

Disorder-induced spin-glass state in amorphous Heusler alloys

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The magnetic dc susceptibility of several amorphous films of Mn-based Heusler alloys exhibits a cusp, characteristic of spin-glass freezing. The cusp temperatures are an order of magnitude smaller than the Curie temperatures of their ferromagnetic crystalline counterparts. The occurrence of the spin-glass state is interpreted in terms of competition between long-range indirect ferromagnetic exchange and direct antiferromagnetic overlap.

Recently, Taylor and Tsuei¹ have reported that some Heusler alloys,² in particular, Cu_2MnZ with $Z = \text{Al}, \text{In}, \text{Sn}$, can be prepared in the amorphous state by rf sputtering. In this paper, we report on the magnetic properties of these "amorphous Heusler alloys," as we shall call them. We have discovered that the ones we have studied are spin-glasses, in contrast to their strongly ferromagnetic crystalline counterparts. The early work of Bradley *et al.*³ had already shown unambiguously that change of structure in Cu_2MnAl , by means of varying heat treatment but without a change in composition, destroyed ferromagnetism in this alloy. Our work, however, is the first study of the magnetic properties of such extremely disordered alloys. We shall discuss the nature of the competing interactions leading to the spin-glass behavior; the analysis sheds some light on the proposed exchange mechanism in the crystalline state as well.

The samples used in this experimental study were

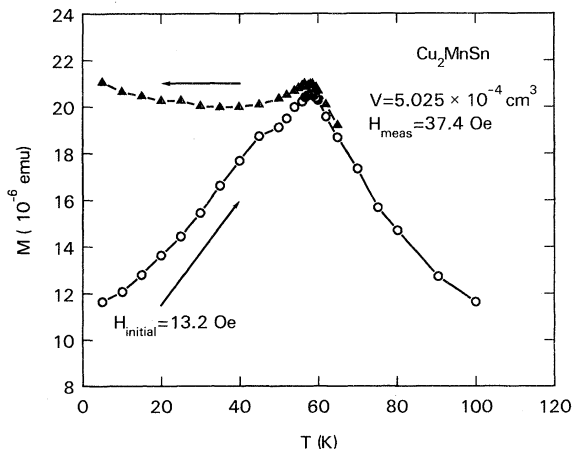


FIG. 1. Magnetization M of an amorphous Cu_2MnSn film in a measuring dc field of 37.4 Oe. The data points displayed as triangles were measured in order of decreasing temperature as indicated by the arrow. The data points indicated by open circles were taken upon increasing temperature, after the sample was cooled to 4.2 K in the field $H_{\text{initial}} = 13.2$ Oe.

Cu_2MnZ , where Z was either Al, In, or Sn. The preparation and characterization of the samples have been described by Taylor and Tsuei.¹ As in previous work, these alloys, when crystallized in the Heusler structure, were found to be strongly ferromagnetic.

The magnetic measurements were performed with a superconducting quantum interference SQUID magnetometer in fields ranging from 10 to 120 Oe, on samples which were rf sputtered onto a sapphire substrate and about $1 \mu\text{m}$ thick. The sapphire contribution to the magnetization was subsequently subtracted out. A typical dc magnetization for a Cu_2MnSn sample is shown in Fig. 1.

The spatial long-range magnetic order of the crystalline state has disappeared. Instead, the data show a cusp in the dc magnetic susceptibility, $\chi_{\text{dc}} = M/H$, at temperatures $T_{\text{SG}} = 65, 60,$ and 59 K for amorphous Cu_2MnZ with $Z = \text{Al}, \text{In},$ and Sn , respectively. These values are roughly one-tenth of the corresponding crystalline Curie temperatures 600 (Ref. 1), 520 (Ref. 1), and 530 (Ref. 9). As in many other spin-glass systems, time-dependent effects (remnant) are apparent when measurements are per-

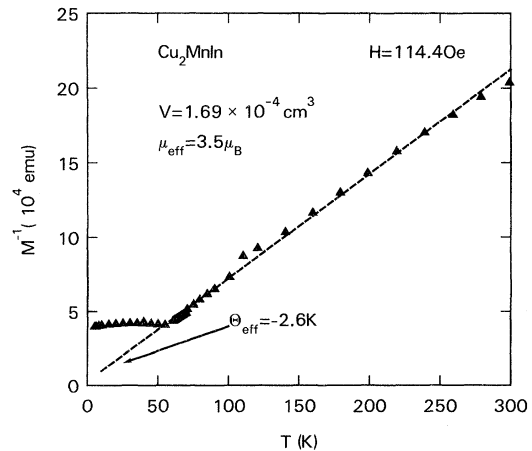


FIG. 2. Inverse magnetization M^{-1} of an amorphous CuMnIn film in a dc field of 114.4 Oe. The Curie-Weiss behavior is observed for all temperatures higher than T_{SG} .

formed in a field H_{meas} , which is higher than the initial field H_{initial} , in which the sample is cooled down to the temperatures much below T_{SG} . If then, at the lowest temperatures, the field is switched to H_{meas} , the magnetization is a strongly increasing function of temperature up to T_{SG} . The rate of increase depends on H_{initial} as well as the rate at which the sample is being warmed up. Furthermore, plots of M^{-1} vs T , as shown in Fig. 2, show a Curie-Weiss law from 300 K (5 times T_{SG}) all the way down to T_{SG} , with the intercept giving paramagnetic Curie temperatures of 15.9, -2.6, and -12 K for the three amorphous compositions ($Z = \text{Al}$, In , and Sn , respectively). The effective magnetic moments, deduced from the Curie constant in the usual way, are $4.7\mu_B$, $3.5\mu_B$, and $4.1\mu_B$, respectively. These values are close to the moment value of $\sim 4\mu_B$ magneton deduced from the low-temperature saturation magnetization of the crystalline samples and established previously by neutron-diffraction experiments² as well as by the recent band-structure calculations.⁴

We interpret our magnetic data on the amorphous Heusler alloys in terms of spin-glass freezing.⁵ This interpretation is based on the observation of a susceptibility cusp at T_{SG} , a generally flat susceptibility below the cusp temperature, as well as remanence, which are characteristic of other classic spin-glass systems.

In what follows, we would like to explain the remarkable consistency of all the alloy systems, with the crystalline alloys showing T_C 's between 500 and 600 K and all their amorphous counterparts showing T_{SG} between 55 and 65 K. Few magnetic transition-metal systems show such a dramatic magnetic change between the crystalline and amorphous states. For example, most alloys of Fe or Co with metalloids or early transition metals show only slightly reduced ferromagnetic transition temperatures in the amorphous state. The Mn-system MnSi is a helical antiferromagnet with $T_N = 29$ K as a crystal while its amorphous counterpart⁶ is a spin-glass with $T_{\text{SG}} = 22$ K.

We follow recent work and use a localized moment model to describe the Heusler alloys.⁷ This is consistent with the fact that the effective moments remain about $4\mu_B$ in both the crystalline and amorphous states. An extensive literature has considered models for exchange interactions $J(r)$ crystalline in Heusler alloys. Here we consider two of the more recent models by Price⁸ and Stearns,⁹ which have been successful in explaining inelastic neutron studies of crystalline spin-wave spectra.^{10,11} Price's double-resonance exchange model⁸ considers an indirect exchange mediated by oscillatory sp conduction electron polarization. As indicated schematically in Fig. 3(a), the oscillations occur with a periodicity of $2k_F r$ where, since sp electrons are involved, the Fermi wave vector k_F is of order 2 \AA^{-1} . The first three neighbors just happen to lie where there are positive

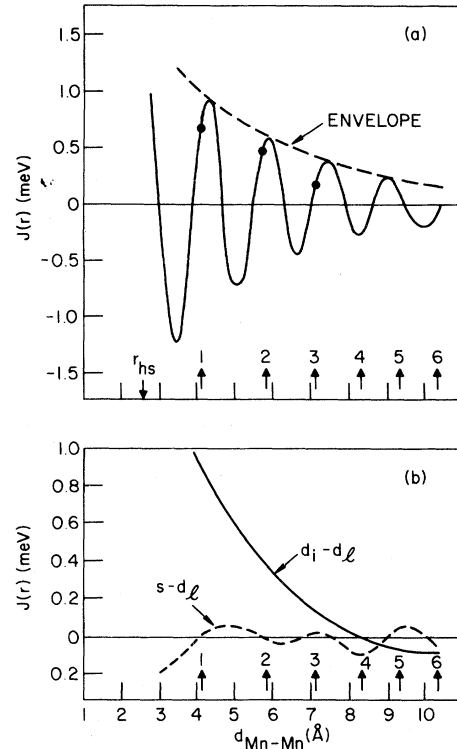


FIG. 3. Theoretical distance dependence of Mn-Mn exchange interactions $J(r)$ in Cu_2MnAl . In (a) the dashed line is a schematic version of Price's Fig. 3 (Ref. 8), scaled in amplitude to match roughly the experimental exchange interactions (points) for Cu_2MnAl . (b) is adapted from Fig. 1 of Ref. 9, showing the slower oscillation of the itinerant- d -local- d exchange interaction. Numbers one through six indicate positions of first through sixth-nearest-neighbor shells.

lobes of the interaction. In this range, the envelope is decaying roughly as $r^{-1.5}$ (as can be deduced from Fig. 3 of Ref. 8) with the power of decay increasing gradually at larger distances until it eventually takes on the same form as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Unfortunately, fits to other more strongly ferromagnetic alloys such as Cu_2MnAl have not been reported, but one could expect that since the first three nearest neighbors give a positive interaction according to fits to the data of Ishikawa *et al.*,¹⁰ a rather similar picture would emerge as shown in Fig. 3(a). This is an apparent weakness of Price's theory, for it is rather implausible that for a series of alloys such as Cu_2MnZ with $Z = \text{Al}$, In , and Sn , all of which are strongly ferromagnetic, but which have different k_F 's, the nearest neighbors should consistently fall on the ferromagnetic lobes of the rapidly oscillating interaction.

Stearns *et al.*⁹ have proposed an alternate model in which the dominant exchange is a d - d RKKY interaction in which itinerant d electrons couple the localized d -electron moments. In the simplest approxima-

tion, this interaction has the form¹²

$$E_{ij} = -2J_{ij}S_i \cdot S_j, \quad (1)$$

$$J_{ij} = V_0[\sin(2k_F r) - 2k_F r \cos(2k_F r)] / (2k_F r)^4.$$

For crystalline Cu₂MnAl, the value of V_0 that Stearns *et al.* require to fit the spin-wave dispersion curve is ~ 220 K, and similar values should apply for the In and Sn analogs because of their similar Curie temperatures. The key assumption of this model is that the itinerant d 's are few in number, so that k_F in Eq. (1) is small (0.3 \AA^{-1} for Cu₂MnAl) and hence the first lobe of the oscillatory interaction encompasses the first three Mn-Mn nearest neighbors, as indicated schematically in Fig. 3(b). It should be noted, however, that it is difficult to determine the precise number of itinerant d electrons *ab initio* from band calculations.

We can test the plausibility of these two rather simplified models by considering what they would predict in the amorphous case. To do this, we make several assumptions which we consider quite plausible:

(1) We assume that in the amorphous state there is a statistical distribution of atoms in a dense random packed structure.¹³⁻¹⁵ This implies on the average three nearest-neighbor Mn around any given Mn at a nearest-neighbor distance of about 2.6 \AA .

(2) We assume nearest-neighbor Mn's interact with an antiferromagnetic exchange interaction J_a which drops off strongly with distance. Such an interaction has been invoked to explain antiferromagnetism in α -Mn, for example.¹⁶ Antiferromagnetic nearest-neighbor Mn interactions explain the transition from crystalline ferromagnet to amorphous spin-glass in a simple conceptual way. In the crystalline Heusler structure, where Mn atoms are kept 4.2 \AA apart, these interactions are absent and ferromagnetism dominates. But in the amorphous state, the antiferromagnetic interactions appear, giving rise to a competition with the ferromagnetic interactions, and such competition is well known to cause spin-glass behavior.

(3) We assume the Fermi energy, the density of s -electron states, and the strength of the s - d exchange are not significantly different in the crystalline and amorphous states. Recent evidence for this supposition has come from EPR measurements in Gd_xY_{1-x-y}Al_y alloys.¹⁷ However, we might expect a significant reduction of the number of itinerant d electrons, for in contrast to the plane-wave-like s electrons, the d electrons have lobes which interact more strongly with the irregular crystal fields of the amorphous sites. Another difference between amorphous and crystalline systems comes in the mean free path. However, this is not likely to be a strong effect, particularly since the resistivities of the amorphous Heusler alloys tend to be low compared to other amorphous alloys, e.g., $130 \mu\Omega \text{ cm}$ for Cu₂MnAl,

implying a mean free path encompassing at least several shells of nearest neighbors. Also, deChatel¹⁸ has pointed out that spin-glass transition temperatures are more weakly affected by mean-free-path damping than are ferromagnetic ones.

(4) To analyze the magnetic properties of the amorphous Heusler alloys, we assume the mean-field formulas for T_{SG} and Θ :

$$T_{SG} = \frac{2}{3\sqrt{3}} S(S+1) \left(\sum_i Z_i J_i^2 + Z_a J_a^2 \right)^{1/2}, \quad (2)$$

$$\Theta = \frac{2}{3} S(S-1) \left(\sum_i Z_i J_i - Z_a J_a \right). \quad (3)$$

Here the T_{SG} formula comes from the spin-glass model of Sherrington and Kirkpatrick¹⁹ involving a distribution of positive and negative exchange interactions with the mean given by Θ . The sum \sum_i represents a sum over the i nearest neighbors, where Z_i is the number of atoms at radius r_i around a given Mn atom and J_i is the oscillatory exchange at r_i (excluding the direct antiferromagnetic exchange). Z_a is the number of nearest neighbors which interact via antiferromagnetic direct exchange J_a . We take $Z_a = 3$ as discussed above.

(5) To treat the ferromagnetic exchange in the amorphous case, we assume a uniform distribution of Mn-Mn distances, r , with the lower cutoff at the hard-sphere radius $r_{hs} = 2.6 \text{ \AA}$ (the estimate is fairly insensitive to the choice of lower cutoff). That is, we replace the sum by

$$\sum_i Z_i \rightarrow 4\pi\rho \int_{r_{hs}}^{\infty} dr r^2, \quad (4)$$

where ρ is the density of Mn atoms per unit volume ($\sim 0.019 \text{ \AA}^{-3}$). Of course, the correct radial distribution function has peaks, particularly at the hard-sphere radius, but these become rapidly damped out with increasing distance.

With these assumptions, we can now proceed to apply Stearns's and Price's models to our experimental results on the amorphous alloys. For the case of Stearns's model,⁹ we evaluate $\sum_i Z_i J_i$ and $\sum_i Z_i J_i^2$ using $J(r)$ from Eq. (1) and relation (4). Inserting the obtained results into Eqs. (2) and (3), using previously given numbers ($2k_F r_{hs} = 1.7$, $\rho/k_F^3 = 0.55$) and $S = 2$, we find to an adequate approximation $\sum_i Z_i J_i = Z_a J_a$ and

$$V_0 \sim 1.2 T_{SG} \sim 70 \text{ K}, \quad J_a \sim V_0/3 \sim 25 \text{ K}.$$

While J_a is plausible, the result for V_0 is low compared to Stearns's crystalline value of 220 K stated earlier.¹² Now the strength of the RKKY goes as n_0^2/E_F , where n_0 is the number of itinerant electrons per atom; so the V_0 values could be an indication of a reduction by a factor of $(220/70)^{1/2} \sim 2$ in the number of itinerant d electrons in the amorphous state. In this estimate, we arbitrarily assume E_F and

k_F stay the same. In fact, nothing is known *a priori* about whether E_F or k_F should change for itinerant d 's in the amorphous state, so this estimate simply indicates the order of magnitude of effect required to account for our data in the context of the Stearns's model.

Turning to the Price model,⁸ we use $J(r)$ as shown in Fig. 3(a), which has the same shape as the one Price calculated for PdMnSn, but with the amplitude of the oscillations scaled up to account for the higher Curie temperature of our crystalline compositions. The envelope of $J(r)$ goes as $(7.8 \text{ K})(4.2 \text{ \AA}/r)^{1.5}$ up to 8 \AA with a faster falloff beyond. Integrating as before, we find from Eq. (3) that $\sum_i Z_i J_i$ averages essentially to zero, implying a very small J_a (of order several degrees K). From Eq. (2), $\sum_i Z_i J_i^2$ integrates to $\sim 600 \text{ K}^2$, implying $T_{SG} \sim 60 \text{ K}$. This is in excellent agreement with our observed T_{SG} . Of course, the result is based on the assumption that the crystalline nearest-neighbor distances are situated at the peaks of the ferromagnetic lobes of the oscillatory exchange [see Fig. 3(a)], as we discussed earlier.

In summary, we have found for the first time that

Heusler alloys exhibit a spin-glass behavior when made amorphous. We have found that with plausible assumptions, both Stearns's and Price's models for the exchange interactions can account qualitatively for the appearance of spin-glass behavior in the amorphous alloys, for the consistency in the values of T_{SG} , and for the low values of Θ . Price's model accounts very well for the magnitude of T_{SG} provided one can ignore the remarkable coincidences required for it to explain the Curie temperatures of the crystalline phase (nearest-neighbors distances always at ferromagnetic lobes of the oscillatory exchange). Because of these coincidences, we presently prefer Stearns's model and take the reduced value of V_0 in the amorphous state as an indication of a factor of 2 reduction in the number of itinerant d electrons. However, we do not exclude that an alternate, more realistic theory of ferromagnetism in Heusler alloys might be developed in the future. Such a theory should be tested in a similar way against the results in the amorphous state.

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¹²The form of the RKKY interaction used throughout this discussion is derived by Fourier transforming the general-

ized susceptibility, $\chi_0(\vec{q})$ of a noninteracting electron gas. If interactions between itinerant electrons are taken into account (Ref. 20), $\chi_0(\vec{q})$ exhibits a substantial maximum at $q = 2k_F$. The result of this correction is to reduce our estimate of V_0 by about a factor of 6–7 in the crystalline case. However, the estimate of V_0 in the amorphous state would be reduced by the same factor, preserving the crystalline-to-amorphous ratio.

¹³Metal-metal alloys tend to have less chemical short-range order (Ref. 14) in contrast to metal-metalloid alloys like MnSi where significant short-range order has been observed (Ref. 6).

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