Amorphous Dy-Cu: Random spin freezing in the presence of strong local anisotropy

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Magnetization and specific heat of an amorphous Dy-Cu alloy containing 41-at.% dysprosium establish that random single-ion anisotropy dominates exchange in this material, which can be approximately considered as a random Ising magnet. Exchange coupling is predominantly ferromagnetic with some antiferromagnetic interactions. Square hysteresis loops at 100 mK which show large values of remanence and giant Barkhausen jumps indicate that the magnetic structure in the magnetized state is asperomagnetic (random ferromagnetic). Remanence and coercivity fall off exponentially with increasing temperature from limiting values of $2.7\mu_B$/Dy and 8000 Oe. Time dependences were studied both of the remanence, which decays with the logarithm of time, and the magnetization in low fields which increases exponentially with time below 18 K when the temperature is increased with a time constant practically independent of temperature. The spin-freezing transition at $T_f = 18$ K is marked by a peak in the irreversible low-field magnetization measured in a SQUID magnetometer but there is no marked anomaly in the specific heat. An attempt to analyze the data near T_f in terms of critical exponents, justified by the large spontaneous magnetization, leads to values which differ from those of a normal ferromagnet, yet do not contradict the scaling-law equalities.

I. INTRODUCTION

Magnetic order in amorphous alloys containing rare-earth ions is governed, as in their crystalline counterparts, by the interplay of magnetic and crystal-field interactions. A key difference is that these interactions in crystals tend to align the moments along a few equivalent crystallographic directions, whereas in amorphous solids that cannot be the case. To begin with, we outline what may happen in an amorphous magnet containing a single magnetic species when one or the other of the two interactions dominates.[1]

In the absence of any crystal field, the simple combination of a noncrystalline lattice and magnetic exchange coupling can give rise to several varieties of magnetic order. Best studied but least novel is the collinear ferromagnetism arising from positive Heisenberg exchange coupling, albeit with a distribution in magnitude.[2] Negative exchange coupling in an amorphous solid is already more problematic. Because of the topology, it is normally impossible to satisfy all bonds simultaneously (the frustration effect[3]) and long-range antiferromagnetism with two antiparallel sublattices does not seem to occur. Instead, random isotropic spin freezing with at most very-short-range antiparallel correlations had been found.[4] For spins in nonmetallic amorphous FeF_3, random spin freezing sets in progressively without any sharp phase transition.[5] Any such random magnetic order where spin correlations average to zero beyond at most a few shells of nearest neighbors will be termed "speromagnetic" in this paper (see Fig. 1).

The third possibility for the exchange is a distribution with positive and negative interactions. This is the spin-glass problem. Spin-glasses[6] can be dilute crystalline alloys where the exchange interactions between impurities, usually via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, are modeled by a broad, symmetric exchange distribution of both signs.[7] In concentrated amorphous metals, such as Y-Fe,[8,9] Gd-Al,[10] and Gd-Cu (Ref. 10) there is convincing evidence that spin-glass-like behavior also exists. Some of these alloys also exhibit a partial magnetic moment which can be construed as random but anisotropic spin freezing so that each domain has a spontaneous moment which is only a fraction of the ferromagnetic saturation value.[8] Any anisotropic random magnetic order in an amorphous magnet will be

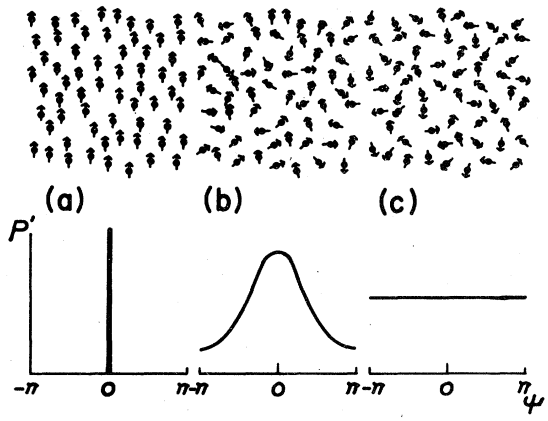

FIG. 1. Illustration of some varieties of magnetic order possible in simple amorphous magnets with a single type of magnetic atom having a one subnetwork structure. (a) Ferromagnetic, (b) asperomagnetic, and (c) speromagnetic. The lower part of the figure shows P, the normalized probability $P(\psi)\sin\psi$ of finding a spin in a domain oriented at an angle ψ with a fixed axis. (a) Ferromagnetic: A spontaneous magnetic moment with colinear alignment of atomic moments. (b) Asperomagnetic: A spontaneous moment exists but the value of the moment does not correspond to complete alignment of the atomic moments. The moments are randomly distributed in direction with an asymetric probability distribution. (c) Speromagnetic: No spontaneous moment exists with a completely random distribution of directions of the atomic magnetic moments. The words asperomagnetic and speromagnetic are intended to describe a frozen spin structure in a solid without connoting any particular class of materials or interaction scheme.

termed "asperomagnetic." These definitions are illustrated in Fig. 1.

The other interaction governing magnetic order in amorphous magnets is that of the magnetic moment with the crystal field. It is most important for non-S-state rare-earth ions. Point-charge calculations on random dense-packed models which approximate the structure of noncrystalline metals have shown that the second-order terms in the crystal field are the dominant ones[11] so that a randomly oriented local easy axis is defined at each rare-earth site. The Hamiltonian for the ith ion may be written as

$$H^i = H^i_{\rm ex} + H^i_{\rm cf} \ . \tag{1}$$

The random anisotropy model has been reviewed by Cochrane *et al.*[12] The orientation of any moment results in general from competition between the two terms in (1). Even when the crystal field is dominant, exchange must still play a part in defining the magnetic structure of a dysprosium alloy (indeed stable magnetic order is impossible without it) because the crystal field cannot lift the Kramer's degeneracy of the energy levels, equivalent to the moment pointing up or down the local easy axis. If the exchange is ferromagnetic and much weaker than the crystal-field interaction, the moments within a domain will be randomly oriented within a hemisphere, an asperomagnetic structure. On the other hand, antiferromagnetic or symmetrically distributed positive and negative exchange will produce speromagnetism, with the moments randomly oriented throughout the sphere.

Amorphous rare-earth alloys are ideal systems for studying the effects of random local anisotropy on magnetic order. Although a number of such alloys have been examined since the first work on Tb-Fe_2,[13] almost all have been magnetic binaries—alloys of rare earths with magnetic $3d$ transition metals[14]—which are magnetically complex because of the presence of two coupled but distinct magnetic subnetworks, yielding ferrimagnetic (or sperimagnetic) structures.[15,16] These alloys have technical potential, but are less well suited to basic study of random anisotropy than alloys of the rare earths with nonmagnetic metals.

Magnetization curves in high fields on $R\,Ni_3$ (where Ni does not carry a moment[17,18]) and $R\,Ag$ (Ref. 19) have clearly shown the effects of random crystal fields. While it is rather easy to induce roughly half the saturation moment by applying a magnetic field at low temperatures, complete saturation cannot be attained even in fields of 400 kOe. These two features suggest asperomagnetic order. Hysteresis and large coercivity appear at low temperature, but it is unclear whether this order sets in at a sharply-defined phase transition.

The present work is a comprehensive magnetic study of a simple amorphous alloy, Dy-Cu, where random local anisotropy can be shown to dominate the exchange. Measurements include magnetization in very weak and very strong fields, including some down to 100 mK, susceptibility, specific heat, resistivity, and Mössbauer spectra. We were particularly interested in the magnetic structure, whether speromagnetic or asperomagnetic and if any evidence could be found for domains to justify these concepts.

We were also interested in time-dependent effects in the magnetization but, above all, we wanted to determine whether random magnetic order sets in at a sharp phase transition in a system with effectively Ising spins. The answers to these questions are discussed in Sec. III, where a number of properties are explained on the basis of Eq. (1). The results themselves are presented in Sec. II. The conclusions form Sec. IV.

II. EXPERIMENTAL RESULTS

A. Preparation and characterization

The amorphous Dy-Cu alloy described here is one of a series of R-Cu alloys which have been prepared

by rf argon-ion sputtering from alloy targets. Films 1–3 μm in thickness were deposited onto both sapphire and silicon substrates from a Dy-Cu target. The composition of the resulting material was found to be $DyCu_{1.44}Ar_{0.05}O_{0.23}$ by electron microprobe analysis.

X-ray analysis gave a diffraction pattern typical of an amorphous rare-earth transition-metal alloy.[20] The density of the films is 8.8 g cm^{-3}, compared with 9.018 g cm^{-3} for orthorhombic $DyCu_2$. Uncertainty in the density and other specific measurements mainly stems from nonuniformity in the film thickness. Using 12-coordination Goldschmidt radii, the packing fraction of the amorphous alloy is found to be 0.76, compared with 0.74 for perfect close packing. The films can therefore be considered as having an amorphous close-packed structure.

The resistivity of the material is shown in Fig. 2. Its large value, $\rho = 150$ $\mu\Omega$ cm, and negative temperature coefficient $1/\rho(d\rho/dT) = -0.75 \times 10^{-6}$ K resemble those found in many other amorphous and disordered alloys.[21] At temperatures below 100 K there is a steeper slope, but no particular anomaly is evident at 18 K, which turns out to be the spin-freezing temperature.

A ^{161}Dy Mössbauer spectrum taken at 4.2 K gave a magnetic hyperfine pattern, poorly resolved because of low absorber thickness, with an overall splitting of 46.2 ±0.6 cm/sec. The value of the hyperfine field correspond to a $M_J = \frac{15}{2}$ state for the Dy at 4.2 K.

B. Magnetic properties

A most significant feature of the magnetism of amorphous Dy-Cu is the existence of a well-defined spin-freezing temperature T_f above which the magnetization is a reversible function of applied field, and below which it is not, at least on the time scales involved in the magnetic measurements. Experimental data on different aspects of the magnetization are presented in the next six subsections. All measurements were made on samples of approximately 1 mg, and, because of the small size, experimental errors limit the absolute values of magnetic parameters to ±5%.

1. *Paramagnetic region:* $T > T_f$

Magnetization was measured in fields between 1 and 18 kOe using a force balance magnetometer. The field was applied parallel and perpendicular to the plane of the film, in an attempt to see whether any bulk anisotropy had been introduced by the preparation procedure. Data corrected for the demagnetizing field are shown in Fig. 3. The susceptibility follows a Curie-Weiss law with average values of the paramagnetic Curie temperature Θ_p and molar Curie constant C_m, respectively, 22 K and 13.9 (cm^3 K). The free Dy^{3+} ion has $C_m = 14.2$. There is no evidence in these data for any bulk, in-plane anisotropy.

2. *Low-field magnetization:* $T \gtrless T_f$

The low-field measurements were made using a SQUID magnetometer in fields ranging from that of the earth ($H_0 = 0.2$ Oe) up to 10 Oe. On initial cooling of the sample in H_0, the magnetization increases normally down to $T_f = 18.0$ K, where it abruptly levels off. Roughly the same form of the susceptibility is found in any other small field, and the curves are fully reproducible on heating. However, if the sample is cooled to a temperature below T_f in H_0, and then the field is increased to H_1, there is a time-

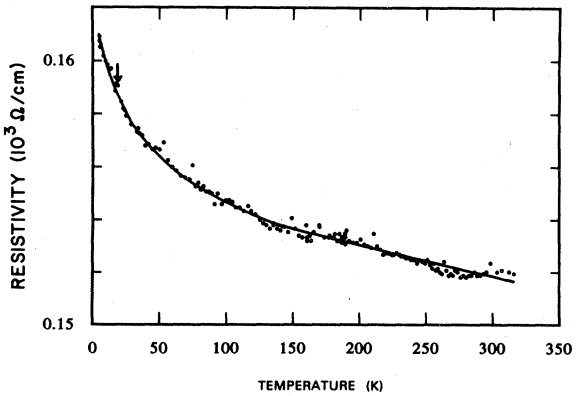

FIG. 2. Resistivity of the amorphous Dy-Cu alloy as a function of temperature. The arrow indicates the spin-freezing transition.

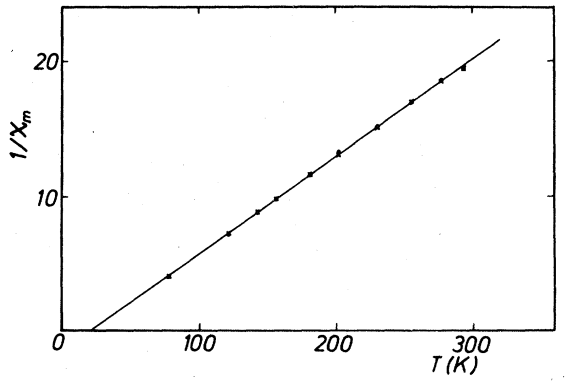

FIG. 3. Paramagnetic susceptibility of amorphous Dy-Cu measured parallel (0) and perpendicular (X) to the plane of the film.

dependent relaxation to a new "equilibrium" (see Sec. II B 5). Following each step of increasing temperature, keeping H_1 constant, the magnetization again increases to a new value until, at T_f, it finally attains the same maximum value it would have attained by cooling from above T_f in H_1.

The magnetization measured as just described is not reproducible on cooling, as indicated on Fig. 4(a), and circles on the dashed curve just indicate the values after some convenient time lapse (five minutes) when it has ceased to evolve perceptibly. Below T_f we can define reversible and irreversible susceptibilities. The first is $\chi_{\text{rev}} = M/H$ measured on heating or cooling where H is a small field applied on cooling through T_f. The second, χ_{irrev} is measured on heating after the sample has been cooled in essentially zero field and a small field is applied at $T < T_f$. The variation of these quantities is shown on Fig. 4(b). They become equal at T_f.

3. *High-field magnetization:* $T \gtrless T_f$

Results in this and the next section were obtained using a vibrating sample magnetometer with a 60-kOe superconducting magnet. A set of data up to 150 kOe was taken at the Service National des Champs Intenses, Grenoble with an extraction magnetometer and a Bitter magnet. Magnetization curves are shown in Fig. 5. Even in the largest fields, it is impossible to saturate the magnetization. The best that can be achieved is $6.9\mu_B$/Dy, whereas the ultimate saturation value is $10\mu_B$/Dy.

Above T_f, the magnetization curves are fully reversible, for increasing or decreasing fields, but only the portion in high fields ($\gtrsim 10$–20 kOe) is reversible below T_f. Initial magnetization curves are shown dashed in Fig. 5. Like the temperature dependence of M in low fields below T_f, the curves cannot be defined precisely because the magnetization depends on time. The curves shown are measured by waiting for 1 min at each field, and the effects of magnetic viscosity are most pronounced near the point of inflection.

Even after subjecting the sample to the maximum field, the magnetization is not immune from the influence of time. On reducing the field again to a value at or near zero, some spontaneous decay occurs. The complete hystersis loop at 4.2 K is shown in Fig. 10(a). Each point on the curve is taken after a 1-min wait.

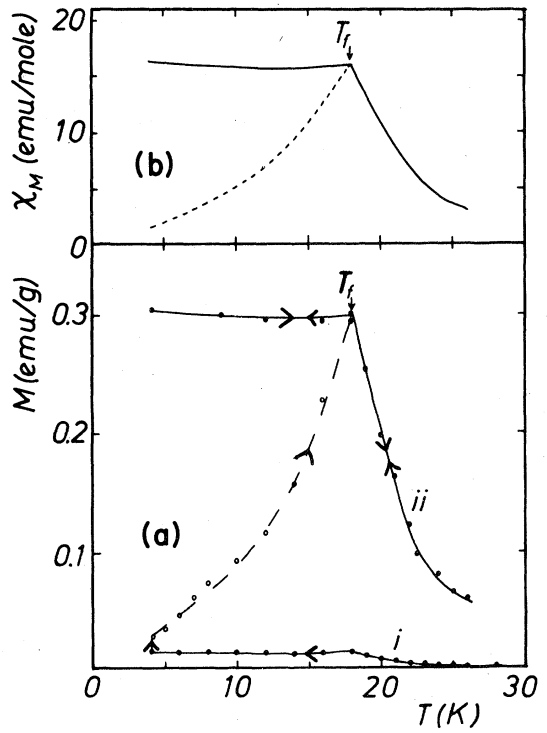

FIG. 4. (a) Magnetization of amorphous Dy-Cu measured (i) in the earth's field and (ii) in 4.94 Oe applied at 4.2 K. The arrows indicate the sequence of measurements. The open circles are obtained on heating and waiting 5 min at each temperature. (b) Reversible (solid lines) and irreversible (dashed lines) susceptibilities, derived from these data.

4. *Coercivity and remanence:* $T < T_f$

Because of the difficulties just referred to, the coercivity and remanence are not truly well-defined

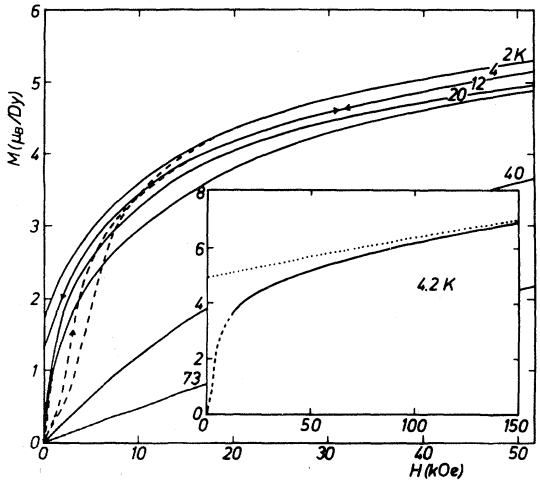

FIG. 5. Magnetization curves of amorphous Dy-Cu at various temperatures. Initial magnetization curves are the dashed lines. The insert shows measurements at 4.2 K up to 150 kOe. The dotted line is explained in the text in connection with Eq. (3).

quantities. Somewhat different values will be found according to the times taken for measurement. Nonetheless the remanence varies by only about 10% in an hour and the measurable variation in coercivity is even smaller. Below T_f however both quantities double in magnitude with each decrease in temperature of a few degrees, so it is reasonable to talk about their temperature dependences, as shown in Fig. 6. Both quantities vary as e^{-T/T_0} with $T_0 = 2.5$ K for coercivity and 4.2 K for remanence.

Besides the time and temperature dependence of the isothermal saturation remanence itself, we have measured the thermoremanent magnetization and the isothermal remanence as a function of field at 1.7 K, as shown in Fig. 7. For the former, the field is applied at $T < T_f$, and the sample cooled to 1.7 K in the field which is then reduced to zero, whereas for the isothermal remanence the sample is cooled to 1.7 K in zero field, the field applied and then withdrawn. The same saturation remanence is attained irrespective of procedure, provided the field exceeds about 20 kOe. A field of similar magnitude is needed to close the hysteresis loop.

5. *Time dependences:* $T < T_f$

Time variations of the magnetization measured under different experimental conditions will be described here in more detail. There is a time-dependent increase with increasing temperature or magnetic field and a decrease when the field is decreased near zero or reversed.

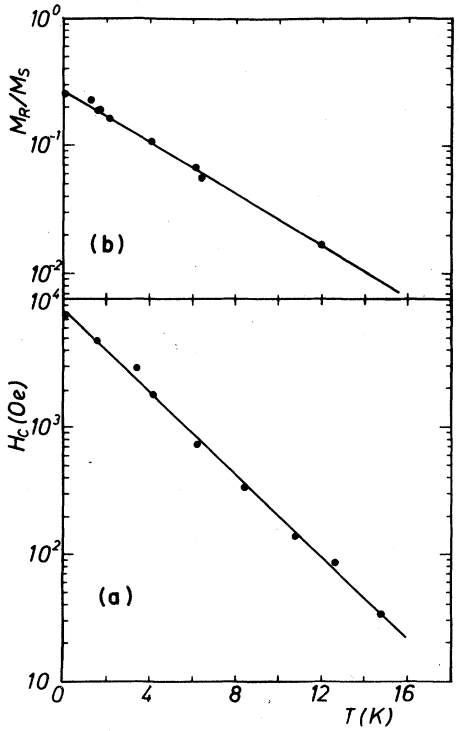

FIG. 6. (a) Coercivity and (b) remanence of amorphous Dy-Cu.

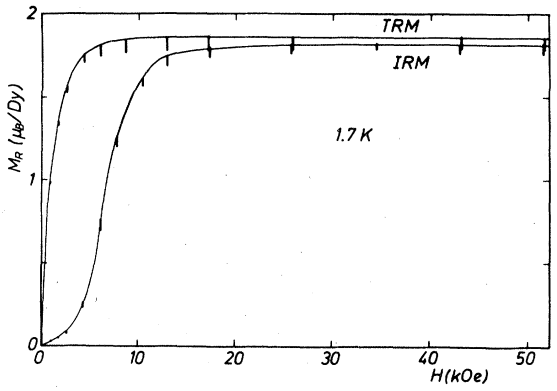

FIG. 7. Thermoremanence (TRM) and isothermal remanence (IRM) of amorphous Dy-Cu, measured at 1.7 K. Vertical lines indicate the time variation in 1 min. The application of the field shown on the horizontal axis is described in the text.

Experimentally it is not possible to measure accurately the response at times below about 30 s with the superconducting magnetometer because of the time required to turn down the field. The response of the sample to small changes of temperature in the SQUID magnetometer is more rapid, on account of the low thermal inertia.

a. Constant weak field, increasing temperature. These measurements were made in the SQUID magnetometer. After cooling to 4.2 K in the earth's field (about 0.2 Oe) a field of 5 Oe was then applied, and the time dependence of the magnetization measured on increasing the temperature by 1 K from 5 to 6, 11 to 12, and 17 to 18 K.

The data shown in Fig. 8 follow a curve of the form

$$M(t) = M(\infty) - \Delta M e^{-t/\tau} .$$

Values of τ were, respectively, 1.7, 2.1, and 1.3 min. They are thus practically *independent* of T and rather insensitive to the precise values chosen for $M(\infty)$.

b. Constant temperatures, with field abruptly reduced to zero. The time dependence of the isothermal remanence is shown in Fig. 9. It decays slowly, approximately following the law

$$\frac{M_R(t)}{M_R(0)} = 1 - c \ln\frac{t}{t'} ,$$

where t' is a starting time, for example, $t' = 10$ s in Fig. 9. A natural choice of time to characterize this

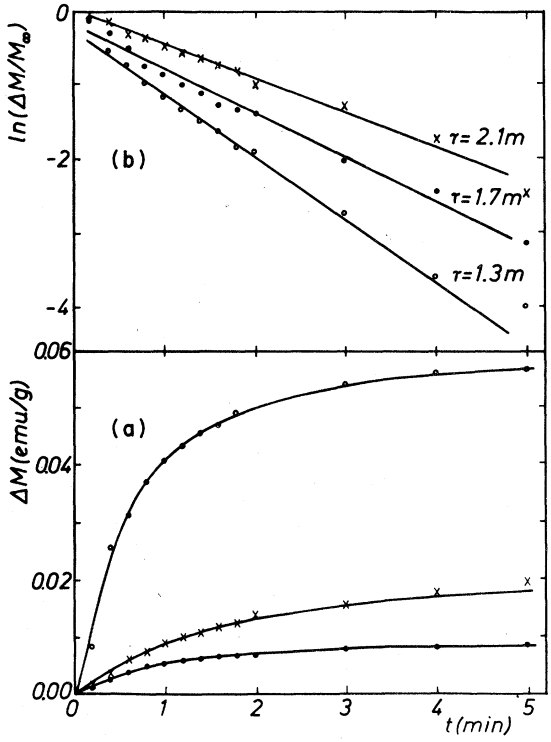

FIG. 8. Sample cooled to 4.2 K in earth's magnetic field. (a) Increase in magnetization in a field of 5 Oe as a function of time on increasing the temperature by 1° from 5 to 6 K; ●; from 11 to 12 K, x; and from 17 to 18 K, ○. (b) The same data plotted on a logarithmic scale to show the exponential approach to the new equilibrium. Solid lines are not calculated curves.

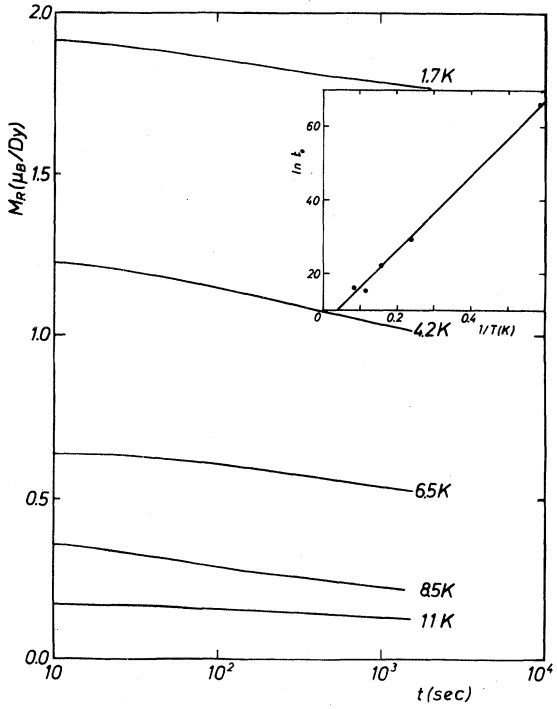

FIG. 9. Time decay of the isothermal remanence of amorphous Dy-Cu at several temperatures. The inset shows how the extrapolated time for the remanence to decrease to zero, depends on temperature.

decay is $t_f = t' \exp(1/c)$, which ranges from 2×10^{20} years at 1.7 K to 0.2 years just 1 K below T_f. Despite the ambitious extrapolation on the ln t axis there can be little doubt that amorphous Dy-Cu exhibits a stable magnetic order after the application of a magnetic field.

The inset on Fig. 9 presupposes that the decay of the remanence is a thermally activated process so that

$$t_r = t_0 \exp(E_n/kT) \quad .$$

The activation energy E_n is about 100 K, whereas the time between "attempts," t_0, is of order 50–3000 s. E_n is similar in magnitude to that expected from anisotropy (or exchange) energy per dysprosium ion, but the physical significance of t_0 is obscure. Possibly significant is the fact τ agrees with t_0, within an order of magnitude.

c. Constant temperature, increasing field. In a third set of experiments, a field in the range 1–8 kOe was applied fairly rapidly (20 s) to a zero-field cooled, unmagnetized sample. The data (not illustrated) show a fairly rapid initial response tailing into a slower ln$t$ increase. At 4.2 K, the initial response is consistent with an exponential $(1 - e^{-t/t'})$ with time constant ~ 100 s, whereas extrapolation of the logarithmic part to the value of the magnetization obtained in the same field, (after first saturating in 50 kOe) gives $\sim 10^4$ s in 8 kOe rapidly increasing times in smaller fields.

6. *Hysteresis at very low temperatures:* $T \ll T_f$

The hysteresis loop measured at 4.2 K is shown in Fig. 10(a) where the part of the curve shown dashed represents the region of significant time-dependent effects.

Next we made measurements in the very-low-temperature range (100 mK) to see whether the remanence increased over that found at 4.2 K which was approximately 10% of saturation. Figures 10(b) and 10(c) indicate that while there is an increase to nearly 30%, the remanence still falls short of the value ($\geq 50\%$) predicted by a simple model of purely ferromagnetic interactions and random anisotropy.[22] The measurements were made on a sample cooled by adiabatic demagnetizing to a temperature of 100 ± 20

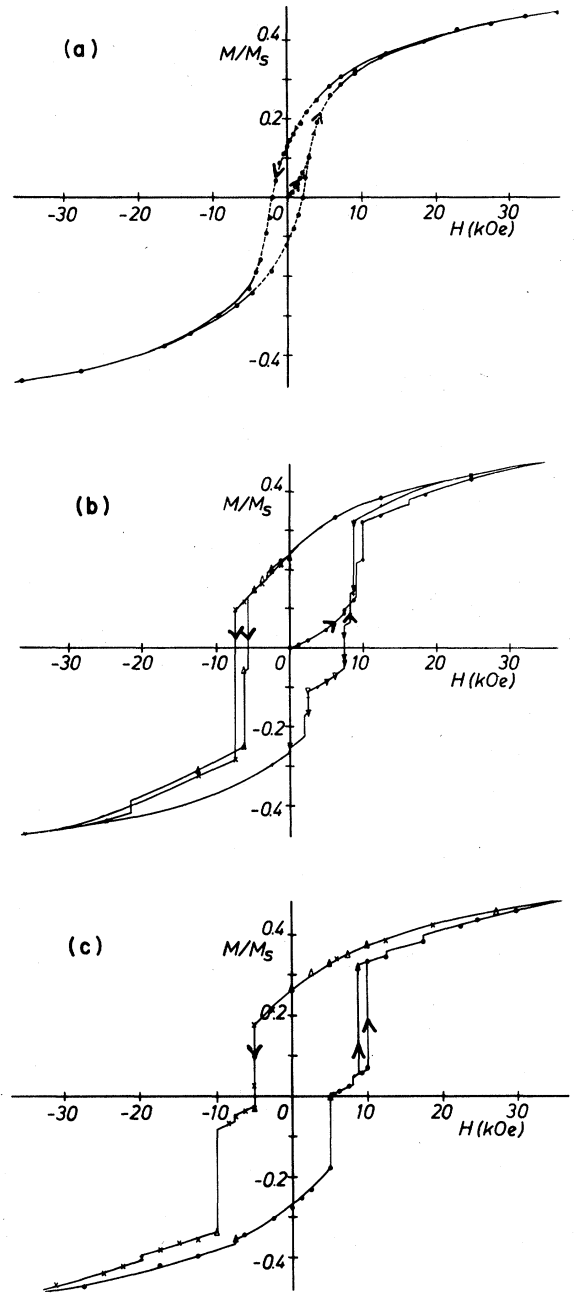

FIG. 10. Hysteresis loops (a) at 4.2 K and (b) at 100 mK cooled from above T_f in 0 kOe and (c) at 100 mK cooled from above T_f in 50 kOe. In (b) and (c) different loops are indicated by triangles, circles, and crosses.

mK. In common with all the magnetization curves, the field was applied in the plane of the Dy-Cu film to avoid demagnetizing fields.

An unexpected and quite remarkable feature appeared in the very-low-temperature loops. Instead of a smooth field dependence in the irreversible part of the loop, the magnetization changes in a series of large discrete jumps. This is reminiscent of the Barkhausen effect in a sample containing about half a dozen domains. Each would have volume 10^{-2} mm^3 and contain some 2×10^{18} Dy ions.

On field cycling, after cooling in zero applied field, the jumps occur in roughly the same places, but if the cooling is repeated, or if the sample is cooled in an applied field, a different pattern of jumps is obtained. No asymmetry of the hysteresis loop is induced in this latter case, however.

Small spontaneous fluctuations of the magnetization as a function of field were observed, particularly in the second and fourth quadrant of the M:H plane.

C. Heat capacity (Ref. 23)

Specific heat was measured at temperatures ranging from 1.4 to 25 K using the thermal relaxation method with an apparatus similar to the one described by Bachmann *et al.*[24]

The sample was taken from a sapphire disk, other parts of which were used for the resistivity and most of the magnetic measurements. The sample mass was 1.4 mg and the mass of sapphire substrate 49 mg. It was mounted on a silicon bolometer using a small quantity of Apiezon N vacuum grease applied by allowing a measured drop of a solution of grease to evaporate. A correction for all the addenda was made by remeasuring the sapphire after dissolving off the Dy-Cu alloy in concentrated HCl and remounting it with the same amount of grease.

Despite a 70-fold disproportion in mass between sample and addenda, the heat capacity of the alloy can be measured successfully in the low-temperature region because of the large magnetic- and crystal-field contribution of the Dy ions, and the rather low characteristic lattice temperature. At 20 K, the addenda account for 80% of the total measured heat capacity, but their contribution becomes relatively less important at lower temperatures so that by 4.2 K they account for only 30% of the total [Fig. 11(a)].

The specific heat of the sample is therefore subject to a relative error which increases with increasing temperature. The result of addenda subtraction is shown in Fig. 11(b). There is no sign at the freezing temperature of the λ anomaly normally associated with a magnetic phase transition. It is possible that there might be a change of slope, but the data in this region are too uncertain to be quite sure.

The specific heat of the sample C_s may be broken down as the sum of three contributions:

$$C_s = C_{\text{latt}} + C_{\text{el}} + C_{\text{exc}} \ . \tag{2}$$

The first term, due to the lattice, will be the largest at high temperatures. Figure 11(b) shows C_{latt} calcu-

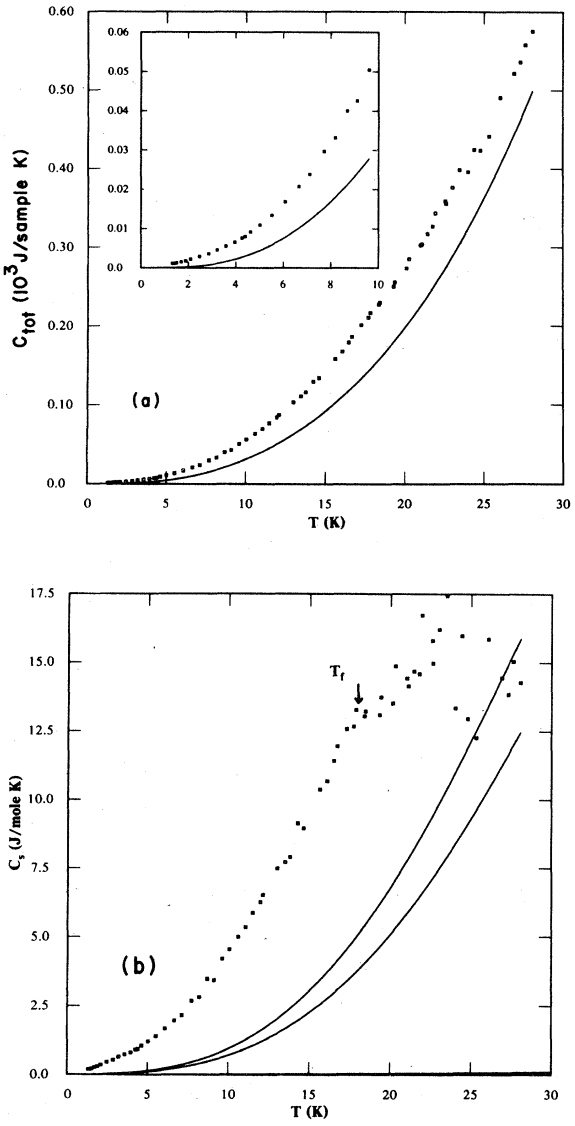

FIG. 11. (a) Total specific heat of amorphous Dy-Cu plus addenda comprising sapphire substrate, mounting grease, silicon bolometer, and leads. The insert, shows C_{tot} with an expanded temperature scale. The contribution of the addenda alone is indicated by the solid curve, a polynomial fit to data points. (b) Specific heat of amorphous Dy-Cu. The two solid lines show two extreme estimates of the lattice contribution corresponding to Debye temperatures of 180 and 200 K. Included in both solid curves is an estimate of the electronic contribution.

lated from the Debye model for two extreme choices of Debye temperature. One limit is given by crystalline Dy-Cu, since amorphous alloys have invariably been found to be "softer" than their crystalline counterparts.[25] The value of 200 K was obtained by scaling data on cubic Y-Cu.[26] Another limit is given by the requirement that the lattice specific heat cannot exceed the entire specific heat of the sample. It follows that $180 < \Theta_D < 200$ K. In the following analysis Θ_D is taken as 190 K, but the choice of any value in this range has an insignificant effect on the data at lower temperatures, below about 10 K.

The electronic specific heat is a small term, proportional to T. The coefficient is taken to be the same as for crystalline Y-Cu, 5 mJ/mole K^2.[26]

All the interest resides in the remaining term C_{exc}. In it are lumped together the magnetic- and crystal-field excitations of the dysprosium. Below 6 K, C_{exc} is the dominant term in the total measured heat capacity, addenda included. In Fig. 12, C_{exc} is plotted as a function of temperature, on both linear (a) and logarithmic (b) scales. Two features are established.

(i) At temperatures well below the freezing temperature, there is a large, almost linear specific heat ($\gamma = 155$ mJ/mole K^2).

(ii) The entropy, obtained by integrating C_{exc}/T up

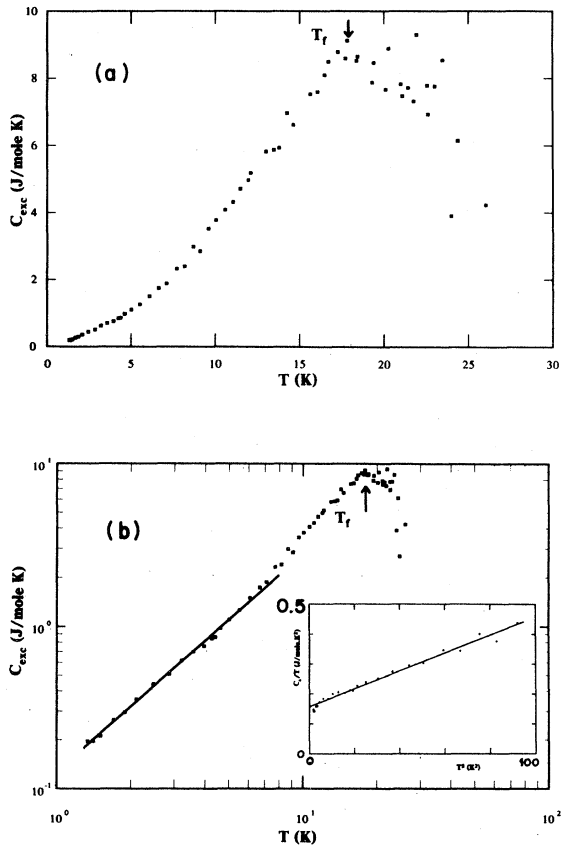

FIG. 12. Specific heat of amorphous Dy-Cu, after correcting for lattice and electronic contributions plotted (a) on a linear scale and (b) on a logarithmic scale. The insert on (b) shows C_s/T plotted against T^2 to give the coefficient of the linear term.

to T_f is 5.8 ± 1.0 J/mole K. The errors allow for the maximum uncertainty in the choice of Debye temperature and composition of the sample. This entropy is much less than $R \ln(2J+1) = 23$ J/mole K for Dy ($J = \frac{15}{2}$). It is however almost exactly $R \ln 2$, a value we discuss in terms of the fundamental Kramers doublet.

III. DISCUSSION

The experimental data establish that some type of magnetic ordering does appear in amorphous Dy-Cu below a spin-freezing temperature which is marked by a discontinuity in the temperature derivative of the low-field magnetization, however it may have been measured. Observation of stable remanence is decisive evidence for magnetic order. In addition the hyperfine splitting of the Mössbauer spectrum indicates that all the dysprosium atoms participate. Although the remanence actually shows some time dependence, the times estimated by extrapolation for its complete decay below 3 K exceed the age of the universe, so it may reasonably be regarded as stable.

The magnetic structure of the ordered state will be discussed first. At the onset, it is clear that amorphous Dy-Cu is not a ferromagnet, at least in the usual sense that all atomic moments are aligned parallel at $T=0$. The Curie constant derived from the paramagnetic susceptibility agrees with that expected for Dy^{3+} ($J = \frac{15}{2}$), and the value of the hyperfine field confirms an essentially pure $J = \frac{15}{2}$ state for the Dy at 4.2 K. A moment of $10\,\mu_B$/atom is associated with this state yet the magnetization which can be induced in very large laboratory fields in only one-half or two-thirds as much with no sign of saturation. At the same time, remanence of up to 2.7 μ_B/Dy testifies to a magnetic structure with a large net moment. In the light of the random anisotropy model below, the likely magnetic structure is asperomagnetic, as illustrated in Fig. 1(b). The moments within a domain are randomly oriented according to an anisotropic probability distribution so that, in this case, they are about three times as likely to point in the northern hemisphere as the southern. Direct evidence for macroscopic domains many hundreds of microns in size is given by the Barkhausen jumps in the low-temperature hysteresis loops of Fig. 10. Their observation puts the concept of asperomagnetic order onto a sound footing.[27]

It is not certain however that these domains preexist in the zero-field cooled, unmagnetized state. We argued earlier[1] that the size of an asperomagnetic domain in the presence of strong random anisotropy should depend sensitively on the range of the exchange interaction. That argument is given in more detail in the Appendix. In the limit of nearest-neighbor ferromagnetic exchange, the unmagnetized state is expected to be composed of regions whose direction of magnetization wanders over distances of order ten lattice spacings. A magnetized state with almost the same energy as the unmagnetized one is obtained by flipping the spins at weak spots where the local anisotropy axis is almost perpendicular to the exchange field. It is just these excitations that dominate the specific heat at low temperatures and leads to the linear temperature dependence of the specific heat as shown in Fig. 12(b).

Is there a phase transition? Certainly there is a well-defined temperature where the irreversible susceptibility makes its appearance on the time scale of a particular measurement (Fig. 4). Absence of any corresponding anomaly in the specific heat [Fig. 12(a)] does not rule out a second-order phase transition. It just means that the specific-heat exponent α must be less than -1.

From the susceptibility which suggests that there may be a phase transition, it is possible to make another estimate of the critical exponents from the magnetic data, since a direct field couples to the net moment. The susceptibility in the earth's field above T_f, from 20–30 K, gives $\gamma = 1.05$ and $M(H)$ curves at 18 K in fields of 250–2500 Oe give $\delta = 1.9$, where the exponents γ and δ are defined by $M(T) \propto (T_c - T)^{\beta}$ and $M(H) \propto H^{1/\delta}$. Using the equalities $\alpha + 2\beta + \gamma = 2$ and $\gamma = \beta(\delta - 1)$, we deduce $\beta = 1.2$ and $\alpha = 1.5$ where α comes from the zero-field specific heat $C(T) \propto (T - T_c)^{-\alpha}$. This specific-heat exponent is compatible with the data, but experimental evaluation of β poses a problem. Figure 5 shows that there is no way of deriving the spontaneous magnetization by extrapolating the magnetization curves to zero field, as is normally done for a ferromagnet. Nor could β be obtained for the temperature dependence of the hyperfine field, which is usually an excellent probe of the stable component of the local moment, which is the order parameter $\sqrt{\langle \mu(0)\mu(t)\rangle_{t\to\infty}}$. Chapert and Boucher[28] have found that the hyperfine splitting in amorphous Dy-Ag persists well above the spin-freezing temperature because the time taken for spin reorientation in the fundamental crystal-field doublet; an improbable transition with $\Delta M_J = 15$, is long compared with the nuclear Larmor precession time. (In contrast, the hyperfine field in transition metals and S-state rare earths is a good measure of the local magnetization because fluctuations due to spin waves are rapid compared with the nuclear Larmor frequency.)

A way of estimating β is from the difference in the reversible and irreversible susceptibilities below T_f. If it is reasonable to take this as proportional to the spontaneous magnetization, then we find $\beta = 1.0(2)$. These factors lend support to the idea of a second-order phase transition taking place at T_f which has quite different critical exponents from that of a normal three-dimensional (3D) Ising magnet.

Up to now we have implied that the magnetism of amorphous Dy-Cu is dominated by strong random anisotropy. We must now consider explicitly the evidence for this. Compelling points are the large coercivity [$(BH_{max} = 19$ MG Oe at 100 mK] and the magnetic entropy at T_f, which is only 25% of the total R ln16 associated with the Dy^{3+} ion, and corresponds to the entropy of a single Zeeman-split Kramers doublet, R ln2. The remainder of the entropy will be developed on population of the other crystal-field levels at higher temperatures. Lack of saturation in high fields is not in itself a proof of random anisotropy. It is found in Gd alloys[29,30] where a distribution of positive with some negative exchange interactions leads also to an asperomagnetic spin structure.

Predominantly ferromagnetic exchange in our present alloy is indicated by the positive paramagnetic Curie temperature $\Theta_p = 22$ K. Work on Gd_xCu_{1-x} alloys[29] may be a guide to exchange in Dy_xCu_{1-x}. The gadolinium alloys are ferromagnetic when $x \gtrsim 0.6$ and "spin-glass"-like when $x \lesssim 0.3$. Exchange in the present alloy with, $x = 0.41$, is therefore expected from the Θ_p value to be predominantly positive, but include some negative interactions. In a study of the whole amorphous Dy_xCu_{1-x} system, von Molnar *et al.*[18] find no evidence for any net moment in alloys with $x < 0.4$, but there is an increased initial susceptibility when $0.40 < x < 0.55$, suggesting a rather narrow range of concentration where the alloys are asperomagnetic. Estimates of an exchange field from Θ_p and the low-temperature specific heat (see below) are 110 and 77 kOe, respectively. Antiferromagnetic exchange will be weaker than this, so the lack of saturation in high magnetic fields must be attributed to crystal-field effects. In fact, the magnetization curve is effectively linear in fields greater than about 50 kOe, as predicted by the random anisotropy model, Eq. (1). The dotted line in the insert to Fig. 5 is calculated from

$$H_1 = g\mu_B \vec{J} \cdot \vec{H} - B_2^0 \hat{0}_2^0 \ , \qquad (3)$$

with $J = \frac{15}{2}$, $T = 0$, $H = H_{app}$ and random orientation of the crystal-field axes. The best fit to the high-field slope is obtained with $B_2^0 = 1$ K (equivalent to $D = 3$ K if the crystal-field term is represented by $-DJ_z^2$). The slight gap between the experiment and calculation at high field may be attributed to uncertainty in the sample mass. The much greater discrepancy at lower fields, and, in particular, the remanence, which is less than half the calculated value, may be attributed in part to the effect of temperature, but mainly to the antiferromagnetic exchange which is responsible for an asperomagnetic structure with some moments in the southern hemisphere. If the exchange were purely ferromagnetic, they would all be in the northern. [This seems to be the case for amorphous $DyNi_3$, for which $B_2^0 = 2$ K (Ref. 15), and other R-Ni amorphous alloys.[31]]

The value $B_2^0 = 1$ K means that the overall crystal-field splitting of the $J = \frac{15}{2}$ multiplet is 168 K. This is equivalent to an "anisotropy field" of 250 kOe, so the crystal-field interaction in Eq. (1) is substantially stronger than the exchange term. In particular, the lowest $\frac{15}{2}$ Kramers doublet is separated from the next higher $\frac{13}{2}$ doublet by 42 K in zero magnetic field, which means that at temperatures of order T_f and below, the alloy will be an excellent approximation to a random Ising magnet, in the sense that the quantization axes are randomly oriented.

It might have been expected that the random anisotropy would produce deviations from the simple Curie-Weiss law for the susceptibility. Numerical calculations on Eq. (3) with $J = \frac{15}{2}, H = H_{app}$ have shown that this is not the case. A Curie susceptibility with $C_m = 14.2$ is found down to temperatures of order B_2^0. Measurements of the paramagnetic susceptibility are therefore useless for discovering the presence of random axial anisotropy, but conversely the parameter Θ_p should provide an accurate indication of the average exchange interaction. Isotropic random dispersion of the anisotropy axes is somehow equivalent to degeneracy of all M_J levels in any direction.

An exception would occur if the dispersion of anisotropy axes were not isotropic, but had some texture which could probably be represented by an ellipsoid of revolution with its axis perpendicular to the plane of the film. (This ellipsoid is just a way of representing the probability that the axis at any site should be oriented in any given direction.) This is one way in which macroscopic bulk anisotropy can be produced in amorphous films,[32] but it does not apply to the present alloy because, as we have seen, the susceptibility is isotropic (Fig. 3).

Turning now to temperature- and time-dependent effects in the irreversible magnetization, several points emerge from the data. First of all, the area of the hysteresis loop at low temperatures corresponds to an energy loss on passing from the positively to the negatively magnetized states of 45 J/mole or 5.4 K/atom. The activation energies deduced from the temperature dependence of the coercivity and remanence (Sec. II B 4) are a little smaller, as might be expected since the decay is to an unmagnetized rather than a reverse magnetized state. In any case, the energy involved is an order of magnitude smaller than the average energy required to flip a single spin in the exchange field (50–75 K). This suggests that the reversed domains grow out from around the weak spots or groups of weak spots where the local anisotropy axis is perpendicular to the exchange field, and spin flip can be achieved at much less than the average energy cost. These weak spots, whose location depends on the instantaneous spin configuration,

constitute a sort of random domain wall.

Time-dependent effects on the magnetization are two sorts. There is an initial, comparatively rapid, component whose characteristic time is about 100 s and does not depend significantly on temperature (Fig. 8). This is followed by a slow ln t decay at longer times whose slope is both field and temperature dependent. A characteristic time obtained by extrapolating the slow component of the remanence to zero follows an activation law with an energy of about 100 K, and an attempt frequency of $10^{-2}-10^{-3}$ s^1 (Fig. 9). The significance of these results may be as follows. The temperature independence of the fast component suggests tunneling rather than an activated process. At longer times, the probability of spin flip by activation becomes more significant. There is a range of energy barriers, essentially given by the splitting $2g\mu_B JH_m\cos\theta$ of the fundamental Kramers doublet by the molecular field. θ is the angle between H_m and the local crystal-field axis. Extrapolation of the remanence to zero may be expected to pick out the maximum of this distribution, $2g\mu_B JH_m$, and in fact the measured value of 100 K agrees with this splitting for $H_m=77$ kOe, as deduced from, e.g., the specific heat.

The specific heat has been calculated from Eq. (3), with the simplifying assumptions that H_m and B_2^0 are constant in magnitude, and that there is no correlation between the directions of the random anisotropy axis and the magnetic field. In other words, only single-ion excitations are taken into account, and the temperature dependence of the molecular field is ignored. Despite these serious approximations, a reasonable fit of the specific heat up to T_f can be obtained with $H_m=77$ kOe and $B_2^0=1.0$ K.

The model used to calculate the specific heat is best at low temperatures, and successfully explains the large nearly linear term below about 5 K.[23] The argument for a constant density of states for magnetic excitations of Kramers ion in a random magnet has been independently proposed by Korenblit and Shender.[33] A clear understanding of the physical origin of such a density of states is provided as follows. Suppose that the second term in Eq. (3) is much greater than the first. The energy levels are then a set of 8 Kramers doublets at $E_i=3B_2M_J^2$, each split by the magnetic perturbation $\Delta E_i=\pm g\mu_B M_J H_m\cos\theta$. The probability $P(\theta)$ of finding an angle θ between random directions is just $\sin\theta$. But $(dE/d\theta)$ is also proportional to $\sin\theta$ within the doublet. The density of states for excitations, $P(\epsilon)$, where $P(\epsilon)\,d\epsilon=P(\theta)\,d\theta$, is therefore a constant, $(2g\mu_B M_J H_m)^{-1}$ within each doublet and zero outside. The corresponding specific heat at temperatures low compared with the doublet spacing is

$$C=Nk^2T/g\mu_B JH_m\ . \qquad (4)$$

H_m is derived directly from $\gamma=82$ kOe, in close accord with the value obtained from the more elaborate analysis.

The excitations at the lowest temperatures are the spin flips of those ions for which $\theta\sim\pi/2$. If one includes the deviation from the straight line below $T^2=3$ K^2, the data in Fig. 12(b) correspond to $C=\alpha+\gamma T+\beta T^3$ with $\alpha/\gamma=0.5$ K, which implies that there exists a small gap in the density of states at zero energy, $\epsilon_g=2.5$ K. The form $C=\alpha+\gamma T$ is an approximation for the specific heat due to single-ion excitations valid at temperatures of order or greater than the gap. If one assumes that the origin of H_m is ferromagnetic, nearest-neighbor exchange, an examination of the equilibrium of an ion with its shell of Z neighbors shows that no ion is stable with θ exactly equal to $\pi/2$, but that the upper limit is approximately $(\pi/2-g\mu_B H_m/6B_2^0JZ)$. With $Z=8$, this corresponds to a minimum splitting of the lowest Kramers doublet of 2.1 K, in accord with the gap at zero energy in the density of states.

The model discussed here also provides some insight into the spin-glass problem. If strong anisotropy in that case can be attributed to dipolar fields rather than to the crystal field, then each moment will be constrained to behave like an Ising spin, just like the dysprosium in its fundamental Kramers doublet. The original explanation of the linear specific heat in spin-glass[6] was based on single-spin excitations in an Ising model with a $P(H)$ distribution which tends to nonzero constant value at $H=0$. There is an analogy with the present situation, where the quantization axes of the Ising spins are frozen at random with respect to the molecular field, instead of being defined by it. The effective field at some site is $H=H_m\cos\theta, P(H)=P(\theta)(d\theta/dH)$ is a constant, $1/H_m$.

In a recent theoretical analysis, Pelcovits, Pytte, and Rudnick[34] have further considered the problem of spin-glass and ferromagnetic behavior induced by random uniaxial. They conclude that there is no phase transition, but that the spin-glass state is favored depending on the degree of disorder which is probably sufficient in many amorphous alloys such as Dy-Cu. In the final analysis, probably neutron-diffraction studies are needed to determine the range of the correlations that exist in the zero-field cooled state of Dy-Cu.

IV. CONCLUSIONS

Amorphous Dy-Cu containing 41 at.% Dy is an alloy where random anisotropy dominates exchange. It is therefore an example of a random Ising system.

There is a sharp peak in the susceptibility at the magnetic transition temperature which our data suggest may be a second-order phase transition with a set of critical exponents which differ from any found in crystalline magnets.

The exchange is predominantly, though not exclusively, ferromagnetic, and the resulting magnetic structure is asperomagnetic, at least after a field has been applied. The spins within a domain are randomly oriented, close to their local crystal-field axis, with an anisotropic probability distribution as caused by the exchange. The net moment of a domain, obtained by extrapolating the remanence to $T=0$, is 25% of the hypothetical, collinear saturation which would only be achieved in fields of order 10^6 Oe. Direct evidence for the asperomagnetic domains in the magnetized state is provided by the large Barkhausen jumps in the hysteresis loop at very low temperatures although this says little about zero-field domain sizes.

A simplified single-ion random-anisotrpy model can explain several of the magnetic properties, notably the approach to saturation, the time dependence of the remanence, and the large linear specific heat at low temperatures which arises naturally from single-ion excitations of the dysprosium, without having to invoke either spin waves or the sort of configurational reorientations which are thought to be important in spin-glasses. No attempt has been made to calculate any collective property, whether the magnetic ground state, collective excitations or the phase transition, but the comprehensive experimental results we have obtained here should serve as a test of any such calculations in the future.

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APPENDIX

We give a crude estimate of the domain size in the unmagnetized state for an asperomagnet with random axial anisotropy and ferromagnetic exchange coupling of each atom with its Z neighbors.

Consider an atom near the edge of the domain whose net moment is along the z axis so that there are $\frac{1}{2}Z$ neighbors outside the domain assumed to produce no net exchange field at the atomic site and $\frac{1}{2}Z$ inside the domain. The z component of the exchange field produced by these is $\frac{1}{2}Z|\frac{1}{2}H_{ex}|$, since $\langle S_z\rangle = S/2$ for the spins within the domain. The x-y component is $\sqrt{Z/2}|H_{ex}|\sqrt{3/2}$. H_{ex} is the magnitude of the exchange field produced by each neighbor. The average angle between the direction of the exchange field and the z axis is therefore $\theta=\tan^{-1}\sqrt{6/Z}$. This is 35° for $Z=12$. The accumulation of these misorientations will ensure that "memory" of the original z direction will then be lost over 10 interatomic distances, although this distance will increase in proportion to Z.

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