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A calorimetric study of the onset of antiferromagnetism in neodymium

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Abstract. The magnetic transitions at T_N and T_2 in high-purity neodymium have been studied with a high-resolution microcalorimeter. The transition temperatures are $T_N = 20.0 \pm 0.2$ K and $T_2 = 19.2 \pm 0.2$ K. The latent heats associated with the transitions are 0.9 ± 0.3 J mol^{-1} and 0.3 ± 0.1 J mol^{-1}, respectively. Small thermal hystereses were also observed at both transitions. The results prove unambiguously that the transitions are of first order.

Below the Néel temperature the rare-earth element neodymium exhibits a series of magnetically ordered phases of great complexity [1]. Neodymium has a double-hexagonal close-packed crystal structure with sites of local hexagonal and local cubic symmetry. In zero magnetic field the moments on the hexagonal sites order antiferromagnetically at 20 K (T_N) with a slight modification of the magnetic structure at about 19 K (T_2). The ordering of the moments on the cubic sites takes place below 8 K (T_3). The interest of the present investigation has been focused on the magnetic transitions at T_N and T_2. It has been discussed widely in the literature whether the magnetization of the ordered state between T_N and T_2 is modulated with wavevectors q of equal magnitude along all three equivalent b directions in the reciprocal lattice or whether it is a 'single-q' state [2]. Renormalization group calculations [3] have shown that, if the magnetic structure is a single-q state, the transition at T_N will be of first order thermodynamically. If the magnetic structure is a triple-q state, the transition should be continuous. Neutron diffraction results obtained at that time indicated that the transition was continuous and it was concluded [3] that the ordered state immediately below T_N was a triple-q state. Recent high-resolution thermal expansion measurements by Zochowski and McEwen [4], however, have revealed a discontinuity at T_N which indicates that this transition is of first order and hence that the magnetic phase immediately below T_N should be a single-q state, and this has later been verified by neutron diffraction work [1]. At T_2 the neutron magnetic satellite reflections split and turn away from the b direction but are still in the basal plane [5], giving rise to a multidomain double-q structure in zero magnetic field which persists down to T_3. The transition at T_2 is, according to the thermal expansion results [4], also of first order.

The discontinuities at T_N and T_2 reported in [4] are small, corresponding to a fractional length change of about 5×10^{-7}, which indicates that these transitions will be weak first-order transitions. Neither heat-capacity measurements [6] nor measurements using other experimental methods have so far been able to demonstrate unambiguously the first-order nature of the transitions at T_N and T_2. We therefore decided to perform detailed measurements of these transitions using a high-resolution microcalorimeter which we have used in previous studies of magnetic transitions in rare-earth metals [7].

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Neodymium of two different qualities was used in this investigation. Sample A was cut from a single crystal produced from starting material obtained from Ames Laboratory. Sample B was cut from a polycrystalline electrotransport-refined material. The neodymium crystals were obtained from Dr D Fort, Department of Metallurgy and Materials, University of Birmingham. The purity of the single crystal was 99.88 at. %, according to a previous chemical analysis [8] while the electrotransport-refined sample had a purity between 99.93 and 99.97 at. %, corresponding to a position somewhere between the 'cathode' end and 'centre' of the crystal from which this sample was taken (cf table 2, p 37, in [8]). The masses of both samples were about 0.07 g. After cutting, the samples were strongly etched but no annealing in vacuum or in an inert atmosphere was carried out so that no unintentional contaminations were introduced into the samples. Experience from our previous studies of magnetic first-order transitions shows that even small impurity amounts can smear the transitions and change a weak first-order transition into one of second order. The calorimetric technique used has been described in some detail in [7]. The experimental conditions in the present investigation were the same as in [7]. All measurements were made in a zero magnetic field as it was not possible to apply an external field to the samples in the calorimeter.

A typical result of the measurements is shown in figure 1 which displays the rate dQ/dt of change in energy versus temperature during cooling from a temperature well above T_N. Figure 1(a) gives the result for sample A, the single crystal, while figure 1(b) shows the result for the polycrystalline sample B. In both cases a marked peak appears at around 20 K caused by an energy release in the samples followed by two or three peaks just above 19 K, also due to energy release. In the single-crystal sample the energy release peaks at 20 and 19 K are clearly separated although somewhat broadened, but in the polycrystalline sample a certain overlap is obtained, probably owing to strains in the lattice or the cutting. The cooling and heating rates were approximately 1 mK s^{-1}. By lowering the rate of change in temperature a better separation between the 20 and 19 K energy release regions can be obtained but then the difficulties in distinguishing the peaks from the background due to the small energies connected with these transitions will increase. The chosen rate of change in temperatures was found to be most appropriate for the present measurements.

The measurements were repeated several times, starting with cooling from room temperature. A small variation in the value of the transition temperature between different runs for the same sample was found. This may be due to strains in the samples, probably introduced during the cooling from room temperature. It has been observed previously [2] that the phase transition at T_2 is suppressed by small strains. The transition temperatures, given as a mean value for more than ten runs, are 20.0 ± 0.2 K for T_N and 19.2 ± 0.2 K for T_2 under cooling. The energy changes associated with these transitions are 0.9 ± 0.3 J mol^{-1} and 0.3 ± 0.1 J mol^{-1} for the transitions at T_N and T_2, respectively. A thermal hysteresis of 0.1–0.3 K for the transitions was observed when cycling the sample through the transitions. The marked energy peaks and the presence of hysteresis prove that these transitions are of first order as indicated by the results from the thermal expansion studies [4]. The transition temperatures in [4] were $T_N = 19.95 \pm 0.05$ K and $T_2 = 19.1 \pm 0.1$ K obtained under heating in a zero magnetic field.

The discontinuous length changes at T_N and T_2 in [4] were approximately of the same magnitude for both transitions. The measurements were made along a b direction. No data for the thermal expansion along the a or c directions in neodymium are reported. It is therefore not possible to calculate the volume changes at the transitions from which an estimate of the energy change at the transitions could be made. It is, however, reasonable to expect that the transition at T_N which involves an ordering of the magnetic moments on

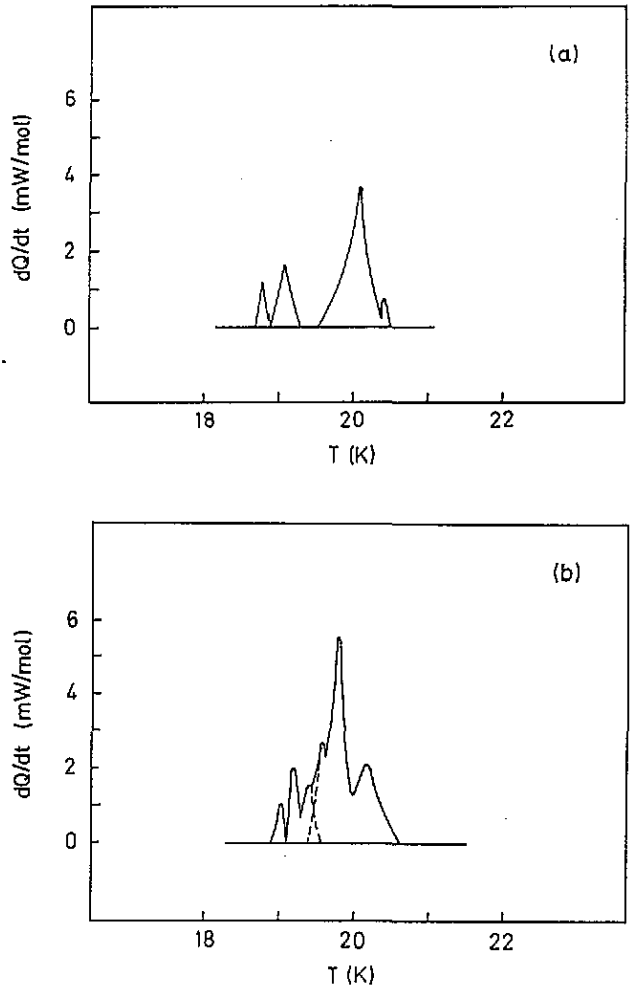

Figure 1. The rate of change in energy versus temperature for neodymium: (*a*) single crystal; (*b*) polycrystalline sample. The results were obtained during cooling. The zero line is drawn as a guide to the eye.

the hexagonal sites will cause a greater change in the magnetoelastic energy, which is the main source for the energy change at the transitions in this case than the rotation of the q-vectors at the transition at T_2. The observed ratio of the latent heats for the two transitions seems therefore not unreasonable. It may finally be pointed out that, although the cause of some of the splitting of the peaks in figure 1 is probably impurity effects, the T_2 transition always showed a more marked splitting in separate peaks for both sample A and sample B. Whether this is an intrinsic effect or associated with impurities is an open question.

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