Correlation of Elastic and Magnetic Properties of Magnetic Glassy Alloys

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A theory of correlation between the elastic and magnetic properties of transition-metal based ferromagnetic glassy alloys is developed. The specific Young's modulus, E/ρ, is shown to be related to the thermal average of the effective spin, $\langle S \rangle$, as $E/\rho = V_E^{0\,2} + K\langle S \rangle^2$, where E and ρ are Young's modulus and the density, respectively, and $V_E^{0\,2}$ and K are constants related to the properties of the materials. The change of E/ρ with composition in $(Fe_{1-x}M_x)_{80}B_{20}$ glasses (M representing Co or Ni) agrees well with the present model.

The elastic properties of metallic glasses have been studied extensively.[1-5] Experimental results and theoretical calculations suggested that the glassy phase is elastically softer than the crystalline phase. Testardi, Krause, and Chen[4] showed that amorphous Pd-Cu-Si alloy and its crystalline phase have an unusually large anharmonicity. Low acoustic attenuation in Pd-Ag-Si glassy alloy was also reported. Mechanically,[6-8] metallic glasses have been demonstrated to possess a fracture strength, $\sigma_F \sim 0.02E$ (where E is Young's modulus), which approaches the theoretical limit. Thus the study of elastic properties is of interest from both the theoretical and technical points of view.

The influence of magnetic energy on the elastic constants of a crystalline material was first recognized by Sato.[9] He showed that the anomalous behavior of the elastic constants of a saturated ferromagnet at the Curie temperature is associated with the appearance of the spontaneous magnetization. Extensive theoretical[10] and experimental[11] effort has been devoted to the study of this anomaly. In this Letter, I derive briefly the interrelation between the Young's modulus of a glassy alloy and its saturation magnetization and report an unusually large magnetic contribution to the elastic constants of transition-metal—metalloid glasses. This work is the first one which shows the close correlation between the elastic and magnetic properties of magnetic glassy alloys.

The calculation of elastic constants requires a knowledge of the detailed structure of a substance. Since the atomic arrangements in a metallic glass have not been fully characterized, an appropriate model has to be used. For simplicity, I assume that the arrangement of constituent atoms is random and that alloying affects only the interatomic potential. If the interatomic potential is known, generally there are two ap-

proaches which can be used for the calculation. The first one is to calculate the energy of a computer-generated structure after the structure is relaxed according to some prescribed criteria and then recompute the energy when the system is under strain. This method requires an assumed arrangement of atoms and yields results in a numerical form; thus, it is not suitable for our calculation. The second one is to ignore the detailed arrangement of atoms and assume that the arrangement can be represented by the atomic density function (ADF). The displacement of each atom upon distortion is described by the macroscopic strain and no other internal displacement is considered. The change of atomic arrangement under strain is fully described by the change of its ADF. Based on this model, the bulk modulus of an amorphous alloy with a ADF of $R(r)$ is given by[3]

$$B = (4\pi/9\Omega)\int_0^\infty r^2 U(r)[3R + 7r^2R' + 2r^4R''] \, dr$$
$$= (4\pi/9\Omega)\int_0^\infty r^2 U(r)F(r) \, dr, \tag{1}$$

where Ω and $U(r)$ are the atomic volume and interatomic potential, respectively. All derivatives in (1) are taken with respect to r^2. Here we calculate Young's modulus through Eq. (1) using the experimentally determined Poisson's ratio, ν.

If we consider a Heisenberg ferromagnet and assume that each transition-metal atom possesses a magnetic moment of $gS\mu_B$ which couples to other moments by an effective exchange integral, J (where g is the gyromagnetic ratio, S is the spin under consideration, and μ_B is the Bohr magneton), the exchange energy between two such magnetic moments is $-2JS^2$. Because the total energy of the system is affected only by the thermal average of the magnetic moment, $g\langle S \rangle \mu_B$, the total internal energy of two atoms in the mag-

netic state can be written as

$$U = U_n - 2J\langle S \rangle^2, \tag{2}$$

where U_n is the part of the energy which is non-magnetic in origin and includes all energy terms which do not depend on the alignment of moments. Because a metallic glass is a macroscopic isotropic material, Young's modulus is given by

$$E = 3(1 - 2\nu)B. \tag{3}$$

The adiabatic Young's modulus of a slender specimen is related to the extensional strain wave velocity, V_E, by a simple relation:

$$E = \rho V_E^2 = (M/N_0\Omega)V_E^2, \tag{4}$$

where ρ is the density, M is the gram formula weight, and N_0 is Avogadro's number. Thus, from Eqs. (1)–(4), we have

$$V_E^2 = (E/\rho) = V_E^{0\,2} + K\langle S \rangle^2, \tag{5}$$

where

$$K = - (8\pi N_0/3M)(1 - 2\nu)\int_0^\infty r^2 J(r)F(r)\,dr,$$
$$V_E^{0\,2} = (4\pi/9\Omega)\int_0^\infty r^2 U_n(r)F(r)\,dr. \tag{6}$$

Equation (5) predicts that the magnetic part of Young's modulus depends on the square of the effective magnetic moment and on K, which in turn depends on $J(r)$ and $F(r)$.

The modulus in Eq. (5) is not truly adiabatic (constant magnetization), since $\langle S \rangle$ may depend on strain and should not be considered as a constant in the integration. Actually, measurements cannot be conducted in a truly adiabatic manner. The magnetization may be changed by the volume strain. The error induced by this simplification can be estimated by Eq. (5), viz.,

$$\frac{\Delta V_E^2 - V_E^{0\,2}}{V_E^2 - V_E^{0\,2}} = \frac{2}{\langle S \rangle}\frac{d\langle S \rangle}{dw}\,\Delta w,$$

where Δw is the volume strain accompanying the propagating elastic wave. $d\langle S \rangle/dw$ is related to the forced volume magnetostriction, $\partial w/\partial H$, by[12]

$$(\partial w/\partial H)_p = \rho(d\sigma_s/dw)B^{-1},$$

where w is the volume strain, H is the applied magnetic field, and p is the pressure. With $(\partial w/\partial H)_p \sim 10^{-10}$ Oe^{-1} and $\Delta w \sim 10^{-6}$, $\Delta(V_E^2 - V_E^{0\,2})/(V_E^2 - V_E^{0\,2}) \sim 10^{-9}$, which is negligibly small.

According to the above calculations, the magnetic contribution to the specific Young's modulus, $V_E^2 \equiv E/\rho$, is proportional to the square of $\langle S \rangle$ and K. Thus the extensional sonic velocity and room-temperature saturation magnetization,

σ_s(RT), of $(\text{Fe}_{1-x}M_x)_{80}\text{B}_{20}$ (M denoting the transition metals Co or Ni) glasses were measured. Glassy alloy ribbons were obtained by rapid quenching of the molten alloys. A pulse-echo overlap technique was used for the sound-velocity measurements in a magnetic field of 120 Oe parallel to the ribbon axis. This field strength is more than enough to saturate the specimen. A Princeton Applied Research vibrating-sample magnetometer was used for the magnetic measurements. All measurements were conducted at room temperature. V_E was observed to vary slightly ($\pm 0.2\%$) from sample to sample. This is attributed to a small variation of the quenching condition and error in length measurement rather than the uncertainty in the transit-time measurement.

Shown in Fig. 1 are V_E and $\langle S \rangle$ $\lfloor \langle S \rangle = \sigma_s(R, T)M/(0.8)\mu_B g N_0 \rfloor$ as a function of composition for $(\text{Fe}_{1-x}\text{Co}_x)_{80}\text{B}_{20}$ glasses. The salient feature of these curves is that each possesses a maximum at $\sim \text{Fe}_{64}\text{Co}_{16}\text{B}_{20}$. The maximum observed in $\langle S \rangle$
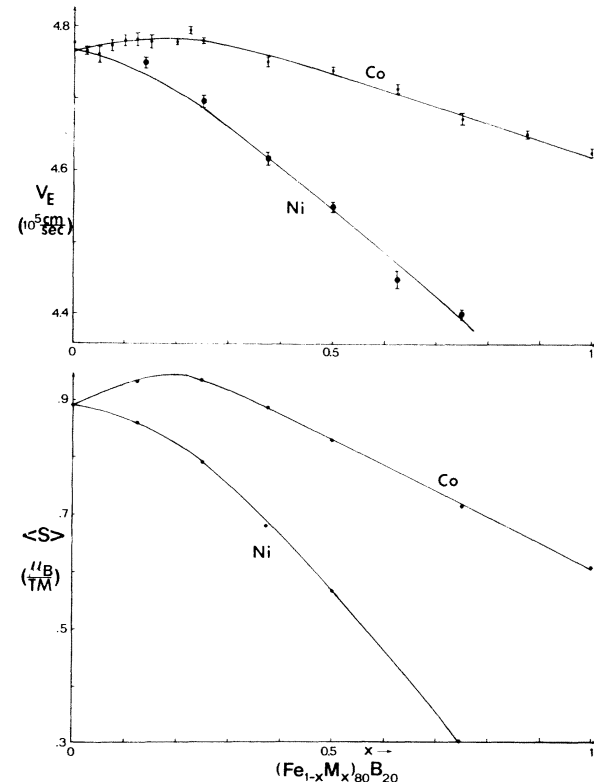

FIG. 1. The room-temperature extensional sonic velocity, V_E, and thermal average of the effective spin, $\langle S \rangle$, of the glassy alloys $(\text{Fe}_{1-x}M_x)_{80}\text{B}_{20}$ (where M denotes the transition metals Co or Ni). V_E was measured in a magnetic field of 120 Oe parallel to the ribbon axis.
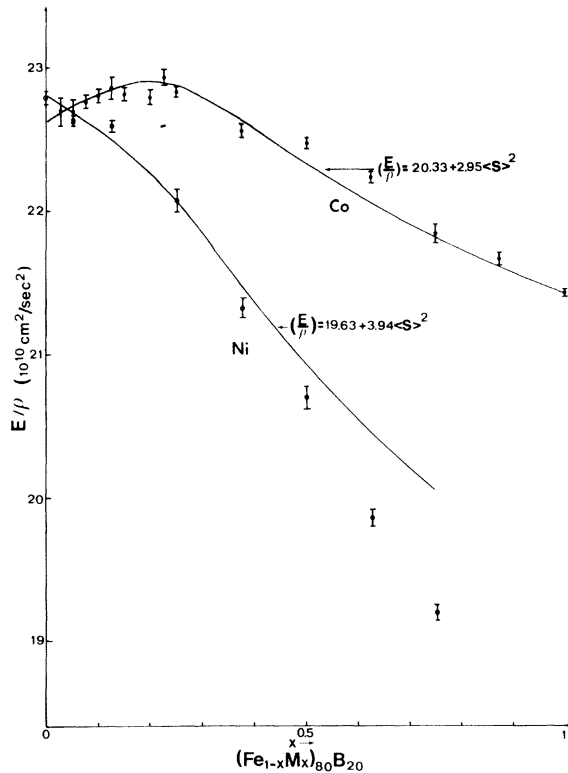
FIG. 2. Calculated V_E^2 of the glassy alloys $(Fe_{1-x}M_x)_{80}$-B_{20} (where M denotes the transitions metals Co or Ni). The solid line represents the theoretical fitting with Eq. (5).

resulted from the combined compositional dependence of saturation moment and Curie temperature in these glassy alloys.[13] Figure 2 shows V_E^2 as a function of composition for these alloys. The solid line represents the theoretical fitting by Eq. (5) with constant $V_E^{0\,2}$ and K. As can be seen from this curve, the variation of the specific Young's modulus of these alloys can be attributed to the variation of the magnetic term $\langle S \rangle^2$. The experimentally determined $V_E^{0\,2}$ and K are 20.33×10^{10} cm²/sec² and 2.75×10^{10} cm²/sec², respectively.

$(Fe_{1-x}Ni_x)_{80}B_{20}$ glassy alloys with high Ni content are difficult to fabricate, and thus only compositions with $x \lesssim 0.7$ were studied. Figure 1 also shows the variation of V_E and $\langle S \rangle$ with x for the Ni-containing alloys. The maxima which characterize the Co alloys are not observed; both curves decrease monotonically with increasing x. In Fig. 2 we plot V_E^2 as a function of x for these glasses. As opposed to the case for the Fe-Co glasses, it is difficult to fit the experimental results satisfactorily across the whole composition range by a single set of constants. The solid line

represents the curve of Eq. (5) with $V_E^{0\,2} = 19.63 \times 10^{10}$ cm²/sec² and $K = 3.94 \times 10^{10}$ cm²/sec². It is evident that the discrepancy between experiment and this curve is severe where $x \gtrsim 0.5$. Based on Eq. (6), this implies that K and/or $V_E^{0\,2}$ varies as the Ni content increases. A variable K [$= f(J)$] may be expected for Fe-Ni glasses; i.e., experimental results[14] suggest that $(J_{Fe-Fe} \sim J_{Fe-Co} \sim J \sim J_{Co-Co} \sim J_{Fe-Ni}) \gg J_{Ni-Ni} \sim 0$, where J_{A-B} is the exchange integral between A and B atoms, in the glassy phase. Thus a larger variation of $J(r)$ with composition might be expected in Fe-Ni than in Fe-Co glasses. While this is consistent with our results, we cannot exclude the possibility that $V_E^{0\,2}$ varies with composition in either case.

Further evidence supporting our interpretation may be obtained by measuring the temperature dependence of elastic constants on a specimen of fixed composition at Curie temperature. One would expect that an anomalous behavior exists at $T \simeq T_{Curie}$. This observation on the present alloy system is not feasible because the Curie temperatures of these glasses are either higher than or close to the crystallization temperature.[15] However, experiments on Fe-Mo-B glasses having lower Curie temperatures indeed showed an increase of modulus as the specimen underwent a paramagnetic-to-ferromagnetic transition.[16]

The strong influence of magnetic energy on elastic constants reported in this Letter, to my knowledge, is not observed in crystalline alloys. One presumes that for such alloys a systematic observation of the kind discussed here is masked by the change of certain structural effects such as a phase change, atomic size difference, etc., which are accompanied by the change of composition. Because of the absence of long-range ordering in the glassy structure, such effects are either minimized or eliminated. One considers that metal-metalloid glasses are all characterized by a qualitatively similar structure.[17] Thus the variation of modulus reflects more of the change of interatomic potential than the change of structure.

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Experimental Test of the Smoothness Hypothesis in CsCoCl₃ · 2D₂O

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Here the results are reported of a neutron-diffraction study of the critical behavior of M and M_{st} along the line of critical points in the magnetic phase diagram of the metamagnet $CsCoCl_3 \cdot 2D_2O$. It is shown that the critical behavior of M and M_{st} can each be represented by a single critical exponent up to the multicritical point, where a breakdown of smoothness and crossover is observed.

The smoothness hypothesis predicts[1-3] that the critical line is a smooth curve and that the singular part of the thermodynamic potential is essentially the same everywhere along a critical line, except for a smooth variation of parameters describing the amplitudes of the various singularities. In particular, the critical exponents α, β, γ, etc. should remain unchanged when one moves along a critical line. However, since the singular behavior depends on the order[2] of the critical transition, this notion of smoothness may not be extended over regions of critical points with different order. Upon the approach of a critical point with different order, the singular behavior changes discontinuously, a feature which is commonly referred to as "breakdown of smoothness."[3] Evidence for the universal nature of the singular behavior along a critical line has been reported for the superfluid transition in He^3-He^4 mixtures as a function of He^3 concentration.[4] At the corresponding tricritical point, a new set of exponents is found.[5] For magnetic systems, for instance, $FeCl_2$,[6,7] the experimental evidence

seems less complete.

In the present Letter, we report the results of a scaling analysis of the critical behavior of the metamagnet $CsCoCl_3 \cdot 2D_2O$ around the multicritical point (MCP), with the emphasis on the discontinuous change of the critical exponents at the MCP and the crossover from critical to multicritical behavior around the MCP.

$CsCoCl_3 \cdot 2D_2O$ has been the subject of a number of experimental investigations.[8-10] It is a pseudo-one-dimensional compound with strongly anisotropic interactions (Ising-like). The relatively small interchain interactions give rise to a three-dimensional antiferromagnetic ordered state below $T_N = 3.3$ K. The compensated noncollinear four-sublattice magnetic array can be described by the magnetic space group $P_{2b}cca'$, as illustrated in Fig. 1. An important characteristic of this structure is that neighboring ions in a chain have their moments arranged in such a way that the chain possesses a net moment directed along the chain direction ($\vec{a}$ direction). It was shown by nuclear-magnetic-resonance[8] and neu-