Magnetostriction of transition-metal-metalloid glasses: Temperature dependence

R. C. O'Handley

Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960 (Received 26 September 1977)

Linear, saturation magnetostrictions λ_s of a variety of $(\text{FeCoNi})_{80}B_{20}$ glasses have been studied as a function of temperature. Magnetostrictions over the range 4.2 K $\leq T \leq T_c$ for selected glasses, Fe₈₀B₂₀, Co₄₀Ni₄₀B₂₀, and Ni₅₀Fe₃₀B₂₀, are shown to follow reasonably well the theory of Callen and Callen for singleion anisotropy of uniaxial-strain symmetry, i.e., $\lambda_s(T)/\lambda_s(0) = \hat{I}_{5/2}(X) \equiv I_{5/2}(X)/I_{1/2}(X)$ with $I_{3/2}(X) \equiv m(T)$, the reduced magnetization. The anomalous temperature dependence of the magnetostriction observed in the cobalt-rich (FeCo)₈₀B₂₀ glasses is attributed to the combination of a positive two-ion (anisotropic-exchange) term plus a stronger, negative, one-ion (crystal-field) term. A change of sign in λ_s occurs along the Co-Ni side of the triangular Fe-Co-Ni(B₂₀) diagram due to a change in sign of the dominant single-ion mechanism. This sign change results from a change in the orbital character of the states at the Fermi energy as it passes from the top of the cobalt or nickel 3d⁴ band to the bottom of the iron 3d⁴ band.

I. INTRODUCTION

Recent interest in metallic glasses¹ (noncrystalline metallic alloys) may be attributed both to their technological potential²⁻⁴ and to the fact that they represent a novel isotropic medium in which to study a variety of physical phenomena. Of growing interest among the magnetic properties of transition-metal-metalloid (TM-M) glasses are their magnetic anisotropy⁵⁻¹⁰ and magnetostriction.^{2, 11-14} Information on the orbital character of the magnetic electrons can be obtained from such measurements while saturation magnetic moments give information about the number of unpaired spins per atom. However, the weak magnetic anisotropy $(10^2-10^4 \text{ erg/cm}^3)$ of TM-M glasses is difficult to measure accurately. Consequently, numerous examples of conflicting, or at least inconsistent, studies of magnetic anisotropy in TM-M glasses⁵⁻¹⁰ exist in the literature.

Magnetostrictions of metallic glasses are generally not much smaller than those of comparable crystalline alloys and thus provide a viable means of studying magnetic anisotropy. Magnetostriction is related to the strain derivative of the anisotropy energy.¹⁵ The magnetic Hamiltonian with exchange and crystal-field terms, respectively.¹⁶

$$H = \vec{\mathbf{S}}_i \cdot \vec{\mathbf{J}}_{ij} \cdot \vec{\mathbf{S}}_j + \vec{\mathbf{S}}_i \cdot \vec{\mathbf{D}} \cdot \vec{\mathbf{S}}_i \tag{1}$$

where \vec{S}_i is the spin operator at site *i*, may therefore be generalized to include magnetoelastic effects by expanding \vec{J}_{ij} and \vec{D} to first order in the strain ϵ_u :

$$H = \vec{\mathbf{S}}_{i} \cdot \vec{\mathbf{J}}_{ij}^{0} \cdot \vec{\mathbf{S}}_{j} + \vec{\mathbf{S}}_{i} \cdot \vec{\mathbf{D}} \cdot \vec{\mathbf{S}}_{i}$$
$$+ \epsilon_{\mu} \vec{\mathbf{S}}_{i} \cdot \frac{\partial \vec{\mathbf{J}}_{ij}}{\partial \epsilon_{\mu}} \cdot \vec{\mathbf{S}}_{j} + \vec{\mathbf{S}}_{i} \cdot \frac{\partial \vec{\mathbf{D}}}{\partial \epsilon_{\mu}} \cdot \vec{\mathbf{S}}_{i} \cdots .$$
(2)

The equilibrium strain is obtained by adding to Eq. (2) the elastic energy $\frac{1}{2}C_{\mu}\epsilon_{\mu}^{2}$, treating the strain derivatives as perturbations, and minimizing the resulting free energy with respect to ϵ_{μ} . Magnetic anisotropy may arise from either of the resulting anisotropic terms $\langle S_{i}^{z}S_{j}^{z} \rangle$ and $\langle (S_{i}^{z})^{2} \rangle$ with appropriate two-ion or one-ion coefficients; magnetostriction may arise from either of the anisotropic terms with the appropriate strain-derivative coefficients.

Measurements of the temperature dependence of magnetostriction in $Fe_{80}B_{20}$ glass have, accordingly, provided the first clear indication of the nature of the anisotropic interaction responsible for magnetostriction (and presumably also for intrinsic magnetic anisotropy) in TM-M glasses.¹³ In the present paper, these measurements are extended to cobalt- and nickel-containing metallic glasses,¹⁷ and conclusions concerning the nature and origin of magnetostriction in TM alloys are drawn.

In Sec. II, some important experimental considerations are presented. Section III briefly summarizes the theoretical basis for interpreting the temperature-dependence results which are found in Sec. IV. Discussion and a summary of conclusions are found in Secs. V and VI, respectively.

Before an investigation of the temperature dependence of magnetostriction in metallic glasses can be pursued, however, it is important to note first the isotropic nature of magnetoelastic effects in metallic glasses. Secondly, it should be made clear that the low-field effects resulting from changes in domain patterns of unsaturated materials by stress-relief and field-annealing¹⁸⁻²⁰ below the crystallization temperature have no bearing on magnetic properties measured above saturation (e.g., λ_s). Thirdly, it should be remarked that the

930

18

temperature dependences observed here are characteristic of the glassy state and in no way resemble the behavior of $\lambda_s(T)$ in the crystallized²¹ samples of the same compositions.²²

II. EXPERIMENTAL

Essential details of the process of fabricating the metallic glass ribbons²³ and of making the magnetostriction measurements¹²⁻¹⁴ have been presented elsewhere. For magnetostriction measurements, semiconductor strain gauges were used at room temperature and metal foil gauges and polyamide adhesive were used for the temperature-dependent studies. Sample temperature was measured with a Chromel-alumel thermocouple $(T \ge 77 \text{ K})$ and a cryogenic linear temperature sensor²⁴ ($4.2 \le T \le 80 \text{ K}$) in intimate contact with the specimen. Magnetization measurements were performed with a commercial vibrating sample magnetometer. Curie temperatures were determined by the equation of state (Arrott) method.

III. THEORETICAL BACKGROUND

The temperature dependence of magnetostriction can reveal information about the nature of the mechanisms causing the magnetoelastic effects as well as, by association [(Eq. (2)], those causing magnetic anisotropy. The basis for obtaining such information is the quantum-statisticalmechanical theory of Callen and Callen.^{16, 25, 26}

This theory is derived from a Hamiltonian for localized-moment, crystalline, magnetic materials. However, in addition to describing well the magnetostriction and anisotropy in a variety of magnetic insulators,^{16, 27, 28} it has proven to be applicable to crystalline rare-earth metals^{17, 26, 29} and, to some extent, to the crystalline transition metal Ni.^{16, 30} The behavior of magnetostriction in crystalline iron³¹ and cobalt³² is complex and not well understood. More recently the theory of Callen and Callen has been shown to describe $\lambda(T)$ in the iron-rich glass Fe₃₀B₂₀.¹³ The present results suggest that the theory is in fact generally applicable to transition metals, at least in the isotropic glassy state.

The theory describes the temperature dependence of magnetostrictive strains (and magnetic anisotropy) in terms of thermally averaged singleion $\langle (S_i^{g})^2 \rangle$ and two-ion, $\langle S_i^{g}S_j^{g} \rangle$ and $\langle \mathbf{\bar{S}}_i \cdot \mathbf{\bar{S}}_j \rangle$, spincorrelation functions. These three terms give rise, respectively, to (i) single-ion anistropy and single-ion anisotropic magnetoelastic effects, (ii) two-ion anisotropy (anisotropic exchange) and linear magnetostriction arising from such anisotropic, two-ion interactions and (iii) zeroth order (isotropic) terms in the magnetic energy and isotropic, volume magnetostriction and anomalous thermal expansion. The effects arising from isotropic exchange $\langle \mathbf{\tilde{S}}_i \cdot \mathbf{\tilde{S}}_j \rangle$ are generally larger than the anisotropic effects, however, they are not discussed further here.^{26, 33}

The anisotropic spin-correlation functions [(i) and (ii) above], show characteristic temperature dependences. Therefore, the temperature dependence of reduced magnetostriction should reveal the single-ion or two-ion nature of the anisotropic spin correlations. Further description of the detailed mechanism (e.g., spin-orbit, spin-other-orbit, or spin-spin interaction)³⁴ is not possible in metals by this method.

IV. RESULTS

Room-temperature magnetostrictions have been reported for the two series of glasses $Fe_{80-x}T_xB_{20}$ (T = Co, Ni).^{12, 14} These data are displayed here on a triangular diagram (Fig. 1) which includes new data on $(CONi)_{80}B_{20}$ glasses and several pseudoternary $(FeCONi)_{80}B_{20}$ glasses. One important feature of Fig. 1 is the line connecting compositions of zero magnetostriction.³⁵ This line is essentially temperature independent and will be discussed in more detail below.

In order to gain insight into the origin of magnetostriction in these materials, particularly with regard to sign changes in λ_s , it is desirable to study the temperature dependence of λ_s in at least three compositions, rich in Fe, Co, and Ni, respectively. However, the Ni-rich glasses in the area roughly bounded by the dotted line in Fig. 1, are not presently fabricable by continuous, rapidquench techniques. Also the Curie temperatures



FIG. 1. Magnetostriction as a function of TM content for (FeCoNi)_{80}B_{20} glasses. Solid line: $\lambda = 0$. Compositions to the Ni-rich side of dotted line are not currently fabricable.

932

TABLE I. Curie temperature T_c , crystallization T_x
and ambient magnetostriction of the metallic glasses
chosen for comparison with theory.

Glass composition	Т _С (К)	^(К)	10 ⁶ λ _s (295 K)	
$\mathrm{Fe}_{80}\mathrm{B}_{20}$	647	720	+ 32	
$Ni_{50}Fe_{30}B_{20}$	575	685	+8	
$\mathrm{Co}_{40}\mathrm{Ni}_{40}\mathrm{B}_{20}$	610	615	-7	
$\mathrm{Co}_{70}\mathrm{Fe}_{10}\mathrm{B}_{20}$	~850	~ 675	+4	
$Co_{74}Fe_6B_{20}$	~840	~650	+0.6	
$Co_{80}B_{20}$	~830	~625	-4	

 T_c of cobalt-rich glasses generally exceed their crystallization temperatures T_x to the extent that the magnetization and magnetostriction vary little from 4.2 K to T_x (see Fig. 7 below). This renders a comparison with theory difficult. Attention was focused, therefore, on the three representative glasses $Fe_{80}B_{20}$, $Ni_{50}Fe_{30}B_{20}$, and $Co_{40}Ni_{40}B_{20}$. Their Curie and crystallization temperatures as well as λ_s (295 K) are shown in Table I. In these glasses, T_c is sufficiently less than T_x that $\lambda(T)$ may be measured up to T_c without danger of devitrification. The temperature dependence of λ_s in cobalt-rich glasses is described separately.

Figures 2-4 show the temperature dependence of magnetostriction and magnetization for the three selected metallic glasses. The quantities displayed here, $\lambda(T, 2 \text{ kOe})$ and $\sigma(T, 8 \text{ kOe})$, do not vanish at $T = T_c$ because of the applied field.³⁶ Below $T/T_c \approx 0.8$ they are equivalent, within experimental error, to saturation values.

Figure 5 shows the reduced-temperature dependence of $\lambda_s(T)/\lambda_s(0)$ and $\sigma(T)/\sigma(0)$ for $\operatorname{Fe}_{80}B_{20}$ glass only. The data points here are taken from the average line drawn through the data in Fig. 2. The inset shows that the magnetostriction varies as $[m(T)]^3$ up to $T/T_c \approx 0.6$. Figure 5 illustrates the intermediate step in preparing the data for comparison with the theory in which the temperature dependence of $\lambda_s(T)$ is expressed in terms of the parameter $\sigma(T)$.

Figure 6 plots the reduced magnetostrictions as functions of the reduced magnetizations for the three samples. Theoretical lines for single-ion anisotropy of uniaxial symmetry $\hat{I}_{5/2}(X)$, and cubic symmetry $\hat{I}_{9/2}(X)$ and for anisotropic two-ion exchange of uniaxial symmetry, $[m(T)]^2$, are shown



FIG. 2. Magnetostriction (left-hand scale) and magnetization in 8 kOe (right-hand scale) as a function of temperature in $Fe_{80}B_{20}$ glass.



FIG. 3. Magnetostriction (left-hand scale) and magnetization in 8 kOe (right-hand scale) as a function of temperature in $Ni_{50}Fe_{30}B_{20}$ glass.



FIG. 4. Magnetostriction (left-hand scale) and magnetization in 8 kOe (right-hand scale) as a function of temperature in $Co_{40}Ni_{40}B_{20}$ glass. Note λ (T) < 0.



FIG. 5. Magnetostriction and magnetization, normalized to their T=0 K values, as a function of T/T_c in Fe₈₀B₂₀ glass. Inset shows on a log-log scale the dependence of $\lambda(T)/\lambda(0)$ on $m(T) \equiv \sigma(T)/\sigma(0)$.

for comparison. The error bars associated with the data reflect maximum uncertainty due to scatter in the data points from run to run on a given sample, variations from sample to sample of the same nominal composition, error due to extra-



FIG. 6. Observed dependence of reduced magnetostriction on reduced magnetization in three metallic glasses. Theoretical dependences are included for comparison.

polation of $\lambda(T)$ to T = 0 in the Ni- and Co-containing glasses, and instrumental uncertainty. The data show no significant contributions to the magnetostriction from strain associated with values of l > 2. Thus, the samples are well characterized as macroscopically isotropic in their magnetostriction: the magnetization direction is a direction of uniaxial strain symmetry. (This is not necessarily the case for anisotropic media.)

The data for all three glasses follow single-ion theory of uniaxial strain symmetry reasonably well over most of the magnetization range.³⁷ $Fe_{80}B_{20}$ deviates from $\hat{I}_{5/2}(X)$ behavior for $m(T) \leq 0.5$ or $T/T_C \geq 0.85$. This may be associated with the strong field dependence shown by magnetic properties of metallic glasses near T_C .³⁶ Only the cobalt-containing metallic glass shows any appreciable tendency toward two-ion magnetostriction behavior although it is within experimental error of the single-ion curve.

Figure 7 displays $\lambda_s(T)$ and $\sigma(T)$ for three Corich glasses (magnetization of $\text{Co}_{74}\text{Fe}_6\text{B}_{20}$ glass is essentially the appropriately weighted average of the two magnetization curves shown). Magnetization data are roughly extrapolated beyond T_x to illustrate approximate T_c 's. [The best fitting Brillouin function, $S \simeq 2$, suggests T_c 's closer to 950 K but the fit is not good. The arguments to follow are not sensitive to the precise nature of the $\sigma(T)$ extrapolation.] The lines drawn through the magnetostriction data illustrate the average, *reversible* trend up to crystallization.



FIG. 7. Temperature dependence of magnetostriction (left-hand scale) and magnetization (right-hand scale) up to crystallization in three cobalt-rich glasses. Magnetization is extrapolated to approximate Curie temperatures (see text).



FIG. 8. Magnetostriction data from Fig. 7 compared with theoretical curves (solid lines) which include a twoion contribution to magnetostriction in cobalt-rich glasses (see Table II).

The marked curvature in $\lambda_s(T)$ for $\operatorname{Co}_{80}\operatorname{B}_{20}$ glass between 400 and 600 K is greater than would be expected considering the data for $\operatorname{Co}_{70}\operatorname{Fe}_{10}\operatorname{B}_{20}$ glass and the approximate Curie temperatures. In fact, the data suggest a magnetostriction-compensation temperature of approximately 660 K for $\operatorname{Co}_{80}\operatorname{B}_{20}$ glass.

The behavior shown in Fig. 7 can be explained by assuming the magnetostriction of $\text{Co}_{80}\text{B}_{20}$ to contain, in addition to a dominant single-ion term, a two-ion component sufficiently small to be consistent with Fig. 6. Because magnetostriction of single-ion origin drops off more rapidly with increasing temperature than does that of two-ion origin, the latter contribution will be proportionately more significant closer to T_{c} . Thus, a magnetostriction of the form

$$\lambda_{s}(T) = C_{1}\hat{I}_{5/2}(X) + C_{2}m^{2}$$
(3)

with $C_1 < 0 < C_2$ and $|C_1| > |C_2|$, will change sign

from negative at low temperatures to positive for $T \leq T_{c}$.³⁸ To describe $\lambda_s(T)$ in the two compositions which contain both Fe and Co, the single-ion terms of $Fe_{80}B_{20}$ and $Co_{80}B_{20}$ must be combined linearly and the two-ion term may vary either quadratically (if only Co-Co anisotropic interactions are important) or linearly (if both Co-Co and Co-Fe anisotropic interactions are important) with cobalt content. The linear variation of two-ion terms [shown in Fig. 8 for the choice of $\lambda_{s}^{Co}(T)$ = 6.8 $m^2 - 10.2 \hat{I}_{5/2}(X)$] gives a better fit to the data than the quadratic one [for which $\lambda_s^{Co}(T) = 4.6 m^2$ $-8\hat{I}_{5/2}(X)$ is a good choice]. Both theoretical forms show the same general features which mark the data of Fig. 7 as not simply of single-ion origin.39

935

Table II summarizes the results of the present magnetization and magnetostriction measurements. The parentheses around the + two-ion contribution for $\text{Co}_{40}\text{Ni}_{40}\text{B}_{20}$ glass signify the inconclusive nature of the results for that composition (Fig. 6). The last column gives the magnetoelastic coefficients for 0 K. Room-temperature elastic constants of metallic glasses generally increase by less than 5% from room temperature to 0 K.^{33, 42} This variation, less than the error bars on the data (Fig. 6), would bring the high-temperature data closer to the single-ion curve and would not alter the overall conclusions drawn from the $\lambda_s(T)$ data.

For the sake of comparison, in iron⁴³ $B_1 \simeq -29 \times 10^6 \text{ erg/cm}^3$ and $B_2 \simeq +32 \times 10^6 \text{ erg/cm}^3$, smaller in magnitude than the value for $\text{Fe}_{80}\text{B}_{20}$ glass. In nickel,⁴³ $B_1 \simeq +62 \times 10^6 \text{ erg/cm}^3$ and $B_2 \simeq 90 \times 10^6 \text{ erg/cm}^3$, much stronger than the value for Ni₅₀ Fe₃₀B₂₀ glass (magnetostriction decreases monotonically on going from Fe₈₀B₂₀ glass toward Ni₈₀B₂₀ glass).^{12, 14}

TABLE II. Summary of present results on four metallic glasses: magnetization as a function of temperature (columns 2 and 3) and magnetostriction as a function of temperature (columns 4-6). Magnetoelastic constants (last column) are derived from the equation $B = -\frac{3}{2}\lambda_s(C_{11} - C_{12}) = -\frac{3}{2}\lambda_s E/(1+\nu)$, where E and ν are Young's modulus and Poisson's ratio, respectively.

				<u> </u>			· .
Metallic glass composition (at.%)	σ(0,8 kOe) (emu/g)	Т _С (К)	10 ⁶ λ _s (0)	Or one-ion	igin two–ion	$\binom{C_{11} - C_{12}}{\binom{10^{12} \text{ erg}}{\text{cm}^3}}$	$\frac{B(0)}{(\frac{10^6 \text{ erg}}{\text{ cm}^3})}$
$\mathbf{Fe}_{80}\mathbf{B}_{20}$	190	647	+48	+	~0	1.28ª	-94.3
$Co_{80}B_{20}$	115	> 800	-4	·	+	1.33ª	+7.98
$\mathrm{Co}_{40}\mathrm{Ni}_{40}\mathrm{B}_{20}$	67.5	610	-10.5		(+)	~1.20 b	+18.9
$Ni_{50}Fe_{30}B_{20}$	97.6	575	+12.2	+	~0	~1.16°	-21.2

^aSee Refs. 40 and 41.

^bExtrapolation of results in Ref. 41 gives $E = 14.8 \times 10^3 \text{ kg/mm}^2$ for Ni₈₀B₂₀. Assuming $\nu = 0.35$, then C₁₁ - C₁₂ = 1.07 × 10¹² erg/cm³ for Ni₈₀B₂₀ and the elastic parameter in the table for Co₄₀Ni₄₀B₂₀ may be obtained by averaging those for Co₈₀B₂₀ and Ni₈₀B₂₀.

 $^{\circ}E = 15.8 \times 10^3 \text{ kg/mm}^2$ from Ref. 41 and we assume $\nu \simeq 0.33$.

V. DISCUSSION

A. Significance of single-ion behavior

The results shown in Fig. 6 indicate that in TM-M glasses the strain derivative of magnetic anisotropy energy (and by implication, the magnetic anisotropy energy itself) arises principally from crystal-field effects and not from anisotropic interatomic interactions. It is reasonable to expect that these two mechanisms would have a similar relative importance in crystalline 3d metals and alloys. That is, the predominance of singleion anisotropy over two-ion anisotropic exchange is a characteristic of the transition metal species; it is essentially independent of any nonmagnetic species which may be present as well as of the long-range order of the material. (When the single-ion contribution becomes small as, for example, when $\langle L_z \rangle$ vanishes, the two-ion contribution may be observable. See, e.g., Fig. 8.)

Yosida⁴⁴ has argued similarly that the mechanism for magnetic anisotropy in 3*d metals* (which at that time had not been determined) should be essentially the same as is observed in *insulators* (single-ion). This is born out by the present results on metallic, TM-M glasses.

Luborsky and Walter⁴⁵ have shown the kinetics and temperature dependence (above 400 K) of the field-induced anisotropy of Fe-Ni base glasses to follow an ordered-pair theory reasonably well, except in the Fe-rich limit. However, their results may also be consistent with the single-ion behavior reported here for the strain derivative of the magnetic anisotropy. This is because, although the anisotropy is of crystal-field origin, field-induced changes in the anisotropy may result from pairs of atoms moving so as to alter the crystal field. A uniaxial, crystal-field anisotropy varies with temperature as $[\sigma(T)/\sigma(0)]^2$ for $T/T_c \gtrsim 0.6$ and therefore cannot be distinguished from an ordered pair anisotropy in this temperature range.

B. Origin of zero magnetostriction

In *insulating* materials and in rare-earth metals, where electrons that give rise to magnetism are localized, it is possible to describe the ionic states in terms of their atomic wave functions. In these cases, as opposed to 3d transition metals and their alloys, theories have been more successful in explaining magnetic anisotropy and magnetostriction.^{34, 44, 46} The magnitude of the anisotropic effects, which are generally attributable to spin-orbit interaction, tends to scale with the expectation value of orbital angular momentum,⁴⁷ and to change sign when the low-lying levels pass from less than, to more than, half filled.⁴⁸

Efforts have been made to understand the magnetostriction of 3*d metals* in terms of simple band models.^{49,50} More recently, Berger has developed a split-band model^{51,52} with which sign changes in magnetostriction are predicted to occur when the Fermi energy passes through the middle of the *d* band of a given species or between the *d* bands (distinct on an energy scale) of two transition elements.⁵³ The model has been applied successfully to the crystalline Fe-Ni-Cu system.⁵²

The split-band model has recently been shown⁵⁴ to predict very well the observed path of the $\lambda_s = 0$ line close to the Fe-Ni side (the split-band region) of the triangular (FeCoNi)₈₀B₂₀ diagram (Fig. 1). The model associates this line with the passage of the Fermi energy through the boundary between the Ni and Fe 3d⁺ bands.

Inasmuch as it is based on an intra-atomic spinorbit interaction of the *d* states at E_F , the splitband model describes a one-ion magnetostriction. It is to be expected, therefore, that removal of the two-ion magnetostriction component observed in the cobalt-rich glasses would improve the agreement between the predicted and observed $\lambda_s = 0$ lines. Figure 9 shows that this is the case. The slope and intercept of the line joining compositions of zero single-ion magnetostriction (dashed line) is well described by the split-band model (dotted lines) in the split-band (Fe-Ni) regime. The remaining discrepancy on the Fe-Co side of the figure may then be attributed to the inapplicability of the split-band model to the Fe-Co system.

The split-band model suggests, therefore, that



FIG. 9. Solid line: Course of observed $\lambda_s = 0$ in (FeCo Ni)₈₀B₂₀ glasses. Dashed line: observed $\lambda_s = 0$ line with two-ion component removed. Dotted lines: predicted $\lambda_s = 0$ lines from split-band model for limiting values of charge transfer (see Ref. 54).

936

the sign change of λ_s along the cobalt-nickel side of Fig. 1 is associated with a change in the oneion orbital character of the *d* states at the Fermi energy.⁵⁵

VI. CONCLUSIONS

(i) Magnetoelastic effects in saturated TM-M glasses are isotropic and are, therefore, fully characterized by a single, temperature-dependent coefficient, $\lambda_s^I(T)$ or $B^I(T)$ with l=2.

(ii) Measurements of $\lambda_s(T)$ in Fe₈₀B₂₀, Co₄₀Ni₄₀B₂₀ and Ni₅₀Fe₃₀B₂₀ glasses suggest that magnetoelastic effects (and anisotropy) of these glasses are dominated by single-ion mechanisms rather than anisotropic interatomic interactions.

(iii) $\lambda_s(T)$ in cobalt-rich (FeCo)₈₀B₂₀ glasses is well described by assuming a positive two-ion contribution in addition to a dominant, negative single-ion contribution.

(iv) A change of sign in λ_s occurs near Co₇₅Fe₅B₂₀; this is due to a change in the sign of the singleion term, not the introduction of the two-ion term.

(v) The dominance of one-ion contributions to

the anisotropic effects (already recognized in insulators containing transition elements) is probably characteristic of transition metals regardless of the presence or absence of long-ranged structural order or even the presence of a significant fraction of nonmagnetic species (e.g., 20 at.%B).

(vi) The sign change in λ_s near the cobalt-nickel side of the triangular (Fe-Co-Ni)₈₀B₂₀ diagram is associated with a change in the one-ion orbital character of the *d* states at Fermi energy as E_F passes from the top of the Co or Ni $3d^{\dagger}$ band to the bottom of the Fe $3d^{\dagger}$ band.

ACKNOWLEDGMENTS

The author is most indebted to C.-P. Chou, R. Ray, and M. C. Narasimhan of this laboratory for supplying the high-quality metallic glass ribbons. At various stages of this work helpful discussions were had with R. Hasegawa, C.-P. Chou, L. A. Davis, E. A. Nesbitt, J. C. M. Li, D. I. Paul, P. J. Flanders, J. J. Rhyne, E. Callen, and F. E. Luborsky. These are all gratefully acknowledged.

- ¹J. J. Gilman, Phys. Today <u>28</u>, 46 (1975); P. Duwez, Ann. Rev. Mater. Sci. 6, 83 (1976).
- ²T. Egami, P. J. Flanders, and C. D. Graham, Jr., Appl. Phys. Lett. <u>26</u>, 128 (1975); AIP Conf. Proc. <u>24</u>, 697 (1975).
- ³R. C. O'Handley, L. I. Mendelsohn, R. Hasegawa, R. Ray, and S. Kavesh, J. Appl. Phys. <u>47</u>, 4660 (1976).
- ⁴F. E. Luborsky, Amorphous Magnetism II, edited by R. Levy and R. Hasegawa (Plenum, New York, 1977), p. 345.
- ⁵M. Takahashi, F. Ono, and K. Takakura, Jpn. J. Appl. Phys. <u>15</u>, 183 (1976).
- ⁶T. Egami and P. J. Flanders, AIP Conf. Proc. <u>29</u>, 220 (1976).
- ⁷F. E. Luborsky, AIP Conf. Proc. <u>29</u>, 209 (1976); F. E. Luborsky and J. L. Walter, Mater. Sci. Eng. <u>28</u>, 77 (1977).
- ⁸R. Hasegawa, AIP Conf. Proc. <u>29</u>, 216 (1976).
- ⁹C. L. Chien and R. Hasegawa, J. Appl. Phys. <u>47</u>, 2234 (1976); AIP Conf. Proc. <u>29</u>, 214 (1976); IEEE Trans. Mag <u>12</u>, 951 (1976).
- ¹⁰A. M. van Diepen and F. J. A. den Broeder, J. Appl. Phys. 48, 3165 (1977).
- ¹¹ A. W. Simpson and W. G. Clements, IEEE Trans. <u>11</u>, 1338 (1975); N. Tsuya, K. I. Arai, Y. Shiraga, and T. Masumoto, Phys. Lett. <u>A51</u>, 121 (1975); N. Tsuya, K. I. Arai, Y. Shiraga, M. Yamada, and T. Masumoto, Phys. Status Solidi A <u>31</u>, 557 (1975); H. A. Brooks, J. Appl. Phys. <u>47</u>, 334 (1975); H. Fujimori, K. I. Arai, H. Shirae, H. Saito, T. Masumoto, and N. Tsuya, Jpn. J. Appl. Phys. <u>15</u>, 705 706 (1976); L. Kraus and J. Sch-
- neider, Phys. Status Solidi A 39, K161 (1977). ¹²R. C. O'Handley in *Amorphous Magnetism* II, edited by
- R. Levy and R. Hasegawa (Plenum, New York, 1977),

p. 379.

- ¹³R. C. O'Handley, Solid State Commun. <u>22</u>, 458 (1977).
- ¹⁴R. C. O'Handley, Solid State Commun. <u>21</u>, 1119 (1977).
- ¹⁵R. Becker, Z. Phys. <u>62</u>, 253 (1930).
 ¹⁶E. Callen, J. Appl. Phys. <u>39</u>, 519 (1968).
- ¹⁷A preliminary report of these results is found in R. C.
 O'Handley, Bull. Am. Phys. Soc. <u>22</u>, 458 (1977).
- ¹⁸B. S. Berry and W. C. Pritchet, Phys. Rev. Lett. <u>34</u>, 1022 (1975).
- ¹⁹B. S. Berry and W. C. Pritchet, AIP Conf. Proc. <u>34</u>, p. 292; H. S. Chen, S. D. Ferris, E. M. Gyorgy, H. J. Leamy, and R. C. Sherwood, Appl. Phys. Lett. <u>26</u>, 405 (1975); F. E. Luborsky, J. J. Becker, and R. O. Mc-Cary, IEEE Trans. <u>11</u>, 1644 (1975).
- ²⁰Field annealing is a thermally activated process characterized reasonably well by the rate equation $\tau = \tau_0 e^{\Delta E/k_B T}$. In Fe₇₅P₁₅C₁₀ $\Delta E \approx 1.0$ eV and $\tau_0 = 7.4 \times 10^{-7}$ sec for field annealing (Ref. 4 and 18) so that τ (500 K) 8.8×10^3 sec. For Fe₄₀Ni₄₀P₁₄B₆ glass (METGLAS alloy 2826) $\Delta E = 1.35$ eV and $\tau_0 \simeq 7.6 \times 10^{-16}$ so that τ (500 K) $= 3 \times 10^{-2}$ sec (Refs. 4 and 7). (METGLAS is a registered trademark of Allied Chemical Corporation).
- ²¹Crystallization is a kinetic process characterized reasonably well in the temperature range 500-700 K by the rate equation $\tau = \tau_0 e^{\Delta E/k_B T}$. For Fe₃₀B₂₀ glass $\tau_0 = 1.75 \times 10^{-17}$ sec and $\Delta E = 2.67$ eV [F. E. Luborsky, Mater. Sci. and Eng. <u>28</u>, 138 (1977) or Ref. 4]. Therefore, τ (600 K) = 4.6×10⁵ sec and τ (650 K) = 8.6×10³ sec. For Co₈₀B₂₀ glass $\tau_0 = 2.21 \times 10^{-18}$ sec and $\Delta E = 2.66$ eV so that τ (600 K) = 4.8×10⁴ sec and τ (650 K) = 9.1×10² sec. [C.-P. Chou, (unpublished)].

²²R. C. O'Handley, (unpublished).

²³S. Kavesh in *Metallic Glasses*, edited by J. J. Gilman and H. J. Leamy (American Society for Metals, Metals) Park, Ohio, 1977) p. 36; H. H. Liebermann and C. D. Graham Jr., IEEE Trans. 12, 921 (1976).

- ²⁴Micro-Measurements Corp., 28905 Chase Road, Rom-
- ulus, Michigan 48174; J. C. Telinde, MDAC paper WD 10205 (McDonnell-Douglas Corp., Huntington Beach, Calif.) (unpublished).
- ²⁵E. R. Callen and H. B. Callen, Phys. Rev. <u>129</u>, 578 (1963); H. B. Callen and E. Callen, J. Phys. Chem. Solids 27, 1271 (1966).
- ²⁶E. Callen and H. B. Callen, Phys. Rev. A <u>139</u>, 455 (1965).
- ²⁷E. R. Callen, A. E. Clark, B. DeSavage, W. Coleman, and H. B. Callen, Phys. Rev. <u>130</u>, 1735 (1963).
- ²⁸Y. Shapira, R. D. Yacovitch, C. C. Becerra, S. Foner, E. J. McNiff, Jr., D. R. Nelson, and L. Gunther, Phys. Rev. B <u>14</u>, 3007 (1976).
- ²⁹A recent review of magnetostriction in rare-earth metals may be found in J. J. Rhyne in *Magnetic Properties* of *Rare Earth Metals*, edited by R. J. Elliott (Plenum, New York, 1972), p. 164.
- ³⁰G. N. Benninger and A. S. Pavlovik, J. Appl. Phys. <u>38</u>, 1325 (1967); E. W. Lee and H. A. Asgar, Proc. R. Soc. Lond. A <u>326</u>, 73 (1971); D. I. Bower, Proc. R. Soc. Lond. A <u>326</u>, 87 (1971); E. DuTremolet De Lachiesserie, Phys. Status. Solidi. B 54, K135 (1972).
- ³¹H. Takaki, Z. Phys. <u>105</u>, 92 (1937); E. Tatsumoto and T. Okamoto, J. Phys. Soc. Jpn. 14, 1588 (1959).
- ³²A. Hubert, W. Unger, and J. Kranz, Z. Phys. <u>224</u>, 148 (1969).
- ³³Isotropic magnetoelastic effects in metallic glasses are reviewed by R. C. O'Handley and C.-P. Chou, J. Appl. Phys. 49, 1659-1664 (1978).
- ³⁴J. Kanamori in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I, p. 127– 203.
- ³⁵Technical properties of the glasses in the cobalt-rich corner have been reported: R. C. O'Handley, L. I. Mendelsohn, and E. A. Nesbitt, IEEE Trans. <u>12</u>, 942 (1976). Triangular diagrams for two other series of Fe-Co-Ni glasses having metalloid content different than that shown in Fig. 1 have also been reported and show similar $\lambda_s = 0$ lines; R. C. Sherwood, E. M. Gyorgy, H. S. Chen, S. D. Ferris, G. Norman, and H. J. Leamy, AIP Conf. Proc. <u>24</u>, 745 (1975); J. Jagielinsky, K. I. Arai, N. Tsuya, S. Ohnuma, and T. Masumoto, IEEE Trans. <u>13</u>, 1553 (1977).
- ³⁶Metallic glasses generally exhibit stronger field dependence of magnetic properties near T_C than do crystalline materials. This is generally attributed to magnetic clustering. Therefore, near T_C , a greater disparity exists between spontaneous (H=0) and saturation ($H=\infty$) values of a given property.
- ³⁷It has been shown that the temperature dependence of the ΔE effect in Fe₇₅P₁₅C₁₀ glass also follows the theoretical curve for single-ion behavior of uniaxial symmetry: B. S. Berry, (private communication).
- ³⁸A combination of one-ion and two-ion magnetostrictions has also been used to explain the temperature depen-

dence of magnetostriction in crystalline gadolinium (see Ref. 26). There $\lambda_s^{\gamma,2}$ is positive below the compensation temperature; therefore, the single-ion term is dominant and positive: $C_1 > 0 > C_2$ and $|C_1| > |C_2|$ in our Eq. (3).

- ³⁹A two-sublattice model in which the reduced sublattice magnetizations $m_1(T)$ and $m_2(T)$ show different temperature dependences is capable of producing magnetostriction bulges and compensation temperatures as suggested by the data of Fig. 7 (see Ref. 27). However, such a model cannot apply to $Co_{30}B_{20}$ glass which has only one magnetic species.
- ⁴⁰C.-P. Chou, L. A. Davis, M. C. Narasimhan, Scr. Metall. 11, 417 (1977).
- ⁴¹C.-P. Chou, Phys. Rev. Lett. <u>37</u>, 1004 (1976).
- ⁴²C.-P. Chou, (private communication).
- ⁴³C. Kittel, Rev. Mod. Phys. <u>21</u>, 541 (1949).
- ⁴⁴Y. Yosida, J. Appl. Phys. <u>39</u>, 511 (1968).
- ⁴⁵F. E. Luborsky and J. L. Walter, IEEE Trans. <u>13</u>, 953 (1977); 13, 1635 (1977).
- ⁴⁶J. C. Slonczewski, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I, p. 205.
- ⁴⁷J. C. Slonczewski, J. Phys. Chem. Solids. <u>15</u>, 335 (1960).
- ⁴⁸Such is the case, for example, when Fe⁺² and Co⁺² ions occupy octahedral sites. The three $d\epsilon$ levels (t_2g) are much lower in energy than the two $d\gamma$ (e_g) levels. For Fe⁺², the low-lying triplet is singly occupied by a spindown electron while for Co⁺² it is singly occupied by a spin-down hole. The two ions in this case contribute to the anisotropy energy with opposite sign. See Ref. 34 p. 170.
- ⁴⁹L. Berger, Phys. Rev. A <u>138</u>, 1083 (1965); Physica (Utr.) 30, 1141 (1964).
- ⁵⁰I. A. Campbell, Solid. State. Commun. <u>10</u>, 953 (1972).
 ⁵¹L. Berger, AIP Conf. Proc. <u>34</u>, 355 (1976); Physica (Utr.) B91, 31 (1977).
- ⁵²H. Ashworth, D. Sengupta, G. Schnakenberg, L. Shapiro, and L. Berger, Phys. Rev. <u>185</u>, 792 (1969).
- ⁵³An interesting case believed to be described by this model in the very-narrow-band limit but not previously so cited is that of the basal-plane distortion $\lambda^{\gamma,2}$ in the heavy-rare-earth metals. $\lambda^{\gamma,2}$ increases from a relatively small value at Gd($4f_1^7$, $4f_1^9$), peaks, then decreases, changing sign between Ho($4f_1^3$) and Er($4f_1^4$) i.e., at midband. (See Table 4.5 in Ref. 29). This behavior is analogous to the ionic example cited in Ref. 48.
- ⁵⁴R. C. O'Handley and L. Berger, International Conference on the Physics of Transition Metals, Toronto, Aug. 18-22, 1977 (to be published).
- ⁵⁵The sign of the spontaneous Hall coefficient R_s , which also depends on the orbital angular momentum at E_F , is also described by the split-band model (see Refs. 51 and 52). Recent Hall-effect measurements in Fe-Co-Ni-B glasses support this description: R. C. O'Handley, Bull. Am. Phys. Soc. 23, 316 (1978); Phys. Rev. B (to be published).