Physics of ferromagnetic amorphous alloys

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After some introductory comments on materials classification and a brief historical outline, this review seeks to identify those fundamental physical phenomena that underlie the major technical properties of ferromagnetic amorphous alloys. Those phenomena are reviewed and an attempt is made to compare existing data and, where possible, to synthesize new perspectives. A fundamental approach is taken in the sense that we move from consideration of the local atomic structure to its consequences for the electronic structure and from the electronic structure finally to the physical properties it determines. We focus on the aspects of the structure-property sequence that set amorphous metallic alloys apart from their crystalline counterparts. Such a review would be incomplete without addressing the new issues and insights raised by the discovery of the quasicrystalline state. The very existence and better understood atomic arrangements of quasicrystals help to define and illuminate their amorphous cousins.

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I. SYMBOLS AND ABBREVIATIONS USED IN TEXT

\begin{tabular}{ll}
\textbf{A:} & Exchange stiffness coefficient. \\
\textbf{Å:} & Angstrom. \\
\textbf{AF:} & antiferromagnetic. \\
\textbf{Amorphous SRO type I:} & SRO similar to that of a crystalline phase. \\
\textbf{Amorphous SRO type II:} & SRO unlike that of any known crystalline phase. \\
\textbf{ASW:} & augmented spherical wave. \\
\textbf{a-AB:} & amorphous alloy AB. \\
\textbf{\alpha:} & single-ion term of magnetostriction. \\
\textbf{B:} & coefficient of \(T^{3/2}\) spin-wave demagnetization. \\
\textbf{B_{\gamma}:} & magnetoelastic coefficient. \\
\textbf{\beta:} & two-ion component of magnetostriction. \\
\textbf{B_{\gamma}(x):} & Brillouin function. \\
\textbf{C_{T}:} & average fractional surface coverage of nn sphere by T species. \\
\textbf{CSRO:} & chemical short-range order. \\
\textbf{D:} & coefficient of local (crystal) field anisotropy. \\
\textbf{D(E):} & electronic state density as a function of energy (DOS). \\
\textbf{DOS:} & (electronic) density of states. \\
\textbf{d:} & reduced local anisotropy \(D/J_0\). \\
\textbf{\delta:} & reduced exchange fluctuation \(\Delta J/J_0\) or rms exchange fluctuation. \\
\textbf{\epsilon:} & free energy or ferromagnetic. \\
\textbf{F:} & magnetic field (applied). \\
\textbf{H,H_{a}:} & Hamiltonian energy density. \\
\textbf{H:} & exchange interaction as in \(JS_S\), its average value. \\
\textbf{J,J_0:} & exchange fluctuation. \\
\textbf{\Delta J:} & total angular momentum vector. \\
\textbf{J:} & magnetic anisotropy coefficient, uniaxial, of order. \\
\end{tabular}
L: orbital angular momentum vector.
L: local magnetization correlation length.
LRO: long-range order.
A: local anisotropy correlation length or spherical harmonic orbital index.
\lambda: magnetostriction coefficient.
M: metalloid species.
Mv,Mz: magnetization vector, saturation magnetization.
m(T): reduced magnetization \( M(T)/M(0) \).
(n)nn: (next) nearest neighbor.
N(A): number of atoms of species \( A(T,R,M...) \) or number of \( A \)-type electrons \( A = s,p,d, or f \).
QC: quasicrystal.
R: rare-earth metal species.
S(A) : total atomic spin quantum number, at site \( t \).
SCF-Xα-SW-MO: self-consistent field, X-alpha, scattered wave, molecular orbital.
SRO: short-range order.
α: specific magnetization (per unit mass).
T: transition-metal species.
Tc: Curie temperature.
TE, TL: early, late transition-metal species.
t: reduced temperature \( k_B T/J_0 \).
\( \mu_A \): magnetic moment per average atom.
\( \mu_T \): magnetic moment per T species.
\( \mu : \) magnetic moment.
\( \mu_B : \) Bohr magneton.
UPS: ultraviolet photoelectron spectroscopy.
V: valence.
V_m: magnetic valence.
x: composition variable concentration.
XPS (XPS-1): x-ray photoelectron spectroscopy (inverse XPS).
\( Z^T_M \): \( T \) coordination about metalloid species \( M \).

II. INTRODUCTION

The technological development of amorphous magnetic alloys (Fish and Smith, 1986) seems to have achieved a major milestone with the recent reports of successful long-term studies of field-tested distribution transformers (Bailey, 1986) and announcement of production and delivery dates. Yet over the past five years the percentage of papers on amorphous magnetic alloys at major magnetism conferences has declined steadily from 12.5% in 1982 to 7% in 1986. A recent National Materials Advisory Board study of magnetic materials in the United States (Bibliography entry, B1) singled out amorphous magnetic alloys for more intense scientific investigation, particularly with regard to their fundamental properties.

This review is an attempt to consider where we are in our fundamental understanding of magnetism in technologically important amorphous alloys. We use the term “amorphous alloy” in a general way to include liquid-, vapor-, or plasma-quenched material, as well as alloys obtained by solid-state synthesis, whose diffraction patterns show characteristic broad rings. The term “metallic glass” is used to denote only liquid-quenched products. The term “noncrystalline” is more inclusive than “amorphous” in that it also includes quasicrystals (vide infra).

Amorphous metallic alloys of the technologically useful variety discussed here may be represented as \( TL_{1-x} \) (TE, R, M). That is why they are typically made up of 1 - \( x \) = 60-90 at. % late transition metal (TL, e.g., Fe, Co, Ni) with the balance \( x \) being some combination of early transition elements (TE, e.g., Cr, Mo, Nb), rare earths (R, e.g., Gd, Tb, Sm), and/or metalloids (M, e.g., B, Si, C). These are the approximate compositional limitations defining ambient-temperature ferromagnetism. These alloys lack long-range atomic order and consequently exhibit: (1) high magnetic resistivity (100-200 µΩ cm); (2) no macroscopic magnetocrystalline anisotropy (residual anisotropies typically amount to \( 10^8 \) erg/cm\(^3\) for 3d-based alloys but can approach \( 10^9 \) erg/cm\(^3\) for certain rare-earth containing alloys); and (3) no microstructural discontinuities (grain boundaries or precipitates) on which either magnetic domain walls or mechanical dislocations can be pinned. As a result, ferromagnetic metallic glasses based on 3d transition (T) metals are generally good “soft” magnetic materials with both low dc hysteresis loss and low eddy current dissipation. In addition, they are characterized by high elastic limits (i.e., they resist plastic deformation) and, for certain compositions, they show good corrosion resistance. Amorphous magnetic alloys containing appreciable fractions of R metals show magnetic anisotropy and magnetostriction that can be varied almost continuously with composition up to very large values. These characteristics combined with the expectation that metallic glasses can be economically mass fabricated in thin gauges, has led to broad commercial interest.

Probably the best ongoing record of progress in amorphous magnetism, both fundamental and technical, is the proceedings of the annual Conference on Magnetism and Magnetic Materials (CM\(^3\)) with more applied topics covered in the Intermag proceedings. Locations of these and other relevant conference proceedings are listed in the Bibliography.

Many good reviews of amorphous alloys are available, covering a variety of physical properties. These recent reviews competently present a wealth of information on metallic as well as on insulating disordered magnetic systems. Alben, Budnick, and Cargill (1978a) treat several fundamental issues in amorphous ferromagnetism, notably the effects of random anisotropy on coercivity, spin-wave demagnetization, and chemical versus structural disorder effects on the temperature dependence of magnetization. Petrokovskii (1981) gives a lucid survey of some fundamental issues related to the effects of amorphous structure on the magnetic state of a system. O’Handley (1983) covers a number of topics such as charge transfer, bonding, and crystal field anisotropy, that emerge from the body of the data available on transition-metal base glasses. Wohlfarth (1983) examines many aspects of magnetism in light of itinerant elec-

Topics of a more applied nature are covered in several good reviews. Luborsky treats anisotropy, moment variations, coercivity and losses. Hasegawa treats a number of basic properties that affect magnetic applications at low frequency (B6, p. 163). Soohoo reviews several issues important to the use of amorphous rare-earth-containing thin films in magnetic recording (B6, p. 203). Fujimori treats magnetic anisotropy and specific applications are reviewed by Boll, Hiltzinger, and Warlimont (B6, p. 183).

In this review we take the somewhat different perspective of considering the physics that underlies the technological promise of magnetic amorphous alloys. This Introduction continues (Sec. II A) with a classification of the atomic structures that characterize various amorphous and crystalline materials. Section II B gives a brief historical perspective leading to an outline of the physical properties that recommend amorphous magnetic alloys for a variety of applications. Our physical understanding of these useful and unique properties is then considered in detail (Sec. III). Major conclusions are outlined in the summary, Sec. IV.

Processing is beyond the scope of this review. What is known about rapid solidification is largely classical, almost engineering physics. Some very good reviews of melt quenching are available (Liebermann, 1983; Kavesh, 1978; Jones, 1984; Davies, 1985). What is known beyond these reviews is not easily found in the literature. Several excellent reviews (e.g., Sommer in 1985) cover the principles of rapid solidification processing from the early works of Uhlinn (1972) and Davies (1976) to the more recent concepts introduced by Perpezzo and Paik (1982) and by Boettinger (1982). Amorphous alloys can now also be produced by new techniques, e.g., ion-beam bombardment (Matteson and Nicosia, 1982) or solid-state synthesis (Johnson et al., 1985). The level of understanding of the latter process (Yeh et al., 1986) has recently been advanced to the point where it enriches our understanding of glass formation in general (Johnson, 1986).

A. Materials classification

Metastable, noncrystalline materials may be classified with other materials according to their short-range order (SRO) and long-range order (LRO) as shown in Table I. (When the SRO cannot be discerned by direct measurement, it is often inferred on the basis of whether or not some physical properties of the noncrystalline alloy that are deter-

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<th>Material Classification</th>
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<td>Crystalline materials</td>
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<td>Macrocrystal</td>
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<td>Amorphous I</td>
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<td>Amorphous II</td>
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<td>Quasicrystal</td>
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*Crystalline SRO may be that of either an equilibrium or nonequilibrium phase.

There is no long-range periodicity but only quasiperiodicity. However, long-range bond-orientational order does exist.

If the SRO is crystalline and persists over distances greater than about 10 μm, we have a macrocrystal. If the SRO is crystalline and persists only up to a few micrometers before another crystallite (having a different structure and/or orientation) is reached, we have what is usually called a microcrystalline material. [Some carry this categorization one step finer and define nanocrystalline materials (Gleiter and Marquardt, 1984) as those whose short-range crystalline order persists up to only 50 Å or so.] These all comprise examples of crystalline materials having different grain sizes.

If the SRO only approaches that of some ordered phase and is frustrated beyond about 10 Å, i.e., there is no LRO, then we have an amorphous alloy. In all of the cases described so far, the local order we refer to may be that of an equilibrium phase or, given nonequilibrium processing, it may be that of a metastable phase. In cases when the local atomic ordering is very much like that of a crystalline phase but the processing is sufficiently nonequilibrium as to preclude the establishment of crystalline order much beyond 10 Å, we classify the materials as amorphous I. The electronic structure and fundamental physical properties of amorphous I alloys should be very similar to those of the corresponding stable or metastable crystalline state because of their similar local atomic order. Many metallic glasses seem to fit into this category. [It is unfortunate that the recently discovered phases which exhibit noncrystalline diffraction patterns (fivefold or tenfold rotational symmetry which persist over hundreds of Angstroms), have been dubbed “quasicrystals.” The related term “quasicrystalline” has long been used to describe the nearly crystalline local order inferred to exist in many amorphous alloys. The term “quasicrystalline” goes back to concepts promoted by Gilman (1978) and Gaskell (1979). In order to avoid confusion, we will refer to the amorphous I phase as “nearly crystalline” in its SRO. The noncrystalline, nonglassy, quasi-periodic phases, will be called “quasicrystals” or “icosahedral phases.”]

The properties of some amorphous alloys suggest SRO unlike that of any known equilibrium or metastable crystalline phase. (A possible noncrystalline local atomic arrange-
ment is one of icosahedral symmetry.) Such amorphous materials are categorized in Table I as being amorphous II. Some evidence supporting the existence of amorphous II alloys will be presented in the section on atomic structure (Sec. III C 2). Because of the difficulty of direct structural determinations on a scale of 10 Å, it is often unclear whether the short-range order of a metallic glass is nearly crystalline (amorphous I) or noncrystalline (amorphous II) and hence this distinction is somewhat speculative. It is used here as an aid to organization of the data.

Finally, it has been observed recently (Shechtman et al., 1984) that a class of materials exists which have noncrystalline SRO (as in amorphous II). In these materials, the orientational correlations appear to be coherent over at least several hundred Angstroms. The orientational order in these "quasicrystals" (Levine and Steinhardt, 1984) has been reported to be icosahedral (fivefold rotational symmetry) (Shechtman, 1984; Bancel, 1985) or decagonal (tenfold symmetry) (Bendersky, 1985). To accommodate such non-space-filling local symmetry over long distances, a quasi-periodic translational order is established by packing of two incommensurate building blocks. Quasicrystals appear to be an intermediate phase between certain glasses and micro-crystalline materials both in terms of the range of their local order as well as in their inferred free energy (Levine and Steinhardt, 1986). Some amorphous phases (perhaps only amorphous II) transform on heating to the icosahedral phase before crystallizing (Lilienfeld, 1985; Poon, Drehman, and Lawless, 1985). Indeed, direct, high-resolution differential anomalous x-ray scattering studies (Kofalt et al., 1986) confirm that the quasicrystalline phase of Pd₆₄U₂₀Si₂₀ has a local order very similar to that of its amorphous (type II) phase out to second neighbors (6 Å).

We may, therefore, further distinguish amorphous I and II alloys by the hypothetical free-energy curves represented in Fig. 1. Type I devitrifies directly to the crystalline state. This presumably reflects its predisposition for crystalline long-range order due to its nearly crystalline initial local configuration. Type II, on the other hand, transforms first to the quasicrystalline (e.g., icosahedral) state. This reflects a growth of its noncrystalline orientational correlations out to several hundred Angstroms. Upon further heating, this metastable quasicrystal structure transforms to the crystalline state.

In this review, we focus on the noncrystalline phases in Table I, particularly amorphous I and II alloys, and consider the physics behind their unique properties and their technological promise. Quasicrystals (icosahedral phases) will be considered to the extent that they shed light on, and define the limits of, the amorphous state.

B. Historical perspective

Although glass science is quite old, the history of metallic glasses and of amorphous alloys is comparatively young. Various researchers appear to have stumbled across noncrystalline metallic alloys in their quest for new materials. Examples include the early observations of Brill (1930), the Ni-P electrodeposits of Brenner (1946), and the superconducting films studied by Buckel and Hilsch (1952). However, it is generally accepted that until Pol Duwez began his extensive research on metastable and amorphous alloys at Cal Tech in the late 1950's (Duwez, 1967), the intrinsic scientific interest and the technological potential of such materials were not appreciated.

Duwez was pursuing two curiosities. First, he wanted to know why metals as similar to each other as copper and silver did not show complete solid solubility in equilibrium as predicted by Hume-Rothery (Duwez, 1960a). To explore the physics behind the equilibrium phase diagram, he set out to use kinetics to suspend the laws of thermodynamics. He did this by rapidly solidifying these alloys using an atomization technique (Duwez, 1951) and using the gun technique (Duwez, Willens, and Klement, 1960a). Duwez's second curiosity involved exploring the Au-Ge, Au-Si, Ag-Ge, and Ag-Si systems to find bcc phases which should exist in the electron concentration range near 1.4 electrons/atom according to the Hume-Rothery rules (Duwez, Willens, and Klement, 1960b). When Duwez applied his gun technique to the Au-Ge system, the previously unobserved phases were discovered, and when he applied it to the Au-Si systems, noncrystalline alloys resulted (Klement, Willens, and Duwez, 1960). Amorphous thin films in the Cu-Ag system were later observed by Mader et al. (1963). A ferromagnetic amorphous alloy was first reported in 1965 (Mader and Nowik, 1965) and splat-quenched ferromagnets with attractive soft ferromagnetic properties were reported by Duwez's group in 1966 (Tsuui and Duwez, 1966; Duwez and Lin, 1967). The subsequent growth of interest in metallic glasses was exponential.

The early studies of local moment formation, structure, and transport phenomena in Duwez's group as well as the insights afforded by the thermodynamic studies coming from Turnbull's group at Harvard (Chen and Turnbull, 1967; Cohen and Turnbull, 1961; Turnbull, 1961) spurred a research and development effort at Allied Corporation's Materials Research Center (Gilman, 1975). Beginning in approximately 1972, publications on structure, mechanical properties, and glass formation began to appear, largely from Allied and the University of Pennsylvania. By 1974, research papers on magnetic properties of potentially useful metallic glasses began pouring out of Tohoku University (Fujimori, 1974; Kikuchi, 1975), the University of Pennsylvania (Egami, Flanders, and Graham, 1975), and Bell Laboratories (Sherwood et al., 1975), and then from Allied Corporation (O'Handley, 1975; Hasegawa and O'Handley, 1976) and General Electric (Luborsky, Becker, and McCarey, 1975). Soon researches at Vacuumshmelzte
from. Distribution transformers rated at 25 kV A have been performing well in long-term field tests since 1983 (Bailey, Lowdermilk, and Lee, 1986). Such transformers are now being mass produced for full-scale commercial use.

C. Summary of magnetic applications and technical properties

The extensive scientific interest in amorphous alloys was motivated in part by the technological prospects for magnetic applications of amorphous alloys. The technological advances in turn have enriched the scientific investigations.

The most promising magnetic applications of 3d-base metallic glasses make use of their unique combination of properties: excellent soft magnetic response, high, stable electrical resistivity, high elastic limit, and generally good corrosion resistance. Rare-earth-containing amorphous alloys are generally of importance in magnetic recording. In such applications their absence of grain boundaries, high electrical resistivity, good mechanical properties and, for some compositions, improved corrosion resistance, combine with the ability to tailor their magnetic properties \( (M_s, K_u, T_C, T_{comp}) \) with continuous composition variations over broad ranges to provide distinct advantages over crystalline alloys.

High electrical resistivity is important in suppressing eddy currents during high-frequency magnetization reversal. It is understood to be a consequence of the atomic disorder characterizing the amorphous state and is well described by the Ziman–Faber theory of liquids and its modifications (Güntherodt and Künzi in B2, 1978; Nagel, 1977; Cote and Meisel, 1981).

The high elastic limit of amorphous alloys appears to be a consequence of the absence of an ordered atomic lattice through which dislocation motion would be relatively easy. Highly elastic behavior (i.e., little plastic deformation) renders metallic glasses less prone to magnetic degradation during handling. However, they are subject to considerable flow and anelastic relaxation at elevated \( (150 \, ^\circ C < 400 \, ^\circ C) \) temperatures (Chen, 1982; Berry in B2, 1978; Greer, 1984).

The attractive corrosion and oxidation resistance of amorphous metals is now understood to result from a variety of factors including the absence of grain boundaries along which contaminants can enter the host. The fine scale of oxide/corrosion layers renders the materials less susceptible to pitting (Hashimoto, 1983a, b) and the general presence of strong oxide formers in solution as glass formers \( (B, Si, P) \) affords a ready source of material for surface passivation (Cotell and Yurek, 1986).

The generally excellent soft magnetic properties of 3d-base amorphous alloys results from their lack of magneto-crystalline anisotropy and their freedom from microstructural defects (e.g., precipitates or grain boundaries) on which domain walls could be pinned. Hence magnetization—by both wall motion and rotation processes—is relatively easy. Coercive fields \( H_c \) of a few milloersteds and anisotropy fields \( H_K \) of a few tens of Oersteds are readily achieved. The rare-earth-containing amorphous alloys offer a wide range of coercivities and anisotropies because the relatively strong local anisotropy is not averaged out by the structural disorder.

The critical cooling rate required for glass formation can be reduced if the kinetics of atom transport in the melt are slowed down. This occurs either above eutectic compositions (where solidification to two phases is the thermodynamically preferred equilibrium process) or, more generally, in complex alloy melts. However, it is also possible to make glasses from the solid crystalline state by careful exploitation of fast diffusion and chemical thermodynamics (Johnson et al., 1985; Johnson, 1986). In either case glass formation is facilitated by alloying two or more species which interact strongly with each other. This chemical interaction has its own consequences for electronic structure and magnetic properties just as the atomic disorder has distinct effects on the physical properties of the noncrystalline state.

Table II outlines the important technical properties required for various applications and the basic science that underpins the suitability of amorphous alloys in each case. References are given after each application and the citations after the Physics column refer to sections in this review.

The characteristics common to most of the applications requirements listed in Table II (namely, easy magnetization by wall motion and rotation processes, high electrical resistivity and low susceptibility to plastic deformation, and the resulting degradation of properties) are a direct consequence of glass formation. Because of the high cooling rates in the processing of most amorphous materials, impurities tend to remain in solution rather than precipitating out, hence, impurities add only to the electrical resistivity but not to the magnetic viscosity. This is due to the fact that conduction electrons probe the solid on a scale of Angstroms while domain walls interact with solid on a scale of thousands of Angstroms.

Decades ago it was appreciated that single-crystal, magnetic metals typically show a low density of highly mobile domain walls and thus look very attractive magnetically under quasistatic conditions but degrade rapidly with increasing frequency (Pry and Bean, 1958; Wycklendt, 1962). This was understood to be a consequence of the concentration of eddy currents around the few active walls involved in the magnetization process. Increasing the number of walls (by grain refinement in crystalline materials) lowered these anomalous losses and improved high-frequency magnetization performance. Well-quenched magnetic metallic glasses behave much like single crystals in this respect. They show a low density of domain walls and a response that quickly de-
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TABLE II. Summary of important technical properties and their underlying physics for some of the major applications of magnetic amorphous alloys.

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<td>a,b</td>
<td>Chem. bonding</td>
<td>III D,E 2,3,4</td>
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<td>power transformers</td>
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<td>High elec. resistivity</td>
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<td>III F 3</td>
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V. REFERENCES

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- Boll et al., 1983.

VI. PHYSICS

A. Magnetism and short-range order

It has long been appreciated that magnetism—even in 3d alloys—is predominantly a local phenomenon determined by the immediate environment about potentially magnetic atoms. Hence the importance and success of local environment models (Jaccarino and Walker, 1965) as reviewed by Kouvel (1969) and used by Hines et al. (1976) and by Stearns (1976). Although many properties of ferromagnets (saturation moment, magnetic anisotropy, order...

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TABLE II. Summary of important technical properties and their underlying physics for some of the major applications of magnetic amorphous alloys.

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VI. PHYSICS

A. Magnetism and short-range order

It has long been appreciated that magnetism—even in 3d alloys—is predominantly a local phenomenon determined by the immediate environment about potentially magnetic atoms. Hence the importance and success of local environment models (Jaccarino and Walker, 1965) as reviewed by Kouvel (1969) and used by Hines et al. (1976) and by Stearns (1976). Although many properties of ferromagnets (saturation moment, magnetic anisotropy, order...
or the Stoner criterion for the existence of a local moment, 
\[ T_C = J(r)Z_T S(S+1)/3k_B, \]
the number, type, distance, and symmetry of the nearest neighbors about a given site. This is illustrated in simple terms by the molecular field expression for the Curie temperature,

\[ I(E_F)D(E_F) > 1. \]

Here \( J(r) \) is the distance-dependent interatomic exchange integral, \( Z_T \) is the coordination (presumably by strongly magnetic species) about the \( T \) site, \( S \) is the orbital spin quantum number, \( k_B \) is Boltzmann's constant, \( I(E_F) \) is the Stoner constant evaluated at \( E_F \) reflecting intra-atomic (Hund's rule) exchange, and \( D(E_F) \) is the electronic density of states at the Fermi energy. \( D(E_F) \) is an average of the states available anywhere in the unit cell, and \( I \) is more a function of those states localized about the atomic sites, yet both are functions of the local environment. The number, type, and distance of nearest neighbors enter Eqs. (1) and (2) explicitly through \( Z_T \) and \( J(r) \) and implicitly through \( D(E_F) \) and \( I(E_F) \). The symmetry of the nearest-neighbour arrangement clearly affects \( D(E_F) \) and \( I(E_F) \) by changing the degeneracy and hence the distribution of the electronic states. Thus local magnetic moment formation is determined by the extent to which intra-atomic exchange is free to operate. The Curie temperature reflects more cooperative, interatomic effects as well as the magnitude of the local moment.

Examples of magnetic property variations with these indices of CSRO abound in the literature and will not be reviewed here. Several examples pertinent to amorphous alloys will be found throughout the present article.

**B. Effects of disorder on magnetization**

It is well known (Moorjani and Coey, B7, 1984; Mizoguchi, 1977) that many antiferromagnetic (AF) compounds become ferromagnetic (F) in the amorphous state. Two factors may be contributing to this: (1) the frustration of perfect AF coupling in a disordered structure and (2) a positive slope to \( J(r) \) near the equilibrium atomic spacing for iron combined with a greater average interatomic spacing in the amorphous state. The first factor leads to fluctuations in the strength of nearest-neighbor interactions and allows for isolated, nearly AF exchange. For atoms whose nearest neighbors are also nearest neighbors to each other (e.g., odd numbered rings in a planar array), frustration of AF coupling sets in. The second factor assumes \( J(r) \) varies according to the Bethe-Slater curve and an increase in mean atom spacing drives the system from AF to F coupling.

**1. Random exchange fields**

The effect of local disorder on the exchange interaction and hence on the reduced magnetization curve \( M(T)/M(0)/M(0) \) was first considered theoretically by Handrich (1969). He found that for an exchange fluctuation \( \Delta J \) about some mean value

\[ J_{ij} = \langle J_{ij} \rangle + \Delta J_{ij} \]

(where \( \langle \ldots \rangle \) is a random bond average), the Brillouin function describing the variation of magnetization with temperature was suppressed:

\[ M(T)/M(0) = m(T) = \frac{1}{2} \{ B_{1}[x(1+\delta)] + B_{2}[x(1-\delta)] \}. \]

Here \( \delta \) is the rms exchange fluctuation

\[ \delta^2 = \langle (\Sigma_{j} \Delta J_{ij})^2 \rangle / \langle (\Sigma_{j} J_{ij})^2 \rangle, \]

and \( x \) is the effective field variable \( \mu H/k_B T \). Many observers have interpreted reduced magnetization data \( m(T)/T_c \) for amorphous alloys in terms of this model (Tsuei and Lillienthal, 1976) [see Fig. 2(a)]. However, Alben, Budnick, and Cargill (1978a) have cautioned against such interpretations noting that chemical disorder alone can suppress \( m(T)/T_c \).

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**FIG. 2. Reduced magnetization \( m(T) = M(T)/M(0) \) vs. reduced temperature \( T/T_c \).** (a) Schematic for crystalline transition metal and amorphous alloy (cf. Tsuei and Lillienthal, 1976), (b) reduced magnetization for amorphous thin-film Gd_{80}Au_{20} thin film (for which 4d magnetic states are weakly affected by structural disorder) compared with data from pure crystalline Gd metal, and (c) reduced hyperfine field for metallic glass Fe_{80}B_{20} (where 3d magnetic states are strongly perturbed by structural disorder) compared with data for crystalline Fe metal. Theoretical curves based on Eq. (4) are shown for cases (b) and (c) (Kaneyoshi, 1985).

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Kaneyoshi (1985) has pointed out that while exchange fluctuations alone can describe the magnetization behavior of rare-earth-based amorphous alloys [Fig. 2(b)], 3d transition-metal-based amorphous alloys behave quite differently with temperature exhibiting much easier thermal demagnetization than predicted by Eq. (4) [Fig. 2(c)]. Several observers have noted that the spin-wave demagnetization coefficient $B$ in $m(T) = 1 - BT^{3/2}$ is approximately four times higher in amorphous 3d-based alloys than in related crystalline materials (Cochrane and Cargill, 1974; McColl et al., 1976; Hasegawa and Ray, 1979). Also, Fernandez-Baca et al. (1985) have noted a significant anomaly in the spin dynamics of amorphous Fe$_{36}$B$_{14}$ Invarlike alloys. The strong, low-temperature demagnetization may be related to an anomalously high density of low-energy spin-wave states in amorphous alloys (Simpson, 1970 and Tahir-Keli, 1972). Birgeneau et al. (1978) found no disparity in the case of FeNi-P-B-Ae metallic glasses. Kaneyoshi’s model is worth reviewing because of the physical insight it affords.

Kaneyoshi notes that for 4f/amorphous alloys, the more highly localized nature of the R magnetic moment leaves its magnitude relatively insensitive to its environment. Hence R moment distributions are observed to be quite narrow in amorphous alloys (Fig. 3). However, in the 3d alloys where the total moment is more easily perturbed by its environment, variations in moment magnitude as well as exchange fluctuations probably play a larger part in determining $m(T/T_C)$. This disorder effect on moment magnitude is understandably more important at low temperatures where the local environment may be most irregular. At higher temperatures, phonons blur the atomic positions and the magnetic moment is determined by a more nearly uniform environment (even though the magnetic interactions occur on a faster time scale than the thermal fluctuations) (Ohkawa and Yosida, 1977). This has been expressed mathematically by Bhatnager, Prasad, and Jagganathan (1984) and Kaneyoshi (1984). Perhaps the most important result of these modified random exchange theories, which effectively make $\delta$ a function of temperature $\delta(T)$ in Eq. (4), is the correct description of the very broad 3d moment distribution. In fact, it appears likely that, at least at low temperature, many Fe atom pairs in a given amorphous alloy experience zero and even negative (AF) exchange coupling. As $T$ approaches $T_C$, the distribution is predicted to become quite narrow leading to sharp Curie transitions but to nonlinear Arrott plots (Aharony and Pytte, 1980). A narrow moment distribution near $T_C$ could result from the above-mentioned thermal averaging of the atomic disorder as well as from the fact that anisotropy due to local crystal field decreases more sharply with increasing temperature than does isotropic exchange.

2. Random local anisotropy

Magnetic anisotropy arising from long-range crystallinity is clearly absent in amorphous alloys. However, the same “crystal field” or more accurately “local field” is effective in noncrystalline materials on a scale of a few angstroms (Harris, Plischke, and Zuckerman, 1973; Imry and Ma, 1975). The sign and strength of the coupling between this local field and magnetic properties is determined largely by spin-orbit interactions. The degree to which this local-anisotropy field affects macroscopic behavior or gets averaged out due to fluctuations in orientation of the local “easy axes” was addressed simply and effectively by Alben et al. (in B2, 1978). The consequences of the local anisotropy field for 3d- and 4f-containing alloys are so dramatic and of such recurring technical relevance (Chi and Alben, 1977; Alben, Becker, and Chi, 1978b) that the arguments are recast here.

The local crystal field is modelled by a uniaxial (dipolar) term of strength $D$. Its orientation fluctuates with a correlation length $l$ determined by the orientational correlations of the structure: $l$ is approximately 10 Å for amorphous alloys. We assume the local magnetic moments to be coupled by an exchange interaction of stiffness $A$ expressed by the familiar form $AF^2/\langle \mathbf{m}(r) \times \mathbf{m}(r) \rangle^2$ where $\mathbf{m}(r) = \mathbf{M}(r)/M_s$ is the local reduced magnetization.

The interesting question is, given a strength for $D$, what is the range for orientational correlation of the local magnetic moments (assuming $L \gg l$)? Mathematically the problem reduces to evaluating two competing terms in the free energy $F$,

$$F = A \langle \nabla \mathbf{m}(r) \rangle^2 - D \langle \mathbf{m}(r) \cdot \nabla \mathbf{m}(r) \rangle^2 - 1/3,$$

where $\nabla \mathbf{m}(r)$ is a unit vector in the direction of the local easy axis. Clearly the first term can be expressed as $A/L^2$. The strength of the local anisotropy expressed by the second term can be evaluated using random walk considerations. The net anisotropy in the region of diameter $L$ due to the cumulative effect (random walk) of the structural fluctuations of the local elements of diameter $l$ is given by the square root of the number of randomly oriented units: $(L/l)^{1/2}$. This large-scale anisotropy is to be attributed to the $(L/l)^{3/2}$ local anisotropies in the region. Hence the macroscopic anisotropy [second term in Eq. (5)] can be expressed as

$$D(L/l)^{3/2}/(L/l)^{3/2} = D(l/L)^{3/2},$$

down scalping down of the local anisotropy by the ratio $(l/L)^{3/2}$. Energy minimization of $F$ with respect to $L$ then gives

$$L = 16A^2/(9D^2l^3) = 10^6/D^2,$$

where we have used $A = 10^{-6}$ erg/cm and $l = 10^{-7}$ cm (amorphous alloys). For a 3d-base amorphous alloy $D$ is of order $10^8$ erg/cm$^3$ while for 4f-rich alloys it is of order $10^7$ and may approach $10^9$ erg/cm$^3$. Hence for these two cases

$$L = 0.1 \text{ cm} \quad 3d\text{-base},$$

$$L = 10-100 \text{ Å} \quad 4f\text{-base}.$$
[While the value $L = 10$ Å violates the initial assumption of the model, $L > l$, it is clear from Eq. (6) that the magnetization correlation length $L$ decreases dramatically with increasing strength of local anisotropy $D$.]

These results indicate that in 3d-base amorphous alloys exchange stiffness can maintain local moment orientational correlations up to millimeters, whereas in 4f-base amorphous alloys the local magnetic moment may fluctuate (following the local anisotropy field) over a much shorter range possibly approaching a few tens or hundreds of Angstroms. Pictures of ferromagnetic domains in 3d-base amorphous alloys support the first estimate (Leamy et al., 1975; Hasegawa et al., 1976; Livingston and Morris, 1985) and the dispersion of rare-earth moment directions observed in many R-T amorphous alloys (Coey, 1978) supports the second. These dispersed moment alloys were called "speromagnets" and "sperimagnets" by Coey (Coey et al., 1976) and are discussed below. The technical implications of these estimates of $L$ lie in the wide range of macroscopic magnetic anisotropies and coercivities that can be realized in amorphous alloys (Chi and Alben, 1977; Alben, Becker, and Chi, 1978b).

Sellmyer and Nafis (1985) have gathered the effects of exchange and local field disorder into a simple model Hamiltonian:

$$H = -\sum_{ij} (J_{0} + \Delta J_{ij}) \mathbf{J}_{i} \cdot \mathbf{J}_{j} - \sum_{i} D(\mathbf{n}_{i} \cdot \mathbf{J}_{i})^{2}. \quad (7)$$

In the first term, the isotropic exchange interaction between magnetic moments at two sites (expressed in terms of total angular momenta $\mathbf{J}_{i}$ and $\mathbf{J}_{j}$) is expanded to include the effects of exchange fluctuations $\Delta J_{ij}$ [cf. Eq. (3)]. The second term allows for disorder in the distribution of local crystal field axes by introduction of the local unit vector $\mathbf{n}_{i}$ [cf. Eq. (5)]. By defining the dimensionless variables $t = k_{B}T/J_{0}$, $d = D/J_{0}$, and $\delta = (\Delta J)/J_{0}$, a ternary phase space can be constructed which illustrates the rich variety of magnetic orderings that can be realized in disordered magnets through the introduction of exchange fluctuations and random magnetic anisotropy (Sellmyer and Nafis, 1985) (Fig. 4). The existence of the multicritical point and the "reentrant" aspect of the phase diagram along the $\delta$ axis [that is, the replacement of the ferromagnetic (F) phase by a metamagnetic (M) or spin-glass (SG) phase] has been observed in many systems (Rao et al., 1982; Geohagen and Bhagat, 1981). These are features that are unique to disordered magnets.

3. Dispersed-moment structures

Consideration of the effects of structural disorder on magnetism led Andreev (1978) to identity the types of magnetic order allowed in macroscopically isotropic, noncrystalline materials dominated by exchange rather than by local anisotropy. They are ordered ferromagnets, $(S_{i} \cdot S_{j} = |S_{i}||S_{j}|)$, disordered ferromagnets $(0 < S_{i} < |S_{i}||S_{j}|)$, disordered antiferromagnets $(\Sigma S_{i} = 0$ over mutually perpendicular AF axes), and spin glasses.

Coey (1978) has added to these categories by considering first the additional effects of local anisotropy $D$, competing with exchange and then allowing for more than one magnetic species. Local anisotropy can promote spatial dispersion of the local moments and the additional presence of more than one magnetic species can lead to beautifully rich magnetic structures with dispersed parallel (speromagnetic) or dispersed antiparallel (sperimagnetic) magnetic sublattices.

The interplay between exchange coupling (tending to align local moments with each other) and "crystal field" anisotropy (coupling the individual moments to their local easy axes which are assumed to vary from point to point) gives rise to a rich variety of magnetic structures which are best illustrated in the R-T amorphous alloys (Coey, 1978; Kaneyoshi, 1985). The mathematical expression for this competition follows the treatment given in the preceding section. As $d$ approaches zero (see Fig. 4), local anisotropy is basically not felt by the strongly coupled spins and one can have either collinear ferromagnetism [Fig. 5(a)] or, in a two-magnetic sublattice alloy, collinear ferrimagnetism [Fig. 5(b)]. There is no strongly preferred direction for the net magnetization.

When the spins on one sublattice (in Fig. 5, $1 = R$ species) couple more strongly to the local crystal field than with each other ($d_{1} >> 1$) or than with the other species, $D_{1}/J_{11} >> 1$, speromagnetism $J_{12} > 0$ (early R-T) [Fig. 5(c)] or sperimagnetism $J_{12} < 0$ (late R-T) [Fig. 5(d)] can result. [These definitions of spero- and sperimagnetism based on net parallel or net antiparallel magnetization are different from those used by Coey (B7, 1984) who defines them as dispersed moment systems with one and two different magnetic sublattices, respectively. The definition favored here is consistent with the fact that a two sublattice magnetic alloy such as FeNi (Collins et al., 1963a,b) (for which $J_{Fe-Ni} > 0$) is a ferromagnet, not a ferrimagnet.] The spins on the second sublattice as well as the first may also be dispersed in direction either by strong coupling to their own local crystal field $J_{12}$ or $D_{2} \ll 1$ and $J_{12}/D_{2} \ll 1$ or by strong coupling to the spins of a dispersed sublattice $1$, $J_{12}/D_{1} \gg 1$ and $J_{12}/D_{2} \gg 1$. For intermediate cases asymmetric spero- and sperimagnetic structures, for which the cone of dispersed moment fills a narrower angle rather than a hemisphere.
(H > 0) or a sphere (H = 0), may exist. Such materials are called asperomagnets (or canted speromagnets) and aspermagnets (or canted spermagnets), respectively.

Examples of such behavior abound in the literature. Most 3d-based alloys exhibit type a [Fig. 5(a)] magnetic structure with full saturation achieved in relatively weak applied fields. Type b [Fig. 5(b)] behavior is exhibited by Gd-Co or Gd-Fe (Orehotsky and Schroeder, 1972; Taylor et al., 1978). Sublattice moment cancellation is observed at the compensation temperature.

Spermagnetism is observed in Fe-Nd and Co-Nd (Taylor et al., 1978). Difficulty in saturating these materials (closing down the cone angle with an applied field) can be considered one of the bases of the newly developed Fe-Nd-B permanent magnets (Croat, 1982; Hadjipanayis et al., 1982). Spermagnetism is typified by Fe-Tb (Rhyne, Shelling, and Koon, 1974) or Co-Dy (Coey et al., 1976; Jouve, Rebullat, and Meyer, 1976). Weaker coupling of the RE sublattice to the random local field occurs for smaller values of atomic orbital angular momentum. When the transition metal involved is Co as opposed to Fe, the cone angle of RE moment dispersion is slightly narrower because of the greater net R-Co exchange.

The special case of Co$_{40}$Gd$_{20}$ amorphous alloys is worth mention because of its technical importance first as a bubble material and now as a candidate medium for magneto-optic recording (Chaudhari, Cuomo, and Gambino, 1973). While Gd is an $S$ state ion ($L = 0$) it has sufficient spin-orbit-induced angular momentum such that $J_{11}/D_1$ is close to unity. Also, although Gd can be thought of as separating the light from the heavy R elements, its moment couples antiferromagnetically with that of cobalt, $J_{12} < 0$. Thus a magnetic compensation temperature exists for which $N_{Co}\mu_{Co} + N_{Gd}\mu_{Gd} = 0$, where $N_i$ is the number of atoms with moment $\mu_i$. The moderate value of anisotropy allows for perpendicular magnetization $K/2\pi M > 1$ without excessively increasing the coercivity or suppressing the wall mobility. More recent interest in higher coercivity perpendicular media, exclusively for magneto-optic memory, has focused on the higher anisotropy Tb-Fe sperimagnetic system (Connell and Bloomberg, 1985).

C. Atomic structure and magnetism of amorphous alloys

Under equilibrium processing conditions, local atomic arrangements are essentially determined by the thermodynamics of interatomic (chemical) interactions. However, under nonequilibrium conditions (e.g., rapid heat removal, rapid solidification front velocity, or solid-state treatment in a time-temperature regime where the time needed for diffusion to the equilibrium crystalline state exceeds that required to reach metastable states), the fabrication process itself can override the tendency for the atoms to order locally the way they do in the equilibrium crystalline ground state. Thus processing can strongly effect the range of atomic ordering through the kinetic limitations it places on the thermodynamics of the situation. Basically the system can be constrained to a configuration that is stable at some elevated temperature (sometimes called the fictive temperature) or, because processing times leave diffusion lengths short compared to the range required to establish equilibrium, a configuration may result which is only locally stable. In such cases entropy plays a significant role in the local structure obtained. Materials having new structures (e.g., metastable crystalline materials or metallic glasses) may result, depending upon the alloy thermodynamics and on the processing kinetics. Their constrained, nonequilibrium local atomic arrangements determine the electronic structure which, in turn, determines the fundamental physical properties.

It was recognized quite early that the local atomic arrangement in amorphous alloys is not completely random. Indeed, even dense packing of hard spheres (Polk, 1972) imposes a degree of steric order typified by certain canonical structures, the Bernal (1960) polyhedra (Fig. 6). The role of chemistry in further definition of the local order was demonstrated by EXAFS measurements on Pd$_{40}$Ge$_{20}$ glasses (Hayes et al., 1978). In that eutectic glass (whether

FIG. 5. Schematic representation of some of the magnetic structures identified in Fig. 4. (a) $J_{12} > 0$, ferromagnet ($J_{11}/D_1 > 1$, $k = 1$ or 2), (b) $J_{12} < 0$, antiferromagnet if $|S_1| = |S_2|$ or ferrimagnet if $|S_1| \neq |S_2|$, (c) $J_{12} > 0$, speromagnet ($J_{11}/D_1 < 1$, $J_{22}/D_2 > 1$), (d) $J_{12} < 0$ sperimagnet ($J_{11}/D_1 > 1$, $J_{22}/D_2 < 1$).

FIG. 6. Bernal polyhedra believed to be likely local structural arrangements in amorphous alloys. (b) and (c) may be more prevalent in type I amorphous alloys for which the local order is nearly crystalline. (d), (e), and the icosaehedron may be more prevalent in type II amorphous alloys where local order is noncrystalline.
arc quenched or sputtered) the germanium environment was found to be very similar to that in crystalline PdGe and, in particular, it contained essentially no Ge nearest neighbors.

Durand (1980) reviewed the results of NMR and Mössbauer studies of SRO in amorphous materials. He pointed out that the local order seen from the metalloid site is very strong and generally resembles that in the corresponding crystalline phase. The environment about the metal sites as determined by these probes is less clearly defined than that around the metalloid sites and appears to fluctuate strongly from that observed in the appropriate crystalline phase. This difference between the metalloid and metal environments thus reflects the fact that the former are dominated by the strong T–M bonding while the latter are influenced by the weaker T–T bonds, and the few remaining strong T–M bonds, around the T atom.

In the Introduction we outlined a hypothesis which posits two general categories of amorphous structures: (1) type I, for which the physical properties and, presumably, the SRO are close to those of a crystalline phase and (2) type II, for which the physical properties, and hence the SRO, are incompatible with long-range crystalline periodicity. These might be called nearly crystalline and noncrystalline types of SRO.

The Bernal polyhedra shown in Fig. 6 might also be similarly categorized. Some of these are quite common in crystalline structures and probably also occur in amorphous I alloys. For example, trigonal prisms are a known basis for the orthorhombic (cementite) and tetragonal structures occurring in Fe–B and also have been used extensively in modeling local structure in metallic glasses (Boudreaux, 1983). The more complex polyhedra as well as the icosahedron can occur in crystals only as subunits within the Bravais lattice—by themselves they violate classical crystallographic point symmetry. These may be more common in type II amorphous materials. Icosahedral structural units occur in Laves, Frank–Kasper, σ, χ, and μ phases (Wells, 1962). There is widespread belief that local icosahedral symmetry exists in metallic glasses (Briant and Burton, 1978; Steinhart, Nelson, and Ronchetti, 1983; Sachdev and Nelson, 1985; O’Handley et al., 1986b; O’Handley, 1986).

We have already reviewed the intimate dependence of magnetism on local order. Now some of the experimental evidence supporting nearly crystalline local atomic order in amorphous type I alloys is summarized. The accumulating evidence for noncrystalline local atomic order (amorphous type II) will be discussed later.

1. Support for nearly crystalline local order

Warlimont (1984) tabulated numerous published results supporting nonrandom local order in a variety of amorphous alloys. In most cases the nonrandom order approaches that of a related stable crystal phase. Nearly crystalline CSRO was demonstrated in an eutectic glass cited above (Hayes et al., 1978). The now classic NMR experiments of Panissod (Panissod et al., 1980) indicate that in metallic glasses of composition close to that of a stable crystalline compound, the metalloid environment generally shows the symmetry of the crystalline state. This was demonstrated for amorphous alloys based on La, Ga (cubic), Mo2B (tetragonal), and Ni3B (orthorhombic) systems (Fig. 7). An interesting sequel to this work studied a series of Ni100–x B x glasses (18.5 < x < 40 at. %) spanning three stable compounds (Ni3 B, Ni3 B, and Ni4 B3). It was shown (Panissod, Bakonyi, and Hasegawa, 1983) that the B environment remained trigonal prismatic (as in orthorhombic Ni3 B and Ni4 B3) over the entire glassy region studied. The uniaxial B environment characteristic of tetragonal Ni3 B did not appear in the glassy alloys. Boron does exhibit an electric field gradient characteristic of uniaxial symmetry in both amorphous and crystalline (tetragonal) Mo2B.

Magnetic moments of many amorphous alloys are close to those of a related crystalline compound, suggesting similar local environments. Indeed, Corb, O’Handley, and Grant (1983a) have built a quite successful model of local order and magnetism in amorphous alloys that describes well the moment variation with metalloid content in several alloys based on cobalt, nickel, and iron by assuming a local coordination in the glass similar to that in a related crystalline compound. This model is described in more detail in Sec. III E 2.

Curie temperatures in Fe100–x B x glasses vary nonmonotonically with x following the pattern established by Tc's of the three compounds FeB, Fe2 B, and Fe3 B (Chien and Unruh, 1981; O’Handley, 1983). The behavior in the lower metalloid content region is discussed in more detail in Sec. III C 3.

Electronic energy-band calculations based on crystalline structures (e.g., Cu, Au) used to model amorphous alloys give state densities closely resembling measured UPS state densities and predict well the magnetic moments observed for many amorphous alloy systems (Moruzzi et al., 1983; Oelhafen, 1983). This subject will be covered in more detail in Sec. III D.

Mössbauer spectra of many glassy alloys resemble broadened versions of those of related crystalline compounds (Durand and Panissod, 1981; Gonser and Preston, in B, 1983). The case of amorphous Fe100–x Px (Eibschutz, Lines, and Chen, 1983) has been carefully analyzed. The hyperfine splitting and isomer shift suggest a local order close to that of Fe3 B. P. Vincze, Boudreaux, and Tegze (1979) argue from their Mössbauer analysis that the iron environ-

![FIG. 7. Comparison of NMR signature of crystalline compounds (left) and amorphous alloys (right) of similar compositions. Top: Ga NMR in LaGa; middle: B NMR in MoB; and bottom: B NMR in NiB (Panissod et al., 1980).](image-url)
ment in amorphous Fe-B alloys closely resembles that of the metastable crystalline Fe₃B compound. However, Eibschutz, Lines and Chen, (1983) as well as Chien and Unruh (1984) find amorphous Fe-B alloys to be an exception to the correspondence often seen between crystalline and amorphous alloys (see Sec. III C 3).

Thus, an impressive body of evidence suggests that the CSRO of many amorphous alloys is close to that of some related crystalline phase.

2. Support for noncrystalline local order

Many notable results point to local atomic arrangements that are noncrystalline (or found only as subunits in complex crystal structures). I refer specifically to icosahedral atomic orderings (Hoare and Pal, 1975) which are inferred to exist in liquids and glasses and known to exist in Frank-Kasper phases as well as in α-Al-Mn-Si (Guyot and Audier, 1975). The stability of finite icosahedral clusters is due to their high symmetry and coordination and was numerically demonstrated by Frank (Frank, 1952; Sadoc, Dixmier, and Guinier, 1973). Later Briant and Burton (1978), Hoare (1979), and more recently Sachdev and Nelson (1985) showed that icosahedral clusters formed very good models of amorphous alloys as judged by the similarity of their RDFs. However, many different atomic arrangements are able to reproduce experimental RDFs.

Steinhart, Nelson, and Ronchetti (1983) have shown the natural preference for icosahedral ordering (particularly bond orientation correlation) in molecular dynamics simulations of solids. Early electronic structure calculations on fcc cobalt clusters showed the local stabilizing effect of distortions to non-space-filling conformations (Eberhart, O'Handley, and Johnson, 1984). Electronic structure and state densities have been calculated for icosahedral atomic clusters of aluminum and cobalt and compared with results for the corresponding fcc structures. In the case of aluminum there is a clear electronic preference (energy stabilization of electronic states) for the local icosahedral arrangement compared to the crystalline one (McHenry et al., 1986a). These results are discussed further in Sec. III G. Results for cobalt clusters (McHenry et al., 1986c) indicate that the state densities and saturation moments are similar for icosahedral and fcc local arrangements (Fig. 8). This suggests that, at least in the case of amorphous cobalt-rich alloys, it would be difficult to distinguish type I (fcc) or type II (icosahedral) local order on the basis of electronic structure or saturation moment alone. However, the local magnetic anisotropy (as probed for example by approach to magnetic saturation) would be smaller in the icosahedral case if the magnetic species occupied the high-symmetry icosahedral sites.

Further evidence pointing to the existence of a noncrystalline SRO in amorphous alloys comes from a consideration of the phases grown upon heating various noncrystalline alloys. Many metallic glasses appear to devitrify directly to some crystalline phase which is assumed to nucleate from the local atomic order of the glass. However, the newly discovered quasicrystalline state appears to be accessible also by devitrification of certain amorphous alloys (Lilienfeld et al., 1985; Poon, Drehman, and Lawless, 1985). That is, for some compositions, the SRO of the glassy alloy is such as to favor growth of a noncrystalline symmetry (type II). This situation is depicted schematically in Fig. 1. In fact, direct structural determinations now confirm that the local order is the same out to second neighbors in icosahedral and amorphous Pd₆₀U₂₀Si₂₀ (Kofalt et al., 1986).

Just as devitrification to the quasicrystalline state can be taken as evidence of type II SRO in the original glasses, so too a similarity or difference between glass and crystal in some fundamental physical property, which is determined uniquely by SRO, could help identify the SRO of the glass.

In Sec. III E 3 we review some data on R-T alloys in their crystalline and amorphous states. We note there that while R-Fe alloys show suppressed $T_c$'s in their amorphous phase (relative to the crystalline form), R-Co alloys show enhanced $T_c$'s in their amorphous phase. Both of these effects are explained by a model which assumes the local structure about the T sites in the glass to resemble the icosahedral (type II) environment about the T sites in the RT$_2$ Laves phase. See Sec. III E 3.

Finally, results of new studies on rapidly quenched Co-Er alloys may also be relevant in this respect. Most of the compositions studied span the range from hexagonal Co$_6$Er to the Laves phase Co$_5$Er where the increasing trend toward icosahedral coordination about the Co sites in this series is complete. The alloys are ferrimagnetic, or more specifically, spermagnetic (Coey et al., 1976; Coey 1978). The magnetization versus T curves for these alloys are strikingly at variance with magnetic behavior of known stable crystalline phases (O’Handley et al., 1986a) and they also differ from the behavior of the amorphous thin films of the same composition studied more than a decade ago by Jouve, Rebuillat,
and Meyer (1976). The newly melt-spun materials show sharp powder diffraction peaks which can be indexed to a hexagonal structure or to icosahedral symmetry. While they are clearly not amorphous and probably not quasicrystalline, they may contain icosahedral clusters. One implication of their magnetic behavior (Sec. III G) is that the local order of amorphous Co-Er thin films (whose properties they approach) is of type II, i.e., similar to that of the quasicrystalline phase.

3. Amorphous Fe$_{1-x}$B$_x$

The local structure of amorphous Fe-base alloys and a-Fe-B, in particular, has been a matter of much experimental activity and at least as much speculation. The first suggestion that the structure differed appreciably from that of bcc-Fe was the observation that with decreasing metalloid content the Curie temperature did not increase (much less extrapolate to anywhere near that of bcc-Fe) whereas it does increase in amorphous cobalt base alloys (Durand, 1976). However, in both Fe- and Co-base glasses the magnetic moment increases with decreasing metalloid content. The Curie temperature anomaly was rationalized by arguing that because amorphous alloys are somewhat densely packed, they would only behave like, or extrapolate toward the behavior of, related close-packed structures (fcc or hcp). Hence, as metalloid content approaches zero the Curie temperature in Fe-base glasses was seen as extrapolating toward the behavior of fcc iron (Fig. 9). The nonmonotonic variation of $T_c$ with boron content shown in this figure can be rationalized in terms of the simple mean field expression for $T_c$ [Eq. (1)]. At high boron content, $T_c$ drops off because of decreased magnetic coordination and weakened exchange as average Fe-Fe distance increases. $T_c$ vanishes when the local moment vanishes. At low boron content $T_c$ drops off due to decreasing, and ultimately negative (AF), Fe-Fe exchange at very close Fe-Fe separation. This occurs despite the persistence of a local moment.

There is also evidence that the structure of amorphous Fe-B differs from that of other Fe-base glasses and from those of crystalline phases of Fe-B. It was mentioned above that the Mössbauer spectra of several amorphous alloys closely resemble those of related crystalline phases (Gonser and Preston, 1983; Eibschatz, Lines, and Chen, 1983). The major exception, amorphous Fe$_{100-x}$B$_x$, is just as notable. Chien and Unruh (1984) show major inconsistencies between the parameters characterizing the Mössbauer spectra of a-Fe-B thin films near the equiatomic composition and those parameters for the crystalline compound FeB. Eibschatz, Lines, and Chen (1983) show that while Mössbauer spectra of Fe$_{100-x}$P$_x$ show features like those characterizing the crystalline phase Fe$_3$P (bct), the spectra for a-Fe$_{100-x}$B$_x$ resemble neither of those of the crystalline Fe$_3$C (cementite, orthorhombic) or Fe$_3$P (bct) phases which represent two of the structures in which metastable Fe$_3$B has been observed. [Takahashi and Miyazaki (1981) also report a metastable Ti$_2$P tetragonal phase to be present in Fe$_3$B.] However, this unfavorable comparison is not entirely unexpected because, despite the structural basis for comparison, the chemical difference of B relative to C or P is significant. Thus, while a-Fe-P alloys may be classified as type I, a-Fe-B alloys may be of type II.

Anomalies also occur in a variety of other physical properties of Fe-B glasses suggesting structural changes even within the easy glass-forming region (12%–28% B). A kink was first observed in the density (Ray et al., 1977) and then in the saturation magnetization (Hasegawa and Ray, 1978) of Fe$_{1-x}$B$_x$ glasses near $x = 18$ at. %. Magnetic moment results differing from those of Hasegawa were reported by Fukunaga et al. (1978) and Hiroyoshi et al. (1978). While only a small discontinuity appears in the Curie temperature, the crystallization behavior (Hasegawa and Ray, 1978) supports a structural origin for these amorphous structure anomalies. The proximity of these anomalies to the equilibrium eutectic composition is suggestive but remains unexplained. Tenhover (1981) has used Mössbauer spectroscopy to identify changes in SRO near the eutectic composition in a-Fe-Y alloys.

D. Electronic structure

The electronic structure of amorphous alloys shows subtle effects due to the noncrystallinity of the material. However, the chemical effects due to the presence of glass-forming species are often more dramatic. It is important, therefore, when discussing features of electronic structure that characterize the glassy state, to distinguish, where possible, chemical effects due to the necessary presence of glass-forming species from the effects due solely to the structural and/or chemical disorder.

Early interpretations of Slater–Pauling-like plots of magnetic moment variation with composition (or electron concentration) invoked charge transfer from the glass former to the 3$d$ band (Mizoguchi, Yamauchi, and Miyajima, 1973) to explain what appears to be a shift of the data for the glasses relative to that for pure crystalline alloys. Interpretations...
tions of alloying effects were facilitated by the fabrication in 1975 of the first series of melt-spun glasses based on a single metalloid, (Fe-Co-Ni)$_{80}$B$_{20}$ (O’Handley et al., 1976c) and (FeCoNi)$_{80}$P$_{20}$ (O’Handley et al., 1977). Amorphous T$_{80}$B$_{20}$ alloys showed magnetic moments that were shifted on a Slater–Pauling curve in a way that was consistent with data for crystalline TB and T$_{2}$B compounds and alloys (Cadeville and Daniel, 1966; O’Handley in B3, 1983). The naive charge transfer models soon gave way to a more realistic understanding of compositional effects in terms of (sp)$d$ bonding (Alben, Budnick, and Cargill, 1978a; Allen, Wright, and Connell, 1980; O’Handley and Boudreaux, 1978; and O’Handley, B3, 1983) which is now widely accepted and evident in theoretical treatments and experimental data on electronic structure and bonding of metallic glasses. Johnson and Tenhover (1983) give a lucid overview of electronic structure and energy stabilization in TE-TL (early transition metal–late transition metal) split band as well as T-M (transition metal–metalloid) alloys. In this section we review the concepts of chemical bonding and electronic structure that form the basis of our present understanding of magnetism in amorphous alloys.

The chemical bonding interactions that affect the electronic states and determine the physical properties can be described by two limiting types: polar bonds and covalent bonds (Harrison, 1980). Covalent bonds are formed between orbitals on two atoms A and C (anion and cation) that have similar electronegativities [i.e., similar electronic energies ($E_{A} = E_{C}$)], as well as satisfying symmetry and overlap conditions. In a covalent bond, charge is delocalized from each of the atomic sites and builds up between the atoms. Bonding and antibonding hybrid orbitals are created. Covalent bonds formed between partially occupied (i.e., near $E_{F}$) valence orbitals will often involve magnetic states. The $d$ states become more delocalized as a result of covalent bonding. This delocalization results in loss of $d$ character [hence weaker intra-atomic exchange $I(E_{F})$] and in a suppression of $D(E_{F})$, both of which weaken moment formation [Eq. (2)].

Polar bonds are formed between orbitals that differ significantly in their electronegativity ($E_{A} \neq E_{C}$). The orbitals must also satisfy symmetry and overlap conditions. In the formation of a polar bond, charge is transferred from the orbital of higher energy (lower electronegativity) to that of lower energy. As a result of this charge transfer the bond is biased toward the more electronegative species A. If a polar bond is formed in a metal, the conduction electrons will redistribute themselves to screen the charge transfer and maintain some degree of local charge neutrality. The screened polar bond still contributes to the chemical stability of the alloy. However, it will only affect the magnetic properties if one of the orbitals involved contributes to the magnetism (e.g., a 3$d$ orbital).

A variety of indirect measurements of various properties sensitive to the density of states at $E_{F}$ (such as magnetic susceptibility or electronic specific heat) have been used as crude experimental probes of electronic structure. Several examples of this can be found in the literature (Güntherodt and Künzi, 1978; Fujiwara, 1979; Mizutani and Massalski, 1980; Rao, 1983; Onn, 1983). A more revealing look at the shape of the entire occupied valence-band density of states (DOS) can be had by photoemission measurements. Before reviewing these photoemission results we mention a further aspect of the DOS profile, namely split bands, which is a function of bonding and stability and which has proven most helpful in the study of amorphous alloys.

1. Split bands

The concept that the valence bands of an alloy $A_{1-x}B_{x}$ split into two resolvable components at different energies when their atomic number difference is greater than or equal to 2 was first put forth by Beeby (1964) and developed in detail by Velicky, Kirkpatrick, and Ehrenrich (1968). Split bands reflect polar $d$-$d$ bonding. The lower-energy state is identified primarily with electrons having greater probability density at the site of the more attractive core (i.e., the anion, which for two metals of the same row is the one with higher atomic number). The split-band model can be thought of as an extension to concentrated alloys of Friedel’s virtual bound state model (Friedel, 1958) which is usually applied in the dilute limit.

Split bands were observed directly in the Cu-Ni system by Seib and Spicer (1968) using photoemission. Their result clearly illustrated the errors associated with the widely used and somewhat successful, but nevertheless naive, rigid band model.

In a series of papers, Berger and colleagues applied the split band model quantitatively to descriptions and predictions of a variety of physical properties in various alloys, notably compositional variation of magnetization (Ashworth et al., 1969), magnetoresistance (Berger, 1977), spontaneous Hall effect and magnetoresistance anisotropy (Berger, 1977; Berger and Bergmann, 1980), as well as specific heat and gyromagnetic ratio (Berger, 1977). These papers showed that while the split-band model could account for the Slater–Pauling curve of magnetization versus composition (just as did the rigid band model), it was also able (which the rigid band model was not) to predict successfully the anomalies observed in several physical properties which reflect the orbital angular momentum of the electrons at $E_{F}$, not just the number of $d$ holes. Orbital angular momentum controls these other properties because of their common origin in spin-orbit interaction. Berger showed that $\langle L_{z} \rangle = 0$ when $E_{F}$ lies in the gap or minimum between the energy split bands.

O’Handley and Berger (1978) extended these concepts to amorphous alloys for which data could be described over broader compositional ranges than could be done in crystalline alloys where phase boundaries obscure some compositional trends. Magnetoresistance data (O’Handley and Berger, 1978; O’Handley, 1978a) and spontaneous Hall coefficients (O’Handley, 1978b) were described in amorphous (Fe-Co-Ni)$_{80}$B$_{20}$ alloys. These results show indirectly that the Fe and Ni contributions to the valence-band DOS are concentrated at different energies (the Ni states being more tightly bound) and that a DOS minimum exists between them. The position of the minimum is a predictable function.
of energy and gives a good account of the compositional variation of magnetostriction and spontaneous Hall coefficient. The compositional dependence of these quantities are not correctly described by the rigid band model.

The first direct observation of split bands in amorphous alloys was made by Güntherodt’s group in Basel using ultraviolet photoelectron spectroscopy (UPS) (Oelhafen et al., 1979) on PdZr and CuZr early/late transition-metal (TE-TL) alloys. Figure 10 (top panel) shows the experimental data for amorphous PdZr (Moruzzi et al., 1983). The lower-energy (greater binding energy) feature reflects the chemical stabilization due to the more attractive core potential at the Pd site compared with that at the Zr site. The calculated state densities shown in the lower panel are discussed below.

The connection between split bands and chemical bonding was also shown by Oelhafen et al. (1979 and 1980) with UPS spectra on a variety of amorphous TE-TL alloys. The shift in d-band energy upon alloying was found to correlate with the valence difference between the two transition-metal species (Fig. 11; Oelhafen et al., 1980). The deviation of the Cu-base glasses from linear dependence would be remedied by using electronegativity difference as the abscissa instead of valence difference. Furthermore, the general increase in binding energy with T valence difference correlates with the compound heat of formation (Oelhafen, 1981) as well as with the stability of the glassy phase.

2. Other chemical bonding effects

A carefully studied magnetic system where chemical bonding effects as well as the consequences of disorder are clearly distinguished is that of amorphous Fe$_{0.79}$Th$_{0.21}$ sputtered films (Connell et al., 1984, 1985). These alloys are of interest as magneto-optic recording media (Mansuripur, 1983) and exhibit the sperimagnetic structure typical of most transition-metal/late rare-earth amorphous alloys (see Sec. III B 3).

Figure 12 shows the XPS and XPS$^{-1}$ generated valence-band structure for amorphous Fe$_{0.79}$Th$_{0.21}$ (solid line). The contribution due to Tb, indicated by the dotted line, was deduced from the data for crystalline Tb (Lang, Baer, and Cox, 1981) which is shown by the dashed line on the same energy scale but with a compressed ordinate.

The striking chemical effect upon alloying with iron is the increase in the separation between the occupied Tb bonding states ($ - 3.5$ eV, $ - 9.5 $ eV) and the unoccupied Tb antibonding states ($ + 4$ eV). (This energy shift upon alloying is what is plotted in Fig. 11 for TE-TL amorphous alloys.) In crystalline Tb these features are located at approximately $- 2.5 $ eV, $ - 7.5 $ to $ - 10.0 $ eV, and $ + 3 $ eV, respectively. It is this chemical bonding between Tb and Fe that is responsible for the stability of the amorphous alloy.

The structural disorder in the amorphous alloy introduces a degree of randomness to the local "crystal" field which is responsible for the dispersion in directions taken by the Tb moments. Such random local fields are observed to have less effect on hyperfine field distributions at R sites than at T (3d) sites as discussed above in relation to Figs. 2 and 3. However, in the case of photoemission, the random local field clearly mixes the spectral features resolvable in the crystal, leaving the amorphous density of states broader and less discrete. Connell and Bloomberg (1985) discuss this in more detail in terms of the final photoemission state of a...
singly ionized Tb atom, screened by that part of the Tb \(d\)-charge density at \(E_F\) which is not tied up in bonding states with the iron. Certainly the final state would be more strongly perturbed by randomness than the initial (localized) state. The implications of such fundamental studies for the development of better magneto-optic media are covered by Bloomberg and Connell (1985).

An important aspect of the behavior of transition-metal \(d\) bands that differs between amorphous TE-TL alloys and T-M alloys is revealed by photoemission studies. In the former case the individual (TE and TL) components of the \(d\) bands become narrowed slightly upon alloy formation whereas in T-M alloys the \(d\) bands are broadened compared to those of the pure metals. Amamou's XPS data on amorphous Zr-Ni illustrate the TE-TL case well (Fig. 13), (Amamou, 1980). TE-TL alloys show a narrower, more atomiclike character in the individual components of their \(d\)-band DOS, with greater valence difference between the two species. The same group (Amamou \textit{et al.}, 1980) showed the 3\(d\) band width of Fe-B and Fe-P amorphous alloys (and crystalline compounds) to be significantly greater than that of pure Fe (Fig. 14). The contributions to the spectral density at \(-9.5\) eV and below in the alloys are due to the \((sp)-d\) hybrid states.

This difference between TE-TL and T-M electronic state densities arises from the nature of the bonding responsible for alloy formation in the two cases: \(d\)-\(d\) bonding in TE-TL alloys and \(sp\)-\(d\) as well as \(d\)-\(d\) bonding in T-M alloys. Apparently in TE-TL alloy formation, the \(d\)-\(d\) bonding is such that electronic wave functions associated with the lower-energy DOS peak (dominated by the strongly attractive TL core potential) have small amplitude at the TE sites. Conversely, the higher-energy wave function has greater amplitude at the TE sites. Once the stabilization \{the one center integral \(\bar{\Gamma}_{\text{sum}}\) of Johnson and Tenhover (1983)\} of the states has occurred due to alloying, the system behaves to an extent like two interpenetrating but only weakly interacting sublattices. The electrons occupying the two energy ranges of high state density respond mainly to the core potentials of their own sublattice. Thus the like-atom overlap (TE-TE or TL-TL covalency) is reduced due to the large average spacing of similar atoms and, therefore, the two components of the DOS are narrower than they would be in a pure metal. That is, Johnson and Tenhover's (1983) two center integrals \(\bar{\Gamma}_{\text{sum}}\) are smaller than in the pure metal for two centers of the same species and negligible for different species.

In T-M alloy formation, on the other hand, \((sp)-d\) bonding dominates. The hybridization between metalloid \(sp\) states and metal \(d\) states reduces the degree of localization of the \(d\) electrons tending to broaden the \(d\) band into a more free-electron-like, less tight-binding-like wave function. This \((sp)-d\) hybridization broadens the DOS in T-M alloys to differing degrees depending upon the extent of hybridization. It also gives rise to the discrete \((sp)-d\) bonding states seen in \(a\)-Fe-base alloys (Fig. 14) at \(-9.5\) eV and lower energies.

While Fe-base compounds and amorphous Fe-P-B alloys show \(d\) bands considerably broader than that of pure iron, there is no such clear distinction for Co and Ni \(d\) bands between the pure metals and the compounds or alloys. Apparently the iron-metalloid \((sp)-d\) hybridization feature in Fig. 14 responsible for the broader valence band in the alloys is less significant in the Co (Fig. 15) and Ni (Fig. 16) cases. This is consistent with the higher degree of \(d\) state localization in Co and Ni compared to Fe. Also the increasing energy separation between the B atomic \(2p\) level (\(-3.9\) eV) and Fe, Co, and Ni atomic \(3d\) levels (\(-7.5, -8.5, \text{ and } -9.5\) eV, respectively) gives weaker covalent \(p-d\) bonding in the case of Co- and Ni-base alloys relative to Fe-base amorphous alloys. This decreasing bonding trend with increasing atom-
Matsuura (1980) has studied the valence-band structure of the amorphous Fe$_{1-x}$B$_x$ system using x-ray photoelectron spectroscopy (XPS). In this system the binding energy of the Fe 3d level does not vary monotonically with $x$ as is the case in other alloy systems, notably Pd$_{1-x}$Si$_x$. This may result from the fact that in Pd-Si covalent $p$-$d$ bonding is much stronger than in Fe-B where, due partly to the small size of the boron atom, the wave functions remain more localized and atomiclike. Thus changes in metal/metalloid ratio would be reflected more strongly in the hybridization (valence-band width) of Pd-Si than Fe-B.

An example of a ternary TL-TE-M alloy is worth citing because it reveals the effects of these bonding differences on magnetic properties. When TE = Nb is substituted for M = B in Co-B (TL-M) alloys, the $d$ electrons transferred from the Nb $d$ band (above $E_F$ in the alloy) to the lower-lying Co $d$ band causes a rapid suppression of the cobalt moment. The suppression of the cobalt moment by boron in the binary alloy is small by comparison with that due to the addition of Nb (Corb, O’Handley, and Moruzzi, 1983b). The enhanced stability due to polar $d$-$d$ bonding is seen in the ability to reduce boron content in the ternary alloy well below the limit for glass formation in binary Co-B.

It is instructive to note the extent to which Oelhafen’s photoemission spectra for amorphous alloys match with calculated augmented spherical wave (ASW) state densities (Moruzzi, Janak, and Williams, 1978). Figure 10 shows an example for Pd-Zr (Moruzzi, et al., 1983) and Fig. 17 shows calculated results for Fe, B (Moruzzi, unpublished) which should be compared with Fig. 14. Note, in particular, the $(sp)$-$d$ bonding states centered below 8.5 eV and localized largely on the metalloid atoms. These states are not present in ASW calculations on pure iron (Moruzzi, Janak, and Williams, 1978). The comparison of experimental and calculated DOS for both TE-TL and T-M alloys illustrates two points. First, the UPS spectra offer a good view of the general features of the valence band for many amorphous alloys. Second, DOS calculations based on the Cu$_x$Au structure can account for many of the features observed in the valence-band spectra of these two classes of metallic glasses.

The similarity of the general features of the observed and calculated DOS in Figs. 14 and 17 should not be taken as strong evidence that the local structure in the glass is like that in Cu$_3$Au or some other simple crystalline compound. Particularly in the case of Fe-B, we have already given numerous examples showing its magnetic properties to be in sharp contrast to those of the corresponding crystalline phases (Sec. III C 3). Experimental electronic DOS alone, given their limitations of resolution due to $k$-space averaging in amorphous alloys, are not sufficiently detailed to allow inference of a particular local atomic arrangement by comparison with calculated state densities.

3. Cluster calculations

Calculations on finite clusters of atoms allow for the direct study of the effects of local topological order or disorder on electronic structure. In cluster calculations, one is faced, however, with handling the new problems associated with proper boundary conditions at the surface of the cluster. The fact that cluster calculations can provide a detailed and accurate description of transition metal electronic structure is well demonstrated by Fig. 18. Exchange split, Gaussian broadened eigenstates for a bcc cluster of 15 iron atoms calculated by the self-consistent, X-alpha, scattered-wave, molecular-orbital (SCF-Xa-SW-MO) method (Yang et al., 1981) are compared with ASW band-structure calculations (Moruzzi, Janak, and Williams, 1978). The detailed similarity even for such a small cluster points to the very local nature of the interactions responsible for electronic structure. The moment calculated for the Fe cluster is 2$\mu_B$/Fe.

Fujiiwara (1982, 1984) has calculated electronic states for clusters of 1500 atoms arranged as determined by dense random packing (Fig. 19). The location of spectral features arising mainly from boron $s$ states, from iron-$spd$ bonded with boron $p$ states, and from iron-$d$ states are indicated. More recent calculations (Krompiewski, Krey, and Ostermeier, 1987) on 2000 atom clusters generated by an algo-
M alloys. The results are 3.9 to -8.9 eV (Fig. 5.2). This is shown in Fig. 21. The degree of d-band character and hence decreases the magnetic properties of T-M metallic glasses. He found that the formation of metal-metalloid bonding states decreases the amount of d-band character and hence decreases the magnetic moment. This occupied (sp)-d hybrid states appear at lower total energy than the corresponding states in the pure metal clusters, accounting for the stabilization upon alloying. This is shown in Fig. 20 for Fe2Ni2 and Fe2Ni2B clusters. Fe-P and Ni-B bonds were found to be stronger than Fe-B and Ni-P bonds. The p-d bonding states (square brackets at -6, -6.5 eV below the vacuum level, Fig. 20) are the small-cluster analogs of the p-d hybrid peak at -6 to -8 eV below EF in Fujiwara's large cluster (Fig. 19) or at -8 to -10 eV in the Fe2B band-structure calculation, Fig. 17. This feature is observed by XPS at -9.5 eV (Fig. 14).

Recently Collins has extended Messmer's work to gain a clearer insight into the differences among various metalloids in bonding with iron (Collins, O'Handley, and Johnson, 1987). Eigenvalues and wave functions in M-centered tetrahedral clusters Fe4M(M = B, Si, C, N) are compared and shed new light on a number of aspects of electronic structure and magnetic properties of T-M alloys. The results are summarized in Fig. 21.

At the far left-hand side in Fig. 21 the atomic energy eigenvalues for the various unbonded species are shown. The extent of covalent mixing of states, when simulating an alloy by formation of an Fe4M cluster, will increase as the difference in energy between atomic states decreases. The degree of polarity in a bond will increase as the difference in electronegativity between the initial states increases. It is expected then that the four metalloid atomic p states immediately above the Fe 3d state will form a predominantly p-d covalent orbital, with the greatest covalent mixing taking place between Fe and N or C. The bonding between the Fe 3d level and the lower-lying metalloid s states will be largely polar in character and again strongest for N and C whose s orbitals are most electronegative relative to Fe 3d. Polar interactions between Fe sp-d and metalloid s-like molecular orbitals are found to contribute strongly to chemical bonding. These in-
teractions involve charge transfer to the lower-lying orbital [compensated for by conduction electron transfer in the opposite direction (Watson and Bennet, 1980) to maintain overall charge neutrality].

The second column of Fig. 21 shows the molecular orbital eigenvalues for an empty Fe$_4$ cluster. The symmetries of the states about the centers of the clusters are labeled according to the tetrahedral group notation. Solid lines indicate occupied states and dashed lines, empty states. Partial occupancy (near $E_F$) is indicated by numbers in parentheses. The cluster DOS obtained by Gaussian broadening of cluster eigenvalues [which are really measures of electronegativity (McHenry, Johnson, and O’Handley, 1987b)] are drawn in lighter lines over the discrete states for comparison. The extent to which Fe$_4$ and larger iron cluster results are accurate and useful in understanding physical properties of surfaces and bulk solids are discussed elsewhere (Yang et al., 1981). (Also see Fig. 18.) Allowing the cluster states to spin split results in a moment for the Fe$_4$ cluster of 2.5 or 3.0 $\mu_B$/Fe, for touching or 20% overlapping atomic spheres, respectively.

The effects of the various metalloids in terms of bonding, paramagnetic DOS, and $D(E_F)$ are shown in the next four columns of Fig. 21. Bonding strength is determined mostly by the polar $s$-$d$ interaction. This $s$-$d$ interaction has secondary impact on magnetic properties which are affected more strongly by $p$-$d$ hybridization. Note that B and Si, whose atomic $p$ states lie well above the atomic iron $3d$ states, show little hybridization and thus leave $D(E_F)$ high; covalent mixing is not large. Calculated charge distribution contours show that the $d$ and $p$ electrons for Fe$_4$B and Fe$_4$Si clusters tend to remain more localized within their atomic spheres than do the electrons involved in the $s$-$d$ interaction. (This electron localization holds less for the larger Si atom than for the smaller B atom.) Consequently the Fe$_4$B and Fe$_4$Si spin-unrestricted clusters (not shown) have large moments, 2.6 and 2.4 $\mu_B$/Fe atom, respectively. Amorphous Fe$_{90}$B$_{20}$ shows a saturation moment of approximately 2$\mu_B$/Fe atom (O’Handley et al., 1976c) and Si additions are observed to enhance this moment slightly (Mitera et al., 1978; Kazama, Mitera, and Matsumoto, 1978). Amorphous Fe$_{1-x}$Si$_x$ thin films show a significantly smaller magnetic moment than is observed in amorphous Fe$_{1-x}$B$_x$ (Marchal et al., 1977). For C, and for N especially, the $pd$ covalent hybridization is large due to the small energy differences between the initial atomic states. This leaves $D(E_F)$ low and results in excess interstitial charge. These C- and N-containing clusters are calculated to have low moments of 0.2 and 0.0 $\mu_B$/Fe, respectively. Amorphous Fe$_{1-x}$N$_x$ has not been fabricated but N additions to Fe base glasses are observed to have mixed effects (Nagakubo and Naoe, 1987; Karamon, Matsumoto, and Makino, 1985). Carbon additions to Fe$_{90}$B$_{10}$ glasses weakly suppress the saturation moment (Mitera et al., 1978; Kazama et al., 1985).

These calculations on iron-metalloid clusters show the mechanisms behind the general observation that chemical bonding weakens magnetism. Figure 31 (Sec. III E 4) illustrates the manifestations of the bonding versus magnetism competition in systems based on transition metals and nonmagnetic metals.

Table III is a summary comparison of the binding ener-

![Image](https://example.com/image.png)

**FIG. 21.** Schematic of molecular orbital states and their Gaussian broadened cluster DOS for Fe$_4$ and for tetrahedral Fe$_4$M clusters M = B, C, N, Si. Shown at far left are the positions of relevant Fe and M atomic levels. See text (Collins, 1986; Collins, O’Handley, and Johnson, 1987).

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**TABLE III.** Binding energy (in eV below $E_F$) for boron $s$ states and Fe-$d$-B-$p$ hybrid bonding states as determined by four different calculations and by XPS studies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>B $s$ states</th>
<th>Fe-$d$-$B$-$p$ hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_4$B cluster</td>
<td>a</td>
<td>10.4</td>
<td>7</td>
</tr>
<tr>
<td>Fe$_4$Ni,B cluster</td>
<td>b</td>
<td>...</td>
<td>6.5</td>
</tr>
<tr>
<td>1500 atom Fe$<em>4$B$</em>{20}$</td>
<td>c</td>
<td>12.5</td>
<td>6.8</td>
</tr>
<tr>
<td>ASW Fe$_4$B band struct.</td>
<td>d</td>
<td>...</td>
<td>8–10</td>
</tr>
<tr>
<td>Experimental Fe$_4$B XPS</td>
<td>e</td>
<td>11.5</td>
<td>9.5</td>
</tr>
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</table>

*Collins et al., 1987.
Messmer, 1981.
Moruzzi, unpublished.
Amamou and Krill, 1980.
gies of the major bonding features in the Fe-B system. Various calculational results are listed for small clusters, large clusters, and band structures. Finally, the experimental results are listed. All three calculational approaches, i.e., band structures based on simple close-packed structures (Fig. 17), cluster calculations on large random clusters (Fig. 19), and cluster calculations on small high symmetry clusters (Figs. 20 and 21), agree quite well on the basis of the electronic physics of bonding and electronic structure. Small clusters always show narrower bands and weaker binding energies for bonding states due to the smaller number of interactions as is the case for the small cluster results here (Figs. 20 and 21). Also, all the calculations agree well with the experimental data on "Fe,B."

In Sec. III D 2, the differences in chemical bonding between TE-ML and T-M alloys were pointed out. However, amorphous TL-M (Pd-Si) and TL-TE (Cu-Zr) alloys were seen to have some chemical bonding similarities in the sense that both the metalloid and the early transition-metal species seem to act as a bridge in mediating bonding of the TL species (Leon and Johnson, 1982). New concepts of glass stability based upon the range of this interaction were first explored by cluster calculations (Eberhart, Johnson, and O'Handley, 1982), and have recently been developed in more detail (Eberhart et al., 1985).

A number of interesting features in cobalt-base amorphous alloys have made them the object of extensive experimental and theoretical investigations. Two in particular are relevant here. First, cobalt-base amorphous alloys show small negative or zero magnetostriiction (O'Handley, 1978a) (Sec. III F 2) and zero spontaneous Hall coefficient (O'Handley, 1978b) (Sec. III F 3). Upon replacing cobalt in CoB glasses with small concentrations of Mn, Cr, or V, the magnetostriiction shows temperature compensation \( \lambda < 0 \) for \( T < T_{\text{comp}} \), \( \lambda = 0 \) at \( T_{\text{comp}} \), \( \lambda > 0 \) for \( T > T_{\text{comp}} \) (O'Handley and Sullivan, 1981). Second, CoMnB glasses also show an increase in saturation moment with increasing \( x \) for \( x < 6 \) at. % and a decrease for \( x > 6 \) at. % (O'Handley, 1981; Obi, Morita, and Fukamichi, 1981) whereas crystalline Co-Mn alloys without boron show a monotonic decrease in moment with increasing \( x \). The first of these anomalies is reminiscent of changes in related crystalline alloys that are associated with the hcp-fcc phase transformation (O'Handley and Grant, 1983). This has led to a search for, and some indirect evidence in support of, a local structural transformation in amorphous cobalt-base alloys (Corb et al., 1983c; O'Handley et al., 1984).

Cluster calculations are well suited to investigating such phenomena in noncrystalline systems. With regard to the second anomaly cited above, clusters containing cobalt, manganese, and boron atoms revealed stronger metal-metalloid interactions than metal-metal interaction (O'Handley et al., 1982). More importantly, the Mn-B interaction is stronger than the Co-B interaction (based on the proximity of their atomic energy levels, consistent with the results of Collins cited above). This difference may be responsible for the moment anomaly seen in Co-Mn-B alloys but absent in Co-Mn alloys. Majority-spin Mn states lie above \( E_F \) in Co-Mn alloys and their electrons fill the Co minority-spin holes, thus suppressing the moment. Boron stabilizes the Mn majority-spin states (bring them partly below \( E_F \)) more than it does the cobalt states so that a moment suppression does not occur until the Mn states broaden and extend again well above \( E_F \). This occurs at approximately 6 at. % Mn. A different interpretation of this moment variation is given by Krishnan et al. (1986). They find strong Co and Mn moments ferromagnetically coupled both above and below the alloy moment peak at 6 at. % Mn in Co-Mn-Fe-B glasses. They suggest that the smaller magnetization beyond 6 at. % Mn is due to perturbation of the iron moment. This explanation does not apply to the Fe-free alloy series.

The relative stability of hcp, fcc, and non-space-filling (e.g., icosahedral) clusters, as well as the possibility of transformations between these local orders, was addressed by Eberhart, O'Handley, and Johnson (1984). Their cluster calculations showed that pure cobalt was more stable in the hcp \( (D_h \text{ cluster symmetry}) \) than in the fcc \( (O_h) \) phase. Furthermore, certain nearest-neighbor distortions that alter these crystallographic \( (D_h \text{ or } O_h) \) symmetries and leave the cluster in a non-space-filling configuration, can lower the local bond energy. While this argument does not apply to \( I_h \) symmetry, which is higher than \( D_h \) or \( O_h \), it does point to an electronic mechanism for structural transformations within the crystalline state and to the pair-potential argument given by Frank (1952) for the local stability of icosahedral clusters.

The electronic eigenstates for 13-atom and 33-atom aluminum clusters of icosahedral symmetry \( (I) \) were calculated by McHenry et al. (1986a) and compared with earlier calculations on clusters of \( O_h \) symmetry (Sahal and Messmer, 1977). The electronic stabilization of the \( I \) clusters relative to the \( O_h \) clusters was dramatic. Calculations on icosahedral cobalt clusters (McHenry et al., 1986c) showed only subtle differences in comparison to band-structure results or cluster calculations on \( O_h \) symmetry (Fig. 8). Other interesting aspects of calculations on icosahedral clusters are covered in Sec. III G on quasicrystals.

E. Some models of amorphous magnetism

Having reviewed some experimental and calculational aspects of bonding in terms of the state densities of various amorphous alloys (Sec. III D), we now consider four models which describe trends in magnetic property variation with alloy content. These models focus on magnetic valence, metalloid coordination, and chemical ordering in explaining magnetic moments and Curie temperatures in alloys. We will find the models to be not mutually contradictory but complementary and rich in physical insight.

1. Magnetic valence

The first model we review (Malozemoff et al., 1983; Williams et al., 1983) is based on Freidel's concept of virtual bound states as generalized by Terakura and Kanamori (1971). It accounts for the Slater-Pauling-like variation of average magnetic moment with alloy content in a variety of alloys by defining an atom averaged magnetic valence
where $V$ is the average electronic valence $V = N_d' + N_p' + N_p^T$, and $N_d'$ is the number of majority-spin $d$ electrons. Substitution of the definition of $V$ in Eq. 8 leads to the relation between $V_m$ and atom averaged magnetic moment:

$$V_m = \mu_{av} - 2N_p^T.$$  

(9)

Equation (9) clearly demonstrates that a plot of $\mu_{av}$ versus atom-averaged magnetic valence $V_m$ necessarily leads to Slater–Pauling-like behavior ($|d\mu_{av}/dx| = 1$) with the x intercept determined by the average number of conduction electrons [Eq. (9)]. Numerous examples of the broad applicability of the model are gathered in Fig. 22. When the data for a series of alloys deviates from the line of slope 1, it may be the result of a change in conduction electron concentration or, as is often the case with iron-base alloys, a change from strong to weak ferromagnetism.

In a later addition to this model (Malozemoff, Williams, and Moruzzi, 1984), it is pointed out that Slater–Pauling-like behavior is related to the existence of a gap or minimum in the conduction-band DOS. Such a minimum would tend to conserve the number of conduction electrons in an alloy series and therefore the entire concentration effect is manifest in $d$-band occupation or magnetic moment. That is, Eq. (9) reduces to $\mu_{av} = V_m + \text{(constant)}$ and all data should fall on a common straight line.

2. Coordination bonding

It is appropriate here to review a model which is in the local environment spirit and which sheds light on the role of coordination in the interesting variations of magnetic moment with metalloid content in a variety of magnetic amorphous alloys. It is also applicable to crystalline alloys.

The essence of the model (Corb et al., 1982, 1983a, 1985) is that for a given metalloid content in a $3d$-base alloy, $T_{1-M}$, the $M$ atom is more or less effective in suppressing the host magnetization depending upon whether $M$ more or less strongly bonds with $T$. Exact quantum mechanical calculations graphically depicting this bonding versus magnetic effect are shown in Fig. 21 for a sequence of state densities for clusters of atoms representative of various Fe$_{50}$M$_{20}$ alloys ($M$ = B, Si, C, N) (Collins, O’Handley, and Johnson, 1987). The extent of $p-d$ bonding is assumed to be proportional to the number of $T$ atoms surrounding an $M$ atom. Hence the magnitude of the average magnetic moment $\mu$ per $T$ atom in the alloy is suppressed below that in the pure host $n_b$ by an amount proportional to $Z_M^T$, the $T$ coordination about the metalloid:

$$\mu_T = n_b \left[ 1 - Z_M^T N_M / (5N_T) \right].$$  

(10)

where $N_M/N_T$ [more commonly written as $x/(1-x)$] is the ratio of the number of $M$ atoms to $T$ atoms. Equation (10) assumes that each of the $Z_M^T$ nearest-neighbor $T$ atoms forms a bond with the central $M$ atom and therefore loses, on average, one fifth of its moment because one of its five $3d$ electron orbitals is tied up in a nonmagnetic, covalent bond.

Figure 23 shows the convincing application of this model to metallic glasses as well as to crystalline solid solutions based on a strongly magnetic host, cobalt. The solid lines represent Eq. (10) for $Z_M^T = 6$ (top) based on the Co$_3$B cementite structure, $Z_M^T = 9$ (middle) based on the Co$_3$P tetragonal structure, and $Z_M^T = 12$ (appropriate to hcp solid solutions) at $N_M/N_{Co} = 0$ to $Z_M^T = 9$ (again as in Co$_3$P) at $N_M/N_{Co} = 0.3$. The implication is that while a boron atom in the glassy alloy bonds with, and therefore suppresses the moment of, six cobalt atoms, a phosphorus atom in the glass bonds with nine cobalts and therefore gives rise to a sharper moment reduction. For the crystalline Co-P alloys the coordination numbers used to fit the data, 12 and 9, agree with the results of direct structural determinations of $Z_M^T$.

The model can be extended to Ni-base alloys (Corb, O’Handley, and Grant, 1983a) and, with further assumptions, to metal-metal systems (Corb and O’Handley, 1985). Thus this simple model provides a clear and easily applied relation between magnetic properties and local atomic structure in crystalline alloys and in metallic glasses. A recent

FIG. 22. Atom averaged magnetization for various Co-base and Fe-base amorphous alloys as a function of magnetic valence $V_m$.

FIG. 23. Average magnetic moment per magnetic atom as a function of concentration $N_M/N_T$ of nonmagnetic metalloid species $M$ to transition-metal species $T$. Solid lines are calculated from Eq. (10) for appropriate $M$ coordination.
compilation of data on numerous Co-TE amorphous alloys (TE = La, Y, Hf, Zr, Ti, Ta, Nb, W, Mo) shows the saturation magnetization of follow closely the moment degradation predicted from this model for \( Z_m = 12 \) (Shiba et al., 1986).

It may appear at first that Corb's model, which focuses on the importance of coordination, is orthogonal to the model reviewed earlier (Sec. III E 1), which is based on the influence of chemical valence on average magnetic moment. In fact, the coordination model illustrates a case where metalloid valence seems to play no role in the rate of decrease in magnetic moment (Fig. 24). This figure shows that for a common structure (hcp cobalt solid solution, \( Z_{\text{Co}} = 12 \)) three metalloid solutes Al, Si, and P, each with different valence, all produce the same moment suppression. Similarly, the valence model plots some data for different structures on a common line, implying that magnetic valence and not coordination tells the whole story.

To resolve this conflict it is first noted that the Co_{1-x}B_x data of Hasegawa and Ray (1979) and the Co_{1-x}P_x data of Pan and Turnbull (1974) appear in both Figs. 23 and 24, as well as in Fig. 22, in each case supporting the respective models. Thus the conflict is due in part to the method of presentation of the data. Corb's model plots the variation of \( M_T \), the moment per T atom in terms of the parameter \( N_M/N_T \) [which for an alloy T_{1-x}M_x is equivalent to \( x/(1-x) \) ] instead of in terms of the more conventional \( N_M/(N_M+N_T) \) (or \( x \)). The valence model plots the variation of the moment per average atom \( \mu_{av} \) in terms of the parameter \( V_m \). Examination of the expressions for moment reduction in each model for the Co-B and Co-P systems resolves the problem (O'Handley and Hara, 1987). Equation (10) for the cobalt moment \( \mu_{Co} \) in the coordination model can be written instead to give the moment per average atom \( \mu_{av} = \mu_{Co}(1-x) \) in terms of the metalloid concentration \( x = N_M/(N_M+N_T) \):

\[
\mu_{av} = n_B(\text{Co}) [1-x(1+Z_{\text{Co}}^T/5)].
\]

Equation (11) predicts

\[
\mu_{av} = (1-2.2x)n_B(\text{Co})
\]

and

\[
\mu_{av} = (1-4.5x)n_B(\text{Co})
\]

for amorphous Co_{1-x}B_x (\( Z_{\text{Co}} = 6 \)) and for amorphous Co_{1-x}P_x (\( Z_{\text{P}} = 9 \)), respectively.

Equation (9) for the atom-averaged moment of Co_{1-x}M_x in the magnetic valence model

\[
\mu_{av} = 2N_{ip} + V_M
\]

can be expressed in terms of \( x \) and evaluated using \( 2N_{ip} = 0.75 \) \([n_B(\text{Co}) = 1.75] \) and \( V_M^{Co} = 1, V_M^B = -3 \), and \( V_M^P = -5 \) to predict

\[
\mu_{av} = 1-4x/n_B(\text{Co}) \quad (12a)
\]

\[
= 1-2.3x,
\]

\[
\mu_{av} = 1-6x/n_B(\text{Co}) \quad (12b)
\]

\[
= 1-3.4x,
\]

for amorphous Co_{1-x}B_x and Co_{1-x}P_x, respectively.

These predictions are compared with the data in Fig. 25. Clearly, for these glassy alloys, the coordination model gives a more accurate fit to the data. However, the magnetic valence model is able to explain more general trends in a wider class of alloys. Both models offer valuable physical insight for models of alloy magnetism in terms of the impact of bonding on moment formation and of the correlations between metalloid size, coordination, and valence.

3. More on coordination

Reference has been made to the local environment model of Jaccarino and Walker (1965). Buschow et al. (1977) have used this statistical approach to fit the moment variation in amorphous Co-Y alloys. Their data are well described by the curve based on eight cobalt neighbors required to support the local moment. This curve, as well as the theoretical curves for 7 and 9 neighbors critical for moment formation, are shown in Fig. 26. The upper panel of that figure shows an interesting but familiar anomaly. The decrease in \( T_c \) for Fe-Y amorphous alloys compared to the increase in \( T_c \) for Co-Y amorphous alloys upon T enrichment is reflected in both T-M alloys (Hasegawa and Ray,
1978, 1979a) and in T-R alloys (Heiman et al., 1974, 1976). The absence of a monotonic approach of $T_C$ to its limiting equilibrium crystalline value (1044 K for $a$-Fe) in iron-base amorphous alloys despite such behavior in cobalt-base alloys is understood to be a consequence of the transition from the dense-packed amorphous phase to the more open bcc structure of $a$-Fe and its solid solutions. The former is characterized by decreasing Fe-Fe separation and hence greater AF exchange as iron content increases. The latter structure is characterized by $T_C$'s increasing toward that of $a$-Fe.

A long-standing problem in understanding the properties of amorphous alloys relative to their crystalline counterparts is the contrary behavior of Fe-R alloys compared to Co-R alloys upon glass formation. Specifically there is observed a general suppression of $T_C$ in glassy Fe-R alloys compared to an enhancement of $T_C$ in glassy Co-R alloys, relative to their crystalline phases. Several interesting examples are worth citing. First, Tao et al. (1973) noted that while the Curie temperature Fe$_3$Tb is smaller in its amorphous phase than in its crystalline (Laves) phase (Rhyne et al., 1972, 1974), that of Co$_2$Gd is greater in its amorphous than its crystalline (Laves) phase. This pattern continued when Heiman and Lee (1974) observed that the Curie temperatures of HoCo$_2$ alloys are significantly higher in the amorphous phase than in the crystalline phase. Jouve, Rebillat, and Meyer (1976) made a similar observation in amorphous Co$_{0.44}$Er films relative to crystalline Co$_2$Er$_3$.

On the other hand, the Curie temperatures of R-Fe alloys are lower in the amorphous (Heiman, Lee, and Potter, 1976) than in the crystalline state (Fig. 27). Such differences between Fe-R and Co-R systems cannot be attributed to different amounts of dispersion of the R moments due to differences in random local anisotropy (Harris, Plischke, and Zuckermann, 1973). While this theory no doubt predicts decreasing moment and Curie temperature in random anisotropy systems (e.g., TbFe$_2$) with increasing ratio of crystal field strength to exchange $D/J$, it fails to explain the magnitude of that decrease for RF$_2$ alloys or the enhanced $T_C$ in amorphous RCo$_2$ systems. The explanation lies in the chemical short-range order about the site that dominates the exchange interaction, viz., the transition-metal site. Such a mechanism was first explored by Tao et al. (1973) on the basis of density arguments and reduced R-to-T charge transfer in the amorphous phase compared to that inferred in the crystalline phase.

Moorjani and Coey (B7, 1984) attribute the $T_C$ effect to the different positions of Fe and Co on a curve of $J(r)$ vs $r_{mn}/r_{ao}$ (Bethe–Slater curve where $r_{mn}/r_{ao}$ is the ratio of interatomic spacing to 3d orbital radius) and to the fluctuations in nearest-neighbor distance inherent in the amorphous state. For Fe-R alloys these fluctuations lead to an average decrease in exchange interaction because for Fe $J'(r) > 0$ and AF coupling occurs for close Fe-Fe pairs. For Co-R alloys an average increase in exchange coupling results presumably because for Co $J'(r) < 0$. It is difficult to justify the dramatic increase of $T_C$ for amorphous Co-R alloys on this basis. Perhaps the key to understanding the $T_C$ effects is to examine the consequences of rapid solidification on chemical short-range order in a model (O’Handley, 1987) that builds on concepts of Tao et al. (1974), from the local environment model (Jaccarino and Walker, 1965), from Corb's coordination bond model (Corb, O’Handley, and Grant, 1983a and Sec. III E 2), and lends itself to quantitative prediction by incorporating techniques from the work of Buschow (1982a,b) and co-workers (Buschow et al., 1977).

The RT$_2$ Laves (MgCu$_2$) phase is characterized by interpenetrating Frieauf polyhedra (CN-16) and icosahedra (CN-12) about central R and T atoms, respectively. The icosahedrally coordinated T atoms have 6 T and 6 R nearest neighbors, while the larger coordination bond model (Corb, O’Handley, and Grant, 1983a and Sec. III E 2).

FIG. 26. Above: Curie temperature vs T content in T$_x$Y$_{1-x}$ (T = Fe, Co) compounds. Below: magnetic moment per T atom vs T content. Moments for both crystalline and amorphous (Buschow, 1982a,b) alloys are shown. Solid and dashed curves in lower panel for T = Co were calculated by Buschow from a statistical local environment model (Buschow et al., 1977).

neighbors (Fig. 28, left), favoring T-R ordering rather than reflecting the overall composition. Variations in composition within the crystalline state are known to increase or decrease the T-T coordination $Z_T^{1T}$ as the net T content increases or decreases. Mean field theory clearly expresses the observed dependence of $T_C$ on $Z_T^{1T}$. Increased T coordination also leads to a contraction of the nearest-neighbor icosahedron about the central T atom because fewer of the 12 nearest neighbors are large R atoms. For T = Fe, this decreased Fe-Fe spacing suppresses $T_C$ in the crystalline material presumably because the increased numbers of short Fe-Fe bonds favors AF coupling. In Fe-R alloys this $J(r)$ dependence of $T_C$ dominates the linear dependence of $T_C$ on $Z_T^{1T}$. For T = Co, the opposite trend is observed: the decreased Co-Co separation dramatically enhances $T_C$ in the crystalline compounds. Here increased $Z_C^{Co}$ and decreased Co-Co separation are working together to enhance $T_C$. An illustration of this effect is shown in Fig. 29 for a series of Co-Er compounds.

Rapid solidification freezes in a CSRO that, due to entropy effects, more accurately reflects the overall composition, namely $Z_T^{1T}$ approaches 8 of 12 nearest neighbors (Fig. 28). The increased $Z_T^{1T}$ will increase the magnetic moment at the T site.

Furthermore, the coordination changes lead to a uniform contraction of $r_{nn}$ not just fluctuations about the equilibrium as proposed by Moorjani and Coey (1984). Thus, amorphous materials based on icosahedral units would behave as though they were richer in T content and thus show significantly lower $T_C$ for T = Fe and significantly higher $T_C$ for T = Co compared with their Laves phase counterparts. This is observed to be the case (Fig. 27).

A similar explanation holds for the moment variation across the pseudobinary Co$_{80}$B$_{20-x}$Nb$_x$ series (Corb and O’Handley, 1985). Figure 30 shows the saturation magnetization of Co$_{80}$B$_{20-x}$Nb$_x$ alloys as a function of Nb content $x$. Above the data is a representation of the ternary phase diagram for this system with a dashed line indicating the 80%-$Co$ series (Stadelmaier and Schobel, 1966). The important feature of the figure is that near the $\tau$ and hcp phase

![Equilibrium and Randomized Phases](image)

**FIG. 28.** Left: Coordination about the icosahedral T site in an equilibrium RT$_2$ Crystal (MgCu$_2$ Laves) and RT$_2$ Cluster (Amorph. or Quasi Crystal).

- Co has 6 T NN
- Co has 8 T NN

**FIG. 29.** Curie temperature vs average Co-Co coordination (or cobalt content) for Co-Er and Co-Gd compounds (O’Handley, unpublished).

fields ($x < 12$ at. % Nb) where the glasses may be of type I, the moments per cobalt atom for the glasses and crystals are comparable whereas, in the $\chi$ (cementite, Co$_2$NbB) and in the Laves (Ni$_2$Mg, Co$_2$Nb) phase field ($x > 12$ at. % Nb) the moments are quite different for glassy and crystalline phases. (Curie temperatures over much of the amorphous series in this range are above the crystallization temperatures so they cannot be compared with those of the crystalline Laves phase.) If the difference in the coordination about the icosahedral cobalt site between the crystalline and amorphous phases in Co$_{80}$Nb$_{20}$ tends toward that described by
4. Chemical ordering

Our understanding of the conditions for existence and strength of magnetism in alloys has often been confused by oversimplified notions of charge transfer (Mizoguchi, 1973; O’Handley and Boudreaux, 1978). When carefully considered, charge transfer can be understood in its proper role (Watson and Bennett, 1980; O’Handley in B3, 1983). However, the choice of electronegativity scales and the detailed balancing of various orbital charge redistributions makes models of magnetism based on such concepts of questionable predictive value. On the other hand, models based on local coordination (number and type) are comparatively simple, rich in physical insight, and capable of quantitative prediction. One particular form of such models successfully applied to amorphous and other magnetic alloys has already been described briefly (Sec. III E 2). Here we review the additional and very important ingredient that Buschow and van Engen (1981) added to such models, namely the role of the heat of compound formation in determining the nature of the chemical short-range order and hence the magnetism.

In considering alloys of transition metals T and nonmagnetic metals M (metaloids are treated separately), $T_{1-x}M_x$, we can construct a sphere of radius r equal to the average nearest-neighbor distance $d_{nn}$ about a central T atom. The average fractional surface coverage of the nearest-neighbor sphere by T atoms $C^S_T$ for a random alloy is given by

$$C^S_T = (1-x) V_T^S [1 - (1-x) V_T^S + x V_M^S],$$  

(13)

where the cross-sectional areas of the T and M species are expressed in terms of their atomic volumes $V_T$ and $V_M$. Equation (13) assumes no chemical interaction $E_{T-M}$ (attractive $E_{T-M} < 0$ or repulsive $E_{T-M} > 0$) between T and M. However, for a favorable heat of formation $\Delta H < 0$, of a similarly composed compound, there will be fewer T-M neighbors and more T-M neighbors than in the noninteracting case:

$$C^S_T (\Delta H < 0) < C^S_T (\Delta H = 0)$$

and

$$C^S_M (\Delta H < 0) > C^S_M (\Delta H = 0)$$

and conversely

$$C^S_T (\Delta H > 0) > C^S_T (\Delta H = 0)$$

and

$$C^S_M (\Delta H > 0) < C^S_M (\Delta H = 0).$$

Thus $C^S_T$ is a convenient parameter with which to describe CSRO in amorphous alloys.

Another ingredient present in this model (but more central to Corb’s picture) is the degree of p-d hybridization between the T and M species (Buschow and van Engen, 1981). Such hybridization—essential to bonding and stability in a compound and measured by the heat of alloy formation—reduces $d$ character (Allen, Wright, and Connell, 1980) and weakens magnetism as described earlier (Sec. III D 3, Fig. 21). Figure 31 (Buschow et al., 1977) shows the correlation between heat of formation and moment reduction for some of the metal additions studied. One drawback of such a model is that it is not clear a priori whether one should measure the tendency toward CSRO by the heat of formation or the heat of solution. Buschow argues in favor of the former. Also there is a question concerning the validity of using a heat of formation for a compound $T_nM_m$ $(n, m$ integers) to model a glass of a different composition. More appropriate to many glass-forming systems may be the question of the appropriate heat of formation (or combination) to be used in modeling eutectic glasses where the local order is determined by a competition between two stable neighboring phases.

In summary, these models add further physical insight to local environment models (Jaccarino and Walker, 1965) and are concrete expressions of the chemico-physical interactions uncovered by the cluster calculations reviewed in Sec. III D 3. Specifically they prescribe the ingredients favoring magnetism in (amorphous) alloys: (1) strongly positive heat of formation to favor like atom clustering (higher $Z^T_T$) as opposed to ordering (higher $Z^T_M$); (2) minimum p-d hybridization (smaller T-M coordination as is usually found for metaloids of small radius); (3) more negative average alloy valence (hence more positive magnetic valence and moment); and (4) small $r_{nn}$ for cobalt-rich alloys but larger $r_{nn}$ for iron-rich alloys.

F. Anisotropic properties

1. Magnetic anisotropy

While it would be satisfying to be in a position to review anisotropic magnetic properties from the same perspective (namely atomic structure, electronic structure, physical
property) as was done above for the fundamental isotropic magnetic properties, the level of our understanding of SRO in amorphous alloys is not sufficiently refined to allow this. One early step in this direction of connecting structural anisotropy with physical properties (Cochrane, Harris, and Zuckermann, 1978) appears regrettably not to have been followed aggressively. The exception to this is the point of view taken in analysis of measurements of magnetostriction, through their single-ion and two-ion components, to make inferences about local symmetry of amorphous structures. These efforts are reviewed in Sec. III F 2.

The important consequences of structural disorder for magnetic anisotropy are based on the concepts outlined and referenced in Sec. III on random anisotropy. Basically for \( D/J << 1 \) (e.g., 3d-base amorphous alloys) the magnetization does not respond to the local anisotropy because of the strong exchange coupling. Hence local anisotropy \((10^4-10^5 \text{ erg/cm}^3)\) is averaged out to a small macroscopic value \((\text{of order } 10^4 \text{ erg/cm}^3)\) as argued in Sec. III B 2. Saturation of the magnetization can be achieved in fields as low as 10 Oe in many cases. (Appreciable high-field susceptibility is observed in some 3d-base amorphous alloys.) However, for \( D/J >> 1 \) (e.g., many 4f-containing amorphous alloys) the local magnetization is more strongly coupled to the local anisotropy than to the neighboring moments. The approach to saturation can be quite difficult, requiring fields of several Tesla.

These approach-to-saturation effects are roughly isotropic on a macroscopic scale where they are described by the \( l = 0 \) term in an expansion of the magnetic anisotropy energy in terms of spherical harmonics:

\[
E_K = K_0 + K_2 Y_2^0(\theta, \phi) + \cdots.
\]  

That is, \( K_0 \) is the degree of difficulty for magnetization in any direction. This term is typically of order \( 10^{-10^4} \text{ erg/cm}^3 \) in 3d glassy alloys. In the process of fabricating the amorphous material, or in post-fabrication processing \((\text{e.g., field annealing (Chen et al., 1975), or stress annealing)}, \) or because of internal stresses, or the shape of the sample itself, a macroscopic anisotropy of magnetization \((K_i, l > 0)\) may be superimposed on the essentially isotropic amorphous material characterized by \( K_0 \). These macroscopic anisotropies are described by the appropriate higher-order terms in Eq. (14). Although the absolute magnitude of the \( K_i \) \((l \neq 0)\) terms is generally small \((10^4 \text{ erg/cm}^3)\), they may dominate the magnetic behavior in 3d-base amorphous alloys because they represent the lowest order of angular dependence for the magnetization and because of the small value of \( K_0 \) (Miyazaki and Takahashi, 1979). These \( l \neq 0 \) terms give rise to characteristic patterns of domains and domain walls in various situations (Hasegawa et al., 1976; Livingston and Morris, 1985).

Egami (1975) and O’Handley (1975) pointed out independently that the most significant contribution to the macroscopic anisotropy in 3d-base metallic glasses is due to magnetostriction coupling \( M(H) \) to internal stresses. This realization led to extensive efforts to develop amorphous alloys of low magnetostriction (Sherwood et al., 1975; Kikuchi et al., 1975; O’Handley, 1976b). While these generally contain appreciable concentrations of cobalt some success has been achieved in developing low magnetostriction \((\text{but not } \lambda = 0)\) glasses based on iron (Inomata et al., 1983; Yoshino et al., 1984). In contrast to the cobalt base \( \lambda = 0 \) glasses, the Fe-base glasses that show low magnetostriction at room temperature do so because of their relatively low \( T_C \)‘s.

It has been appreciated for a long time that an understanding of the microscopic origin of intrinsic anisotropy in amorphous 3d alloys is difficult to achieve because of the small magnitude of \( K_0 \) and the presence of other effects which are measured along with \( K_0 \).

In 1974 Berry observed that it was possible to alter the properties of a metallic glass by field annealing. Gyorgy et al. (1976) later illustrated this with dramatic micrographs of the magnetic domains in amorphous ribbons annealed in longitudinal and transverse fields. The role of pair ordering in field annealing was illuminated by pioneering studies of induced anisotropy in the Fe-Ni-B series of glasses (Luborsky, 1977; Fujimori 1977; Takahashi and Miyazaki, 1978).

Uniaxial magnetic anisotropy can be induced by stress annealing as well as by field annealing certain compositions (Gyorgy et al., 1976; Nielsen et al., 1983). Luborsky and Walter (1977) review the evidence for pair ordering as the responsible anisotropy mechanism. The enhanced atomic mobility in the amorphous state allows for pair ordering in certain cases at relatively low temperatures compared to crystalline alloys. The role of the metalloids in this process should clearly be important because of their strong chemical interaction with the T metals (Alia and Vinai, 1978; Becker, 1978). Further basic understanding is needed in this technologically critical area and it is no doubt closely connected with the extensive body of work (not reviewed here) on relaxation effects (Egami, 1984) and magnetic aftereffects (Kronmüller, 1968; Moser and Kronmüller, 1980).

In the case of rare-earth-containing amorphous films, a uniaxial anisotropy often can be developed by controlling the film growth (evaporation or sputtering) conditions. Strong perpendicular anisotropy, useful in magnetic recording materials, can be achieved. Early work by Chi and Cargill (1976) pointed to shape, specifically columnar growth, as the source of the anisotropy in sputtered Gd-Co films. Several publications have revisited this important problem seeking a clearer understanding of the columnar growth mechanism or other possible explanations for the perpendicular anisotropy (Soohoo, B6, 1983; Bona et al., 1986). Mizoguchi and Cargill (1979) pointed out the importance of dipolar coupling in establishing perpendicular anisotropy in ferrimagnetic alloys with columnar microstructure. The origin of induced anisotropy remains a challenging issue even in today’s actively studied perpendicular media such as Co-Cr (Iwasaki, 1980; Hoffman, 1986). The factors contributing to perpendicular anisotropy will probably remain controversial until more is understood about the methods of fabricating these important materials.

2. Magnetostriction

While the intrinsic, macroscopic magnetic anisotropy energy is quite small in 3d-base amorphous alloys, that need
not be the case with its strain derivative, the magnetoelastic coefficient \( B_i \):

\[
B_i = \frac{\partial E_K}{\partial \varepsilon_i}.
\]  

As such, \( B_i \) represents a more easily measured probe of the microscopic interactions responsible for anisotropic magnetic properties in amorphous alloys. \( B_i \), is related to magnetostriction by the elastic constants

\[
\lambda_i = \frac{B_i}{C_{ij}}.
\]

From a fundamental point of view then, one can study the microscopic or local magnetic anisotropy mechanisms with greater sensitivity through the magnetostriction than through measurements of anisotropy itself. Unfortunately, a model is needed to describe how the local magnetoelastic strains are manifest on a macroscopic scale when they do not add coherently as they do in a crystal. Recently, Furthmüller, Fähnle, and Hertzner (1986) have gone beyond earlier attempts to address this fundamental problem of magnetoelastic interactions in amorphous and microcrystalline ferromagnets. Their theory appears to account correctly for the magnetoelastic strain arising from the randomly oriented local structural units [treated as noninteracting by O’Handley and Grant (1985)] as well as for the elastic interaction between these local units (assumed by Fähnle and Egami (1982) to be so strong as to destroy local strain correlations].

By measuring the temperature dependence of the magnetostriction, O’Handley (1978a) was able to determine the relative importance of single-ion (crystal field) and two-ion (anisotropic exchange) contributions to anisotropy—identified earlier by Callen (1968)—in a variety of 3d-base metallic glasses. This work has been reviewed recently (Lacheisserie, 1982; O’Handley, 1983; Lachowicz and Szmyczak, 1984). The magnetoelastic behavior of iron-base glasses is dominated by a strong positive local crystal-field term of uniaxial symmetry. In cobalt-base glasses this single-ion term appears to be much smaller and negative. Also a positive two-ion term of comparable magnitude is needed to consistently fit a wide range of phenomena in several different cobalt-rich alloys (O’Handley in B3, 1983). Competition between these mechanisms was shown to account for the vanishing of magnetostriction in cobalt-base glasses as well as for the anomalous temperature dependence, including magnetostriction compensation points, also observed there (O’Handley and Sullivan, 1981).

It was pointed out (Egami, private communication) that the method of measuring magnetostriction in all the above cases is uniaxial. Thus only the uniaxial component of the strain is measured and more complex distortions of the sample due to higher-order (cubic, etc.) strains are not detected. This criticism is certainly true. Thus the sign and magnitude of the microscopic mechanisms (one-ion, two-ion) identified to be responsible for the magnetostriction are in fact only those of the uniaxial component alone. However, the magnitude of higher-order terms is expected to drop off sharply with increasing \( l \).

The use of the concept of split bands (Sec. III D 1) in determining compositions of zero magnetostriction in T-M amorphous alloys was pointed out by O’Handley and Berger in 1976. The single-ion component of magnetostriction has its origin in the spin-orbit interaction (§ L-S) which couples the direction of magnetization (S) to the distortion of the local structure through the electron orbitals (L). The split-band model makes use of perturbation theory for spin-orbit corrections to the electronic band structure in order to predict magnetostriction zeros. To the extent that two-ion anisotropic exchange contributes to the magnetoelastic effects, predictions based on the split-band model will be in error. Because two-ion contributions appear to play a secondary role in magnetostriction even where they are detected, the split-band model has met with reasonable success in accounting for compositions of zero magnetostriction. Application of the split-band model to prediction of magnetostriction zeros has been reviewed by O’Handley (1983).

An interesting question arises relative to the magnetostriction of ferrimagnetic materials. Specifically, how does \( \lambda \) behave near magnetization compensation, especially if the magnetoelastic effects are due disproportionately to one sublattice (e.g., the R species)? (It should be born in mind that magnetoelastic strain is an even function of the magnetization, i.e., one does not simply associate negative \( \lambda \) with negative \( M \).) Takagi et al. (1979) measured \( \lambda \) in \( a \)-Gd-Fe and \( a \)-Tb-Fe sputtered films using a cantilever method. While amorphous Gd-Fe shows a weak positive magnetostriction with a minimum (\( \lambda = +7 \times 10^{-6} \) dipping to \( 4 \times 10^{-6} \)) at compensation (23 at. % Gd), \( a \)-Tb-Fe shows a much larger positive magnetostriction with no minimum at compensation (\( \lambda = 100 \times 10^{-6} \) at 21 at. % Tb), and a maximum, instead, of \( \lambda = 400 \times 10^{-6} \) at 34 at. % Tb. These results suggest that the contributions to magnetostriction of the R and T species in Gd-Fe are of opposite sign and in the same proportion as their contributions to the magnetization. However, for \( a \)-Tb-Fe, clearly the Tb contributes a large positive magnetostriction, adding to that of Fe, thus precluding magnetostrictive compensation. The magnetostriction thus increases with Tb content; apparently beyond at 34 at. % Tb the Curie temperature and net magnetization decrease sufficiently to bring the net magnetization down.

Twarowski and Lachowicz (1979) report the magnetostriction of \( a \)-Gd-Co to have a peak (\( \lambda = 31 \times 10^{-6} \)) near the composition 23 at. % Gd. It is expected that Fe and Co would contribute to \( \lambda \) in an R-Fe alloy with opposite signs \( \lambda(TbFe_x) = 693 \times 10^{-6} \) whereas \( \lambda(TbCo_{1-x}) = 63 \times 10^{-6} \) (Clark, 1980) implying for these alloys contributions relative to \( \lambda(Tb) = \lambda(Fe) > 0 \) and \( \lambda(Co) < 0 \), and the result quoted above for GdFe implies \( \lambda_{Gd} < 0 \). Thus these data for \( a \)-GdCo cannot be understood in such simple terms. Because of the importance of magnetostriction in establishing perpendicular anisotropy (Takagi, 1979), more should be learned about the local moment angular distributions and the effect of these on magnetoelastic strain. Also, care must be taken to exclude temperature effects by extending the magnetostriction measurements to low temperatures, as was done by Lacheisserie (1983) in \( a \)-Fe_{0.6}B_{0.4}La_{0.7}Tb_5.
Because of the technological importance of low magnetostriction, extensive efforts have been made to reduce the magnetostriction of amorphous alloys based on iron. Iron has a higher saturation magnetization and is more abundant in nature compared to cobalt; magnetostriction of Fe$_{82}$B$_{18}$ is approximately $32 \times 10^{-6}$ at ambient temperature (O’Handley, 1977a,b). Because of the presence of holes in the majority-spin band of iron-base glasses, it is not possible to apply the split-band model without serious assumptions. A purely empirical approach to the problem has been made instead. Room-temperature magnetostriction of iron-base glasses was shown to scale with $M^2$ (O’Handley, 1977b) so that $\lambda = 0$ could only be approached with the loss of magnetization. Nevertheless, it has been found that for certain TE substitutions for Fe, the coefficient of $M^2$ is quite large and $\lambda < 5 \times 10^{-6}$ can be achieved while retaining reasonable values of magnetization (Inomata et al., 1983; Yoshino et al., 1984). In these Fe-TE-metalloid alloys the decreased room-temperature magnetostriction is due partially to the suppressed Curie temperature.

A different approach to low magnetostriction in iron-base alloys had been considered earlier. It is known that rare-earth species can show very large positive (e.g., Tb) or negative (e.g., Sm) magnetostrictions (Clark, 1980; Clark et al., 1976). Kazama and Fujimori (1982) exploited this and have shown that the magnetostriction of sputtered amorphous Fe$_{83}$B$_{17}$ $(31 \times 10^{-6})$ could be enhanced $(40 \times 10^{-6})$ or suppressed $(20 \times 10^{-6})$ by substitution of as little as 1.3 at. % Tb or 5 at. % Sm, respectively, for Fe. R contributions to the magnetostriction are estimated to be $\lambda$(Tb) = $200 \times 10^{-6}$ and $\lambda$(Sm) = $-100 \times 10^{-6}$, Lacheiserie (1983) found the room-temperature magnetostriction of a-F$_{6}$-B to be reduced by the addition of 5 at. % of both Tb and La. This may be due to the suppression of the Curie temperature from 650 to 500 K.

More recent work on magnetostriction has focused sharply on the details of its behavior with composition, temperature, and thermal relaxation, especially in cobalt-rich, low magnetostriction alloys. New, more sensitive methods (compared to earlier work which relied on strain gauges and capacitance techniques) were developed for these demanding studies. The new methods are based on the inverse Wiedemann effect (Barandiari, Hernando, and Ascasibar, 1979; Hernando and Barandiari, 1980) and is measured by small-angle magnetization rotation (SAMR) using a transverse applied field (Hernando et al., 1982, 1983) or by sensing the rotation of a current-carrying ribbon in a longitudinal magnetic field.

New details of the composition dependence of stress-induced anisotropy (Nielsen et al., 1983) and of the behavior of single-ion and two-ion components of magnetostriction with temperature, thermal annealing (Hernando et al., 1984), and quench rate (Madurga et al., 1987) are emerging from these extensive and ongoing experiments. It appears that both single-ion ($\alpha$) and two-ion ($\beta$) magnetostriction components vary in similar ways with temperature during relaxation of the CSRO. The net effect, however, since $\alpha < 0$ and $\alpha + \beta = 0$, is for $\lambda$ to become more positive and then drop sharply negative before crystallization. Consequently, new compensation temperatures at which $\lambda$ vanishes have been observed in several new compositions (Hernando et al., 1984; Chen and Rao, 1986). Extension of such measurements can be expected to shed light on the physical significance of the separation of magnetostriction into single-ion and two-ion components.

With the growing use of low magnetostriction amorphous alloys in videotape heads, in switched-mode-power supply components (Boll, Hiltzinger, and Warlimont, 1983), and possibly in other very high-frequency, thin-film transformers (Tago, Nishimura, and Yanagisawa, 1985), it is critical to continue such fundamental investigations to allow for better alloy design and improved performance of zero-magnetostriction alloys.

3. Electron transport

Amorphous alloys have electrical resistivities falling typically in the range from 100 to 200 $\mu\Omega$ cm (3–5 times those of crystalline magnetic alloys). Metallic glasses are characterized by small positive or negative temperature coefficients of resistivity (TCR) (Mooij, 1973; Tsuei, 1986) which bear a close resemblance to those observed for liquid metals and alloys of similar composition (Güntherodt and Künzli, 1978). This similarity led those authors to apply the Ziman liquid-metal theory to the understanding of electrical transport in metallic glasses.

One immediate outcome of this theory was a simple explanation of the systematics of occurrence of positive or negative TCRs depending upon the values of the Fermi wave vector relative to the peak of the structure factor (Güntherodt and Künzli, 1978). Lin, Bewk, and Turnbull (1979) gave a valuable insight into the direction of resistivity change upon structural relaxation based upon this model. Faber’s extension of the Ziman theory was applied extensively to metallic glasses and significant insights into the static and dynamic structure factor emerged from extensive work by Nagel (1977). The interesting effects of hydrostatic pressure are treated in the diffraction model of electrical transport and related to the Mooij correlation by Cote and Meisel (1982). Other aspects of electron transport in amorphous solids are competently reviewed by Harris and Strom-Olsen (1983), Cote and Meisel (1981), and Rao (1983).

It is not intended that this field be reviewed again here. The above references are cited to give the interested reader a place to start. Also we only briefly mention the anisotropic electron transport effects characteristic of ferromagnetic materials, viz., the magnetoresitivity $(\rho_\parallel - \rho_\perp)$/$\rho = \Delta \rho/\rho$ (where $\parallel$ or $\perp$ refers to the field orientation relative to the direction of current) and spontaneous Hall effect because these were reviewed recently by McGuire, Gambino, and O’Handley (1980).

In a nonmagnetic material the application of a magnetic field perpendicular to the primary current can alter the longitudinal resistance $\Delta r/r$ and induce a Hall voltage in a direction orthogonal to both the current and applied field. In nonmagnetic materials these anisotropic effects can be understood as consequences of the Lorentz force on the primary current carriers. In a ferromagnetic material these ordinary anisotropic transport effects are generally
overshadowed by phenomena with similar geometrical dependencies but arising from the much stronger spin-orbit interaction between the current carrier (orbit) and the local magnetization (spin). Because of their origin in spin-orbit interaction (Hurd, 1972; Berger and Bergmann, 1980), the compositional dependence of anisotropic ferromagnetic transport effects can be well understood by the split-band model (O’Handley, 1978b). These transport effects probe the symmetry of the local crystal field because the spin-orbit interaction is a function of the local electric field gradient. Such indirect probes of local structure have never been fully exploited in advancing our understanding of SRO in amorphous alloys. Again the data for amorphous alloys are more easily compared with theory than are those for crystalline alloys because of the absence of phase boundary discontinuities in the former.

G. Quasicrystals

Quasicrystals (QCs) are a newly discovered class of materials first observed in the Al-Mn system (Shechtman et al., 1984). They show sharp powder diffraction peaks as do crystals (however, the peaks may be interference maxima (Stephens and Goldman, 1986), not Bragg peaks) and the diffraction patterns exhibit fivefold or other symmetry not allowed by classical crystallography. The diffraction peaks do not index to any known crystalline phase, instead they occur at intervals that are multiples of the golden ratio \( \tau = (1 + \sqrt{5})/2 \) (Bancel et al., 1985). The scattering can be explained by structures of randomly assembled icosahedra (Shechtman and Blech, 1985; Goldman and Stephens, 1986) or by Penrose tilings comprised of two rhombohedral bricks arranged so as to preserve long-range fivefold orientational order with translational quasiperiodicity rather than periodicity (Levine and Steinhardt, 1984, 1986). A third structural model proposed by Guyot and Audier (1985) describes the Al-Mn QC structure as a quasi-periodic distortion of the \( a\)-Al-Mn-Si crystal structure. In this structure there are no central atoms present in the icosahedral units. All three of these models give diffraction patterns in good agreement with scattering studies. The actual decoration of the Penrose lattice or of the icosahedral glass structure with various species of the QC alloy is an important issue not adequately resolved yet. Recent high-resolution scattering studies on \( Pd_{40}U_{20}Si_{30} \) quasicrystals strongly favor a three-dimensional Penrose tiling decorated with U atoms at the vertices and Pd and Si elsewhere in the structure (Kofalt et al., 1986). Another QC composition \( (Ti_{1-x}V_x)_{2}Ni \) (Zhang, Ye, and Kuo, 1985) does appear to have a Ni atom in the icosahedral site (Kuo, 1986). Different quasicrystal structures are suggested to apply to the Al-Mn-Si class and the \( (AlZn)_m (Mg)_n \) class of icosahedral phases because of the different values of their quasilattice constants (Elser, 1986; Henley and Elser, 1986). Levine and Steinhardt (1986) call these structure categories “local isomorphic classes” and consider their physical significance.

Quasicrystals appear to be metastable phases clearly distinct from the amorphous state. The fact that some metallic glasses transform directly to the crystalline state while others can pass through the quasicrystalline (icosahedral) state before crystallizing (Lilienfeld et al., 1985; Poon, Drehman, and Lawless, 1985) supports the classification of local amorphous structures into two types: amorphous I (nearly crystalline SRO) and amorphous II (noncrystalline SRO). Much of the research on quasicrystals began as an effort to model the structure of amorphous (presumably type II) materials (Nelson, 1983; Sadoc, 1980; Sethna, 1983; Levine and Steinhardt, 1984, 1986).

QCs appear to form at compositions where the preference for local icosahedral order is strong. This is the case for many Frank–Kasper (1958) phases (e.g., \( \chi, \alpha, \) and Laves phases). A classic example is the \( a\)-AlMnSi structure (for which the MacKay icosahedron is the important building block) which was proposed by Guyot and Audier (1985) as a basis for understanding the structure of QCs. One means of achieving the QC structure rather than long-range crystalline order is by some form of nonequilibrium processing, e.g., melt spinning (Shechtman et al., 1984), ion implantation (Budai and Aziz, 1986), ion mixing by energy beam irradiation (Knapp and Follstadt, 1985), or solid-state diffusion (Knapp and Follstadt, 1986). Thus, the QC state appears to be an intermediate phase between the glassy and crystalline states both in terms of the degree of atomic order and the extent of nonequilibrium processing needed to achieve that order (Fig. 1).

Most reported quasicrystals [e.g., \( Al-Mn-(Si, Al-(Fe,Cr,U,Mo,Ru), Pd-U-Si, Al-Li-Mg-Cu, (Ti_{1-x}V_x)_{2}Ni \) \( (x < 0.1) \), or \( (AlZn)_{49}Mg_{32} \)] are not strongly magnetic. However, the possibility of studying magnetic systems with such high site symmetry (as found in Frank–Kasper phases and some QCs) or with such high macroscopic symmetry (as found in QCs) has driven a search for strongly magnetic icosahedral phases (McHenry et al., 1986b). This search is supported by the observation of enhanced magnetic susceptibility in icosahedral Al-Mn alloys relative to their orthorhombic \( Al_{4}Mn \) crystalline phase (Hauser, Chen, and Waszczak, 1986; Youngquist et al., 1986). While crystalline \( Al_{4}Mn \) is nonmagnetic and has no Mn atom at the center of its McKay icosahedron, I-Al-Mn alloys show the presence of a local moment that increases with the square of the Mn concentration (Hauser, Chen, and Waszczak, 1986). However, Mössbauer studies (Swartzendruber et al., 1985) show an appreciable electric field gradient, i.e., no icosahedral symmetry, at the Fe (Mn) sites in I-Al-Mn. Also, NMR studies (Warren, Chen, and Hauser, 1985) have found no tendency toward stronger magnetism in QC AlMn relative to the crystalline state. Some results of a program to produce strongly magnetic icosahedral quasicrystals have appeared recently (O’Handley et al., 1986a; McHenry et al., 1987a).

Symmetry requires (McHenry et al., 1986a) that an atom in an icosahedral environment would have fully degenerate \( d \) orbitals (no crystal field splitting) and any orbitals of \( f \) symmetry would be split into a fourfold degenerate state and a threefold degenerate state unlike the \( f \) splitting in cubic symmetry (2-2-3). Consequently the DOS should be highly peaked and unusual magnetic and other physical properties would result depending upon the position of these peaks relative to \( E_F \) as well as upon the bonding or antibonding nature of the states at \( E_F \).
Icosahedral clusters of Al atoms show significant electronic stabilization relative to fcc clusters (McHenry et al., 1986a). The electronic density of states (Fig. 32) changes dramatically from \( D(E) \propto E^{1/3} \) behavior for \( O_h \) symmetry to a more peaked structure with an envelope varying as \( E^n \) with \( n > 1 \) for \( I \) symmetry in this free-electron system. This change in \( D(E) \) could give rise to a significant increase or decrease in \( D(E_F) \) in icosahedral aluminum-base alloys depending on the position of the Fermi energy. Calculations on Mn-centered icosahedral clusters indicate the Mn states occur at \( E_F \). Hence they give rise to appreciable local moments. The local moment observed in I-Al-Mn may therefore imply the occupation of some icosahedral sites by Mn in this system. [An alternative explanation for the observed moment given by Hauser, Chen, and Waszczak (1986) is that it results from Mn atom pair exchange interaction rather than site symmetry. See also McHenry and O’Handley (1987c).]

More recently McHenry et al. (1986c) have completed icosahedral cobalt cluster calculations. They found the electronic state densities to be similar in this \( d \)-electron system for clusters of fcc (\( O_h \)) and icosahedral (\( I_h \)) symmetry with slightly larger magnetic moment in the latter case (1.56 vs 1.61 \( \mu_B \)/Co atom, respectively) (Fig. 8).

The high degree of symmetry in the icosahedral group implies small values of the magnetic anisotropy. This is evident from an expansion of anisotropy energy in spherical harmonics such as Eq. (14) where highest symmetry terms, \( l = 0, 2, 4 \), would vanish for icosahedral symmetry. Furthermore, the multiplicity of symmetry axes in an icosahedral sample can be shown to give rise to a variety of new types of domain walls and to lead to easy magnetization by wall motion or rotation processes (McHenry et al., 1987a).

IV. SUMMARY

We have seen that the structures of metallic glasses lie between those of the more disordered liquids, stable at higher temperatures, and those of the more ordered quasicrystals and crystals, relatively more stable at lower temperatures. Metallic glasses transform upon heating either directly to the crystalline state or sometimes through an intermediate QC phase. It was pointed out that the absence of point defects and grain boundaries in amorphous alloys was crucial in allowing easy motion of magnetic domain walls while providing no path for dislocation motion. This leads to the unique combination of magnetic softness and mechanical hardness with high elastic limit which characterizes amorphous alloys and makes them so attractive for a variety of applications.

The paper then focused on the fundamental magnetic properties of metallic glasses moving from their roots in the atomic structure through the resulting electronic structure, and finally on to the specifics of magnetic moments, Curie temperatures, and the anisotropic properties.

We saw that far from being random in their atomic structure, amorphous metallic alloys are characterized by well-defined short-range order that can bear a resemblance to one of the stable or metastable crystalline compounds of similar composition (amorphous type I) or to some non-crystallographic arrangement (amorphous type II) such as icosahedral. Amorphous type I alloys are expected to have electronic structure like that of the related crystalline phase and fundamental magnetic properties that also bear a close relation to their magnitude and compositional dependence to those of that same crystalline phase. Amorphous type II alloys are expected to be somewhat more unique in their electronic structure and magnetic properties. The unusual magnetic behavior of Fe-metalloid glasses was reviewed. First noted was the disparity between the high Curie temperature of pure bcc Fe and the decreasing Curie temperature toward the low metalloid content limit of its glass forming range. This is now understood to be a consequence of the dense packing in the glassy phase, leading to increased antiferromagnetic exchange interaction with increasing Fe content. Next the more puzzling behavior exhibited by the Mössbauer spectra of Fe-M glasses was reviewed.

From atomic structure the review moved to a consideration of chemical bonding and electronic structure. It was pointed out that strong chemical and electronic differences exist between TE-TL glasses and T-M glasses. The former are bonded by ioniclike \( d-d \) electronegativity differences which result in electronic states being somewhat localized spatially around each species as well in a clustering of the electronic states into narrower and more separated energy ranges than obtain in the pure metallic constituents. The DOS shift toward greater binding energy upon alloying is greater for two species of greater valence difference. The charge transfer implicit in this electronegativity driven metallic bonding leaves the TE species with fewer \( d \) electrons and the TL species with fewer \( d \) holes. Thus there is a tendency to weaken the magnetic state as the \( d-d \) bonding strength increases in TE-TL alloys. T-M glasses show state densities dominated by the T metal \( d \) band and, unlike the TE-TL glasses, their \( d \) band is broadened relative to that of the pure metal to an extent that depends on the degree of \( (sp)-d \) hybridization. This hybridization is most pronounced when the interacting atomic states of the pure constituents are separated by small energy differences. The stronger the hybridization, the more strongly is magnetism suppressed in the alloy compared to that in the pure T metal. Polar \( s-d \) bonding also occurs in T-M alloys. Analogous to the \( d-d \) bonding in TE-TL alloys, its strength increases with increasing energy separation between the initial states. The competition between magnetism and bonding in TE-TL and T-M amorphous alloys reflects the close correlation between moment

\[
\text{FIG. 32. Density of states calculated by SCF-Xa-SW-MO method on 13- and 33-atom clusters of Al (McHenry et al., 1986a).}
\]
magnitude and heat of formation observed in transition metal alloys with nonmagnetic metals.

Four models of magnetic moment and Curie temperature variation in amorphous alloys were reviewed and compared. The relation between the magnetic valence model (applicable to a wide range of TE-TL and T-M alloys) and the coordination model (more accurate in predicting moment variation in a narrower class of alloys) was explored. Concepts of chemical ordering as expressed by nearest-neighbor coordination and heats of formation were reviewed. These models suggest a prescription for alloy formation with minimal degradation of magnetism of the pure constituent(s): small metalloid size for small T coordination about M sites and thus minimal p-d hybridization, while preserving high T-T coordination. These factors would be reflected in positive or in small negative alloy heats of formation and large magnetic valence. Moreover, for Fe-rich alloys, Fe-Fe spacings must not be so small as to introduce AF exchange coupling. Small Co-Co spacing is favorable to moment and Curie temperature strength.

Anisotropic properties were reviewed in a more superficial way because of excellent earlier treatments of those fields and the elementary state of relating our understanding of the anisotropic aspects of atomic and electronic structure to their influence on these physical properties. A final word was offered on what may become a sequel to amorphous magnetism, namely, the possibility of magnetism in icosahedral structures. While no strongly magnetic quasicrystals appear to have been fabricated yet, new metastable alloys with magnetic properties clearly distinct from their amorphous and equilibrium phases have emerged.

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