NEEL AND CURIE TEMPERATURES FOR SIX OF THE CRYSTAL STRUCTURES OF CERIUM AND PRASEODYMIUM

G. Meaden, N. Sze, G. Krithivas, M. Zuckermann

To cite this version:

HAL Id: jpa-00213946
https://hal.archives-ouvertes.fr/jpa-00213946
Submitted on 1 Jan 1971

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
NEEL AND CURIE TEMPERATURES FOR SIX OF THE CRYSTAL STRUCTURES OF CERIUM AND PRASEODYMIUM

G. T. MEEADEN, N. H. SZE, G. KRITHTIVAS
Department of Physics, Dalhousie University, Halifax, Nova Scotia

and M. J. ZUCKERMAN
Eaton Laboratory, McGill University, Montreal, Quebec

Abstract. — By various means we have succeeded in obtaining Ce and Pr in different crystal structures at 4 °K. Electrical measurements have permitted detection of the magnetic transitions. Resistance effects characteristic of antiferromagnetism are apparently displayed by α-Ce (fcc), β-Ce (dhcp), α-Pr (dhcp) and γ-Pr (bcc) below 23, 14, and 18 °K respectively. For β-Pr (fcc) and possibly γ-Ce (fcc), the resistance anomalies are more like ferromagnetic ones with transitions at 9 and 8 °K. The importance of these preliminary results for α- and γ-Ce is indicated.

I. Introduction. — At 300 °K annealed Ce is fcc (γ-phase) and trivalent with one 4f electron/atom [1]. On cooling below 260 °K γ-Ce becomes unstable and begins transforming to dhcp β-Ce (also trivalent), while below 100 °K β- and γ-Ce partially transform to α-Ce (collapsed fcc). Neutron diffraction work by Wilkinson et al. [2] has shown that β-Ce is antiferromagnetic (AFM) below ~13 °K, but little is known about ordered magnetism in α- and γ-Ce. It has however been deduced that at high temperatures and pressures α-Ce has no disordered moments to any appreciable extent [3] whereas γ-Ce does (~2.5 μB) [4]. α-Pr (dhcp) is AFM below ~25 °K, according to neutron diffraction studies [5]. A fcc form (β-Pr) which has recently been identified by Bucher et al. [6] is ferromagnetic (FM) below 8.7 °K. Nothing is known of the γ-phase (bcc).

II. Results on Praseodymium. — Firstly, the high-temperature phase diagram had to be clarified in order to delineate the equilibrium crystallographic transition temperatures. By differential thermal analysis we found the β ≳ γ transformation at 1 128 ± 1 °K, but could not detect the α ≳ β change. A possible lower limit is 975 °K because quenching produced the α-phase and subsequently the 22 °K magnetic transition. Although the Pr was polycrystalline, the resistive transition had the familiar hump-back form of numerous AFM monocrystals. Quenching from 1 115 °K retained only β-Pr because a single magnetic transition appeared at 9 °K with a form suggestive of FM (cf the susceptibility work of Bucher et al. [6]). Quenching from the γ-field (at 1 150 °K) was only partially successful because 3 magnetic transitions appeared (Fig. 1), those at 9° and 22 °K corresponding to β- and α-Pr. The new transition suggests AFM and implies a Néel point for γ-Pr at 18 °K.

III. Results on Cerium. — Annealed Ce when slow-cooled produces at 4 °K an α-β phase mixture with very little γ (0-5 %) [2] [7]. Figure 2, curve 1, shows a nearly linear resistivity with an anomaly below 14.5 °K due to AFM β-Ce. The next curve shows the effect of quenching from 300° to 4 °K at a very high rate (~10 seconds). This partially inhibits β-formation and increases the α-fraction at 4 °K. The main new feature is the anomaly below 23 °K, which resembles AFM Mn, Dy, etc. Lastly, curve 3 was obtained after lightly cold-working a quenched sample by scratching its surface at 4 °K. This process converts almost the entire sample to α-Ce, according to McHargue and Yakal [7]. The result strongly suggests that α-Ce is AFM below ~23 °K. Note that the curves are normalized to unity at 4 °K; in absolute terms the resistivity of β-Ce is higher than that of α-Ce [8].

The next experiments were designed to increase the fraction of γ-Ce retained at 4 °K. Unannealed Ce was used. Firstly, the control curve (Fig. 3, no. 1), obtained
after slow cooling, revealed a magnetic transition at 15 °K (β-Ce) and another transition of unknown origin at 35 °K (possibly related to the appearance, on warming, of an intermediate α-γ form [9]). Next, the specimen was clamped rigidly in a special frame and cooled to 4 °K. It was hoped that the constraint would impede to some extent the fcc γ → α transition which, if free, occurs with a 16% volume contraction; the γ-Ce lattice might conceivably submit to a kind of negative pressure effect. As a result, two extra transitions appeared, one near 21 °K and one at 8 °K (curve 2). Next, a third run was done without the clamping constraint (curve 3), and the 8 °K anomaly was found to be no longer detectable. Other runs have confirmed the qualitative nature of these results. Previously, a heat capacity anomaly at 7 °K has been noted [10]. The form of the 8 °K resistance anomaly suggests FM, but AFM without appreciable magnetic superzone scattering (as in Eu [11]) is not excluded. The crystal phase is not yet known but fcc γ-Ce is a possibility because of the nature of the clamping experiment. The fcc forms of Pr and Nd are already known to be FM below 8.7° and 29 °K respectively.

IV. Discussion. — Apart from the work of Elliott et al. [8] on β-Ce these are the first observations of the effects of magnetic transitions on the transport properties of Ce and Pr. Emphasis has been on determining the techniques for obtaining the various phases at low temperatures. For β-Ce and α-Pr the work confirms the Néel points, and for β-Pr the Curie point, provided by other means. It also appears that α-Ce and γ-Pr could be AFM, and γ-Ce either FM or AFM at 8 °K. However, we stress that the work is preliminary as the inferences drawn here are based mainly on resistance and thermopower measurements and the planned low-temperature X-ray and magnetization experiments have yet to be done.

Although magnetic measurements have never been made on pure α-Ce, it has appeared likely that at high pressures and high temperatures α-Ce may be without (disordered) localized 4f-electrons while possessing either spin-compensated or band-like 4f-states [3] [12] [13]. This may be reconciled with an AFM low-temperature, low-pressure ground state by noting that, because the α-γ first-order phase boundary in Ce is akin to the Mott metal-insulator transition (as in V₂O₅) [14] [15], our low-temperature ordered phases may constitute an entirely new phase (ζ-Ce, say) which is the equivalent of the AFM, low-temperature, low-pressure, insulating region of V₂O₅. On heating, the ζ-phase would have a first-order transition to either the disordered, magnetic γ-phase or the non-magnetic α-phase, depending on the temperature and pressure. All the Ce phases are metallic, as opposed to V₂O₅, because conduction electrons are always present. The delocalizing process would be one where the localized f-electron (in γ- or ζ-Ce) moves into an existing conduction band or spin-compensated state (in α-Ce). These possibilities will be examined in our further studies.

We thank D. J. W. Geldart for discussions and the National Research Council of Canada for a grant in aid of this research.
References