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J.M.D. Coey, S. von Molnar

To cite this version:

HAL Id: jpa-00231509
https://hal.science/jpa-00231509
Submitted on 1 Jan 1978
LINEAR SPECIFIC HEAT OF AN AMORPHOUS MAGNET DUE TO SINGLE-ION EXCITATIONS

J. M. D. COEY
Groupe des Transitions de Phases, C.N.R.S., B.P. 166, 38042 Grenoble Cedex, France
and
S. VON MOLNAR
IBM, T.J. Watson Research Center, Yorktown Heights, N.Y. 10598, U.S.A.
(Reçu le 17 mai 1978, révisé le 10 juillet 1978, accepté le 3 août 1978)

Résumé. — Il existe une contribution linéaire importante \( \gamma = 155 \text{ mJ/mole K}^2 \) 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 \( \gamma = 155 \text{ mJ/mole K}^2 \) at temperatures well below the sharp spin-freezing transition at \( T_f = 18 \text{ K} \). 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 \( \varepsilon \) 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 \( T_f = 18 \text{ K} \), marked by a cusp in the low-field \( (H_{\text{app}} < 10 \text{ Oe}) \) 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 DyNi\(_3\) [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 $\lambda$-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 K$^2$. Of this only about 5 mJ/mole K$^2$
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
subtracting the electronic and lattice contributions
from the specific heat. The errors include the uncer-
tainty 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 Dy$^{3+}$ ion
indicates that the crystal field is playing and 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
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

$$\mathcal{H} = -g\mu_B \mathbf{J} \cdot \mathbf{H}_m - B_2 O^2 \mathbf{\theta}$$

(1)

where $\mathbf{H}_m$ is the molecular field acting in the $z$-direction,
$B_2$ is the crystal field parameter and $O^2 \mathbf{\theta}$ 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 $\theta$
with $z$. It is assumed to begin with that there is no
correlation between $z$ and $z'$, so $\theta$ takes any value
between 0 and $2\pi$. The off-diagonal term $O^2 \mathbf{\theta}$
will be 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 $\theta$, the $16 \times 16$
complex matrix derived from (1) was diagonalized to
obtain the eigenvalues as a function of $\theta$ 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 $T_f \sim 0.3$. In fact

![Fig. 1. — a) Molar heat capacity measured on a 1.4 mg sample of
amorphous DyCu$_{1.44}$Al$_{0.93}$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.
](image)

![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.
](image)
the specific heat will rise more sharply with tempera-
ture if $H_m$ is allowed to vary, so the value of $B_z$ 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

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

Equation (2) gives $T_f \sim 20 \, \text{K}$, 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
$E_i = 3 B_z M_i^2$, each split by the magnetic perturbation
$\Delta E_i = \pm g \mu_B M_i H_m \cos \theta$. This structure is already
apparent in the lower-lying energy levels of figure 2.

The density $P(\theta)$ of finding an angle $\theta$ 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, $P(\theta)$, where $P(\theta) \, d\theta = P(\theta) \, d\theta$, is
therefore a constant, $(2 g \mu_B M_i H_m)^{-1}$ within each
doublet and zero outside. The corresponding specific
heat at temperatures low compared with the doublet
spacing is

$$C = N k^2 T/g \mu_B J H_m$$

(3)

$H_m$ derived directly from $\gamma$ 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 $\alpha/\gamma = -0.5 \, \text{K}$, which implies that there exists
a small gap in the density of states at zero energy,
$\varepsilon_g = 2.5 \, \text{K}$. The form $C = \alpha + \gamma T$ is an approxima-
tion 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 $g \mu_B H_m/3 B_z J \rightarrow 0$.

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 $\theta$
exactly equal to $\pi/2$, but that the upper limit is approxi-
mately $(\pi/2 - g \mu_B H_m/6 B_z J Z)$. 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 con-
strained 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 quanti-
zation 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 amor-
phous 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 exci-
tations [4] should be some orders of magnitude smaller.

The essence of the model is the strong crystal field
generally uncorrelated with the molecular field direc-
tion 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 neces-
sary degeneracy at $\theta = 90^\circ$ does not occur.

Acknowledgments. — The authors wish to thank
R. J. Gambino for the sample preparation and charac-
terization. They are also grateful to T. R. McGuire
for permission to quote his unpublished SQUID
magnetometer data.

The work was performed during a stay by J. M.
D. Coey at the IBM T. J. Watson Research Labora-
tory.

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