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LINEAR SPECIFIC HEAT OF AN AMORPHOUS MAGNET DUE TO SINGLE-ION EXCITATIONS

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Résumé. — Il existe une contribution linéaire importante ($\gamma = 155$ mJ/mole K²) à la chaleur spécifique d'un alliage Dy-Cu amorphe. Celle-ci apparaît bien au-dessous de la température de blocage des spins qui se situe vers 18 K. On l'explique simplement par les excitations à un ion d'un ion de Kramers soumis à la fois à un fort *champ cristallin* aléatoire et à un faible champ magnétique d'échange.

Abstract. — The specific heat of an amorphous Dy-Cu alloy includes a large linear contribution ($\gamma = 155$ mJ/mole K²) at temperatures well below the sharp spin-freezing transition at $T_f = 18$ K. This can be simply explained in terms of single-ion excitations of a Kramers ion interacting with a random oriented *crystal field* and a weaker magnetic field.

Low-temperature specific heats approximately proportional to temperature are a feature of various disordered and amorphous solids. They are well-known in dielectric glasses [1] and spin glasses [2]. It has recently been argued that this behaviour is an inevitable consequence of the zero-point entropy in an amorphous solid [3].

The linear specific heat derives from a constant density of states of low-energy excitations. The exact nature of these excitations remains something of a mystery in both glasses and spin glasses, and it has been impossible so far to calculate their density of states from first principles. Current ideas identify the excitations in glasses with tunnelling of single atoms or groups of atoms to new spatial configurations with almost the same energies [4], whereas those in spin glasses are thought to be analogous configurational rearrangements of groups of spins [5].

The purpose of this paper is to present data on another kind of disordered material which shows a very large linear specific heat at low temperatures — an amorphous magnet with strong local anisotropy. It will then be demonstrated that a constant density of states of single-particle excitations follows directly

from a model Hamiltonian for the system, and is capable of accounting for the magnitude of the effect. In other words, at low temperature there is a constant probability $P(\varepsilon)$ that an ion find an excited state ε above its ground state.

The material is an amorphous Dy-Cu alloy, prepared by r.f. argon ion sputtering [6] from a DyCu target. The composition of the resulting film was DyCu_{1.44}Ar_{0.05}O_{0.23}.

The sample has a sharply defined spin freezing temperature at $T_f = 18$ K, marked by a cusp in the low-field ($H_{app} < 10$ Oe) d.c. susceptibility and the onset of irreversible effects in the magnetization, including remanence. The order is not collinear ferromagnetism as the magnetization could not be saturated. In higher fields, the magnetic properties closely resemble those of amorphous TbAg [7] or DyNi₃ [8]. They will be presented in detail elsewhere, together with an analysis of the magnetic structure. For the present purpose, it is sufficient to note that the rare earth moments are frozen with essentially random orientations [8].

The specific heat of the alloy was measured from 1.4 to 25 K by the thermal relaxation method [9]. The

data, after subtracting an estimate of the lattice heat capacity calculated from the Debye model with $\theta_D = 190$ K, are shown in figure 1a. They are linear in temperature below 5 K, and resemble that of a spin glass [10] insofar as there is no λ -anomaly at the freezing temperature, but, unlike a spin glass, there seems to be a change of slope. A plot of C/T versus T^2 (Fig. 1b) gives the coefficient of the linear term, $\gamma = 155$ mJ/mole K². Of this only about 5 mJ/mole K² can be attributed to the conduction electrons [11]. A deviation from the law $C = \gamma T + \beta T^3$ appears at the lowest temperatures.

The excess entropy up to T_f is the second important datum. It was found to be 5.8 (1.0) J/mole K after the subtracting the electronic and lattice contributions from the specific heat. The errors include the uncertainty in the lattice subtraction and in the sample composition. That the entropy is much less than $R \ln 16$ (23.0 J/mole K) anticipated for the Dy³⁺ ion indicates that the *crystal field* is playing an important role. In fact the entropy up to 18 K is just $R \ln 2$ (5.8 J/mole K) as would be expected for Zeeman splitting of a single Kramers doublet. The remainder

FIG. 1. — a) Molar heat capacity measured on a 1.4 mg sample of amorphous DyCu_{1.44}Ar_{0.05}O_{0.23}, after an estimate of the lattice contribution has been subtracted. T_f is the spin freezing temperature. The solid line is calculated from energy levels of figure 2. b) The total specific heat plotted to give the coefficient of the linear term.

of the entropy will be developed upon population of the other crystal-field levels, at higher temperatures.

Crystal-field effects in amorphous magnets have been extensively studied by the McGill group [12, 13]. They have demonstrated by point charge calculations on an amorphous model structure that second-order terms dominate the crystal field and define a local easy axis at each site. Consider therefore the site Hamiltonian

$$\mathcal{H} = -g\mu_B \mathbf{J} \cdot \mathbf{H}_m - B_2 \mathbf{O}_2^0 \quad (1)$$

where $\mathbf{H}_m$ is the molecular field acting in the z -direction, B_2 is the crystal field parameter and $\mathbf{O}_2^0$ is Stevens operator equivalent for the diagonal term in the second order crystal field, referred to the local crystal-field axis z' , which makes some angle θ with z . It is assumed to begin with that there is no correlation between z and z' , so θ takes any value between 0 and 2π . The off-diagonal term $\mathbf{O}_2^2$ is neglected, and for simplicity it is further assumed that $\mathbf{H}_m$ and B_2 have constant magnitude at every site, and are independent of temperature. Calculations with realistic distributions of $\mathbf{H}_m$ or B_2 give essentially the same results in the low-temperature limit, provided $3 B_2 J / g\mu_B H_m > 1$.

After a rotation of the z' axis by θ , the 16×16 complex matrix derived from (1) was diagonalized to obtain the eigenvalues as a function of θ for a range of values of B_2/H_m . The specific heat calculated from the energy-level scheme of figure 2, which corresponds to $H_m = 77$ kOe and $B_2 = 1.0$ K is given by the solid line in figure 1a. The values of B_2 and H_m needed to fit the data are plausible ones. The crystal field is the dominant interaction splitting the $J = 15/2$ multiplet by 300 K, and separating the $|\pm 15/2\rangle$ ground doublet from the next, $|\pm 13/2\rangle$ doublet by 50 K at $\theta = \pi/2$. This explains why the entropy associated with the loss of magnetic order is only of order $R \ln 2$. However, the assumption that H_m is independent of temperature is not realistic above $T/T_f \sim 0.3$. In fact

FIG. 2. — Energy levels of dysprosium calculated from (1), with a molecular field $H_m = 77$ kOe and a crystal field parameter $B_2 = 1.0$ K.

the specific heat will rise more sharply with temperature if H_m is allowed to vary, so the value of B_2 just derived is actually a lower limit on the crystal-field parameter.

A rough estimate of the spin-freezing temperature from molecular-field theory is

$$T_f \sim g\mu_B H_m(J + 1)/3 \text{ K} . \quad (2)$$

Equation (2) gives $T_f \sim 20$ K, remarkably close to the experimental observation. Some reduction of T_f should result however from the random relative orientation of the moments and the molecular field.

A clearer understanding of the physical origin of the constant density of low-energy states is provided by the following argument. Suppose that the second term in (1) is much greater than the first. The energy levels are then a set of 8 Kramers doublets at $E_i = 3 B_2 M_j^2$, each split by the magnetic perturbation $\Delta E_i = \pm g\mu_B M_j H_m \cos \theta$. This structure is already apparent in the lower-lying energy levels of figure 2. 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, $(2 g\mu_B M_j H_m)^{-1}$ within each doublet and zero outside. The corresponding specific heat at temperatures low compared with the doublet spacing is

$$C = Nk^2 T/g\mu_B JH_m \quad (3)$$

H_m derived directly from γ is 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 $T^2 = 3 \text{ K}^2$, the data in figure 1b 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. No such gap appears when z and z' are completely uncorrelated, that is, in the limit $g\mu_B H_m/3 B_2 J \rightarrow 0$. However, the exchange is not strictly negligible, compared with the local anisotropy in DyCu, so some weak correlations between the two directions are to be expected. If one assumes that the origin of H_m is ferromagnetic, nearest-neighbour exchange, an examination of the equilibrium of an ion with its shell

of Z neighbours shows that no ion is stable with θ exactly equal to $\pi/2$, but that the upper limit is approximately $(\pi/2 - g\mu_B H_m/6 B_2 JZ)$. 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 glasses [14] was based on single-spin excitations in an Ising model with a $P(H)$ distribution which tends to a non-zero 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 $H = H_m \cos \theta$, so $P(H) = P(\theta) (d\theta/dH)$ is a constant, $1/H_m$.

In summary, the large linear specific heat in amorphous DyCu can be explained in terms of 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. Any contribution from structural excitations [4] should be some orders of magnitude smaller. The essence of the model is the strong crystal field virtually uncorrelated with the molecular field direction at each site. This situation should prevail in any of the possible ground states [15] of amorphous magnets with dominant local anisotropy, so a large linear specific heat is expected to be a common feature of many amorphous and disordered alloys containing rare earth Kramers ions.

The same effect is not expected in non-Kramers ions because the energy levels should all be separated by the low symmetry of the *crystal field*, thus the necessary degeneracy at $\theta = 90^\circ$ does not occur.

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