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Calorimetric investigation of the low temperature excitations of Pr^{3+} ions in the amorphous matrix $\text{La}_{80}\text{Au}_{20}$

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Résumé. — Nous présentons des mesures de chaleur spécifique entre 0,3 K et 10 K, dans des champs magnétiques atteignant 7 teslas, sur trois alliages amorphes $\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$, avec $x \leq 10$. Les différentes contributions à la chaleur spécifique ont été séparées et analysées. On montre que l'état fondamental des ions Pr^{3+} est un état singulet. La séparation entre le fondamental et le premier niveau excité varie d'un site à l'autre. Dans les alliages les plus concentrés les forces d'échange sont suffisamment fortes pour polariser les ions Pr^{3+} sur un certain nombre de sites.

Abstract. — We present specific heat measurements between 0.3 K and 10 K, in magnetic fields up to 7 teslas, on three amorphous $\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$ alloys, with $x \leq 10$. The various component contributions to the specific heat have been separated and analysed. The crystal field ground state of the Pr^{3+} ions is shown to be a singlet. The separation between the ground state and the nearest level varies from site to site. In the more concentrated alloys the exchange forces are strong enough to polarize the Pr^{3+} ions on a number of sites.

The topological disorder in the amorphous state produces randomly distributed electric field gradients at the atomic sites. In rare earth amorphous alloys it has been shown that the physical situation is fairly well approximated by the random uniaxial model [1] for rare earth ions with large values of the angular momentum J , but that substantial deviations from the predictions of this model can be expected when J is small especially for non Kramers ions [2]. In the latter case a continuous spectrum of low energy crystal field excitations is predicted to exist as a function of the asymmetry parameter η which measures the departure from uniaxiality and is expected to be rather widely distributed from site to site in the material. Such a situation ought to be reflected in the low temperature specific heat by a plateau extending down to very low temperature, instead of the typical exponential decrease of a Schottky anomaly [3]. We have previously reported measurements on the amorphous $\text{Pr}_{21}\text{Ag}_{79}$ alloy between

0.3 K and 10 K which strongly support these predictions [4]. However, in order that the actual physical situation may be amenable to the theoretical picture of single ion excitations, without any appreciable effect arising from exchange interactions, it was highly desirable to study more dilute systems. The present paper is devoted to an investigation of the low temperature specific heat of three amorphous $\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$ alloys with $x \leq 10$.

The samples were prepared by the splat-cooling technique and the amorphous structure was ascertained for each foil by X-ray scanning. The a.c. calorimetry technique was used for the measurements. The salient features of the experimental set-up and procedure have been described in a previous paper and references therein [5]. The requirement that the sample assembly be in thermal equilibrium on a time scale much shorter than the period of the temperature oscillations sets an upper limit to the appropriate frequency to be used [6]. This limit has been experimentally determined before each run and the working frequency was chosen to be well below this limit. This was typically 0.2 Hz at the lowest temperatures. The heat capacity of the substrate

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and its addenda was measured separately and subtracted from the data. The three samples used had the nominal compositions $x = 1, 5$ and 10 . Hereafter they will be labelled Pr_1 , Pr_5 and Pr_{10} . They weighed respectively 12, 9.5 and 7 mg. Additional data were taken in magnetic fields, applied perpendicular to the plane of the foils and ranging from 0 to 7 teslas.

Fig. 1. — The molar specific heats of two $\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$ amorphous alloys below 10 K : $\text{Pr}_5(x = 5)$ in zero field, $\text{Pr}_1(x = 1)$ in zero field and in a field of 7 teslas.

Fig. 2. — The molar specific heats of three $\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$ amorphous alloys below 3 K : $\text{Pr}_{10}(x = 10)$ in zero field, $\text{Pr}_5(x = 5)$ in zero field, $\text{Pr}_1(x = 1)$ in zero field and in a field of 7 teslas.

The zero field results, plotted in figures 1 and 2, show that samples Pr_1 and Pr_5 become superconducting at about 3.4 and 1.7 K respectively with transition widths between 0.1 and 0.2 K. Below these transitions the specific heat does not exhibit the steep decrease commonly observed in superconducting materials. Moreover the specific heat of sample Pr_1 for instance is between three and four times larger than that of $\text{La}_{80}\text{Au}_{20}$ between 0.3 K and 1 K. This behaviour implies that praseodymium is responsible for some additional contribution to the specific heat, varying rather slowly with temperature and remaining substantial down to the lowest temperature of the measurements. Such a component,

hereafter designated by C_E , will be imputed to crystal field excitations of the Pr ions in the following discussion. Thus, this simple qualitative observation raises doubts on the relevancy of the uniaxial model in the system.

Another striking feature of the zero field data is the low temperature upturn which is observed in the specific heat of sample Pr_{10} . We believe that this anomaly is mainly nuclear in origin for the two following reasons. (i) First, the bulk magnetic measurements performed down to 1.8 K on a foil taken from the same batch as sample Pr_{10} exhibited some low temperature departures from the Curie-Weiss law [7]. Such departures, although not accounted for by a pure uniaxial model in the sense of Harris *et al.* [1], are typical of crystal field effects. No evidence was found down to 1.8 K of any trend toward magnetic clustering of the spin glass type, whereas, for the amorphous $\text{Pr}_{80}\text{Au}_{20}$, a susceptibility maximum was found to occur at 5 K, which is thought to be indicative of a concentrated spin-glass or mictomagnetic regime [8]. Thus, for sample Pr_{10} , with only 10 at. % Pr, the crystal field effects are likely to prevail over any possible exchange contribution at low temperature. (ii) Second, applying a strong magnetic field (7 teslas) merely enhances the anomaly in the specific heat of sample Pr_{10} , instead of shifting it towards higher temperatures and spreading it over a wider temperature range; moreover it makes similar upturn grow in sample Pr_1 just in the same temperature range (Fig. 2). Consequently the main part of the zero field low temperature upturn in Pr_{10} is not likely to result from thermal excitations of magnetic clusters, as previously observed for instance in nearly magnetic amorphous alloy $\text{Y}_{0.22}\text{Ni}_{0.78}$ [9]. Instead it may be reasonably identified with a nuclear contribution.

Then, in an attempt to proceed further towards a quantitative analysis, we assume that the normal state data, obtained with or without an applied magnetic field H , may be fitted to the expression :

$$C = A(x, H) T^{-2} + \gamma T + \beta T^3 + C_E(x, H, T).$$

The normal state electronic term γT and the lattice one βT^3 are supposed to be field independent and identical in the three samples, while we let the nuclear contribution $A(x, H) T^{-2}$ and the electric field contribution $C_E(x, H, T)$ be both concentration and field dependent. For given values of x and H the data are analysed in two steps : at the lowest temperatures we get a fairly good estimate for A and a less good one for γ , at the higher temperatures the usual plot of C/T versus T^2 yields informations concerning β and C_E . Though we are unable to ascribe a definite form to $C_E(x, H, T)$ it should be proportional to x wherever it may be imputed to the crystal field excitations of non interacting Pr ions. Thus it appears that, starting from the experimental curves of two samples only, such an assumption, as far as it is

correct, does provide the basis for a rather accurate determination of γ , β and C_E/x . Then the range of validity of the assumption may be assessed more or less soundly by checking whether or not the corresponding results are consistent with the experimental data obtained on the third sample. Actually such a fitting procedure works fairly well for temperatures higher than 1 K, and a coherent picture emerges from the whole body of our experimental results. In particular it is gratifying that our estimate of γ , β and C_E/x in zero fields, obtained from a fit to the normal state measurements, obey, within experimental accuracy, the requirement that the entropies associated with the superconducting and normal states must be equal at the superconducting transition points.

The electronic and lattice contributions that we derive are close to, but smaller than published values for the corresponding terms in amorphous $\text{La}_{80}\text{Au}_{20}$ [10], yielding $\gamma = 5 \text{ mJ.mole}^{-1} \text{ K}^{-2}$ and $\theta_D = 119 \text{ K}$, instead of $\gamma = 7 \text{ mJ.mole}^{-1} \text{ K}^{-2}$ and $\theta_D = 96 \text{ K}$. The difference between the values of γ is rather meaningless since the electronic contribution in our alloys is only a small fraction of the total specific heat. But the lattice term as it is given in reference [10] for $\text{La}_{80}\text{Au}_{20}$ is definitely too large to fit our experimental results, especially in the high temperature range. It should be noted however, first, that this term has been estimated from data points on $\text{La}_{80}\text{Au}_{20}$ spanning a temperature range of less than 2.5 K, second, that we have indications that θ_D may be slightly temperature dependent (although such a dependence cannot be taken into account by the present analysis) and third, that our estimate of the Debye temperature is in better agreement with the value $\theta_D = 123 \text{ K}$ derived from Mössbauer measurements on amorphous $\text{La}_{78}\text{Au}_{22}$ at 18 K [11].

The component C_E/x is displayed on figure 3 where, for each of the samples, we have represented by error flags the effect of an uncertainty of $\pm 1\%$ in the whole heat capacity, inclusive of the addenda, in order to appreciate the limits of validity of the present analysis. The following features should be underlined : C_E/x increases only gently with temperature along a structureless perfectly smooth curve, it is not affected, within experimental accuracy, by applying an external field of a few tenths of a tesla, but it is strongly depressed below 4 K by a field of 7 teslas (see Fig. 3). On the other hand the uniaxial anisotropy model, gives the same crystal field energy levels at each site with a doublet $J_z = \pm J$ as the ground state, implying first that C_E/x , in zero applied or exchange field, should be a Schottky anomaly, increasing exponentially with temperature at low temperature, and second, that it should be appreciably altered by the removal of the twofold degeneracy of the ground state when applying even a weak magnetic field. Thus our experimental observations

Fig. 3. — The contribution C_E/x of the crystal field excitations per mole of Pr to the specific heat of Pr_5 and Pr_1 . The dashed curve represents the same contribution with an applied field of 7 teslas.

rule out the relevancy of the uniaxial model and rather suggest the presence of two low-lying non degenerate levels with the separation between them distributed from site to site around some non zero average value. This is in qualitative agreement with the crystal field level structure calculated by Cochrane *et al.* [12] when using computer generated clusters of randomly close-packed hard spheres to take into account the disordered structure of the amorphous state. Finally it can be seen from figure 4 that, below 1 K, the C_E/x curves pertaining to the

Fig. 4. — The contribution C_E/x to the specific heat of Pr_{10} , Pr_5 and Pr_1 below 1 K.

different samples start to deviate from each other, the higher the Pr concentration the greater C_E/x at the lowest temperature. This behaviour, taken in conjunction with the relative magnitude of the nuclear terms to be discussed now, suggests that, in this low temperature regime, exchange interactions interfere appreciably. However the circumstances under which a magnetic moment may be induced on the Pr^{3+} ions will not be examined here.

Since only the high temperature tails of the nuclear contributions are observed, the data have been fitted

Table I. — *The experimental values of the nuclear specific heat coefficient A in $\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$ as compared to the corresponding theoretical values A_{max} when complete polarization of the Pr^{3+} ions is assumed. f is the fraction of Pr^{3+} electronic moments which should have to be fully developed in order to take proper account of the experimental values of A .*

$\text{Pr}_x\text{La}_{80-x}\text{Au}_{20}$	A mJ.K/mole of alloy	$\frac{A}{A_{\text{max}}}$	f
—	—	—	—
$x = 10$ $H = 0$	4.83	4.5 %	21 %
$x = 5$ $H = 0$	0.78	1.5 %	12 %
$x = 1$ $H = 0$	0.04	0.4 %	6 %
$x = 1$ $H = 7 \text{ T}$	2.3	22 %	47 %

to the first term AT^{-2} in the expansion of the nuclear specific heat as a power series of T^{-1} . The results obtained for the coefficient A are summarized in table I. Both the magnetic and quadrupole hyperfine interactions may contribute to A . But, on the basis of available data for crystalline samples, the latter contribution is likely to be unimportant in our temperature range, though Au and Pr nuclei both carry quadrupolar moments. Now the occurrence of a magnetic hyperfine contribution concerns the Pr nuclei only, and requires that the 4f electronic shells are partially polarized even in zero external field. As already mentioned there is actually some indication that the Pr-Pr exchange interactions are sufficient to cause a spontaneous moment to appear on at least a few sites in the most concentrated alloys. In table I the experimental values of A have been compared to the theoretical values A_{max} which should be obtained assuming complete electronic magnetization. Since the magnitude of A is proportional to the average value of the square of the electronic moment over the rare earth sites, we have also noted the fraction f of Pr electronic moments which should have to be fully developed in order to take proper account of the experimental results. It appears that, in zero field, the nuclear term is large in sample Pr_{10} only, while it becomes substantial in sample Pr_1 as well when a field of 7 teslas is applied. It is noteworthy that our estimate of the average value of the electro-

nic moment in sample Pr_{10} is in fairly good agreement with the magnetization data according to which the moment reaches about 30 % of the ionic value when applying a field of 5 teslas at 1.8 K.

Finally the following picture emerges from our results. Nearly all the Pr^{3+} ions have singlet ground state and display essentially Van Vleck paramagnetism. But the magnitude of the gap between the ground state and the nearest level is distributed from site to site. Consequently spontaneous admixing of the higher state into the ground state may occur, with a resulting magnetic polarization of the ions, on the sites where the ratio of the exchange energy to the crystal field gap exceeds a critical value. Similarly the magnetic polarization of the ions is increased by an external magnetic field, leading to an enhancement of the nuclear contribution to the specific heat.

In conclusion, our measurements show evidence of substantial departures from the uniaxial model of Harris *et al.* [1] for rare earth amorphous alloys. According to this model the ground state of the rare earth ions should be $J_z = \pm J$, a situation which is definitely ruled out by our data. Fert and Campbell [2] have shown that important deviations from the uniaxial predictions have to be expected in the case of non-Kramers ions with small values of J . Fert and Spanjaard [3] calculations, assuming values of the asymmetry parameter η equally distributed between -1 and $+1$, yield a better approach than the Harris model. But the fact that the majority of Pr^{3+} ions are found to lie in a singlet ground state when diluted in the amorphous $\text{La}_{80}\text{Au}_{20}$ matrix suggests a narrower distribution of η than assumed by Fert and Spanjaard. It has been shown by Cochran *et al.* [12] that the distribution of the crystal field splitting is a quasi-Gaussian one when the disordered structure of the amorphous state is of the type given by the random close packing of atomic spheres. Calculations by Bhattacharjee and Coqblin [13] are now in progress to test if assuming such a distribution provides the basis for a more realistic model.

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