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THE EFFECT OF CRYSTAL FIELD SPLITTINGS ON THE ELECTRICAL RESISTIVITY OF NdB_6*

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The contribution to the electrical resistivity of NdB_6 arising from temperature dependent crystal field level populations is experimentally measured and accounted for by theory.

NdB_6 CRYSTALLIZES in a cubic structure which may be regarded as a CsCl arrangement of Nd atoms and B_6 octahedra. Theory[1,2] and experiment[2,3] agree that tri-valent metals form hexaborides with one conduction electron per unit cell.

Above approximately 125°K the magnetic susceptibility of NdB_6 is Curie–Weiss like with an effective moment close to that expected for the Hund's Rule $4f$ ground state $^4I9/2$.[4] Below this temperature the behavior deviates from Curie–Weiss type. Antiferromagnetic ordering sets in a $T_N = 7.5$°K.[5]

Westrum measured the heat capacity of NdB_6 from 5 to 300°K.[6] He found the entropy associated with magnetic ordering ($T_N = 8.4$°K for his (sample) to be 1.63 cal/g.f.m.° K $= R \ln 2.28$. Westrum subtracted of the specific heat of LaB_6 from that of NdB_6 and then found the best fit to the difference given by assuming that the 10-fold degenerate $4f$ ground state of Nd is split in the cubic environment into a ground state doublet and two quartets at 116 and 323°K above the ground state respectively. Nickerson[7] and Nickerson and White,[8] adapting an idea of Williams and Hirst,[9] show how an octahedral crystal field of negative charges arising from the conduction electrons in the hexaborides can account for this level scheme semi-quantitatively. In the notation of Lea, Leask and Wolf,[10] this is the case $x = -1$. The energy separations of the two quartets above the doublet have, from the tables of Lea, Leask and Wolf, a ratio of 3.42, compared to Westrum's fit with ratio 2.78. In what follows we will consider only this $x = -1$ case.

Hirst has calculated the elastic and inelastic contribution to the electrical resistivity from s–f exchange coupling in dilute rare earth alloys.[11] This has also been done by Andersen *et al.*[12] whose notation we will use. They express the resistivity due to scattering from the magnetic ions as $\rho_{mag} = \rho_0 tr(PQ)$, where the trace is taken over the $2J + 1$ crystal states whose energies are E_i. The matrices P and Q are:

$$P_{ij} = \frac{\exp(-E_i/k_BT)}{\Sigma_k \exp(-E_k/k_BT)} \cdot \frac{(E_i - E_j)k_BT}{1 - \exp[-(E_i - E_j)/k_BT]}$$

and

$$Q_{ij} = |\langle i|J_z|j\rangle|^2 + 1/2|\langle i|J_+|j\rangle|^2 + 1/2|\langle i|J_-|j\rangle|^2.$$

Q_{ij} is calculated here using the eigenvectors tabulated in reference 10. As mentioned before, we do this for $x = -1$. ρ_0 is a constant from which we can estimate the s–f interaction strength.

Figure 1 gives our data on the electrical resistivity of NdB_6 and LaB_6 single crystals, measured by the four probe, a–c technique. The crystals were grown from molten Al.[13] Because of the somewhat irregular shape of the NdB_6 measured, its absolute resistivity was determined by the method outlined below.

We assume for our analysis that the resistivity of

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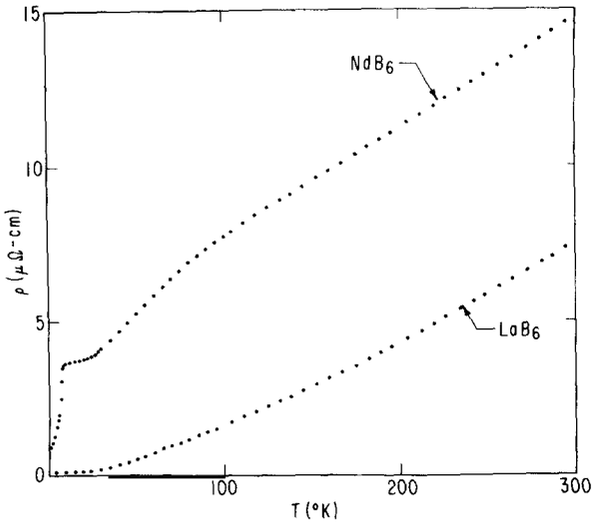

FIG. 1. Temperature dependence of the electrical resistivity of NdB_6 and LaB_6 single crystals. Absolute value for NdB_6 determined by method discussed in text.

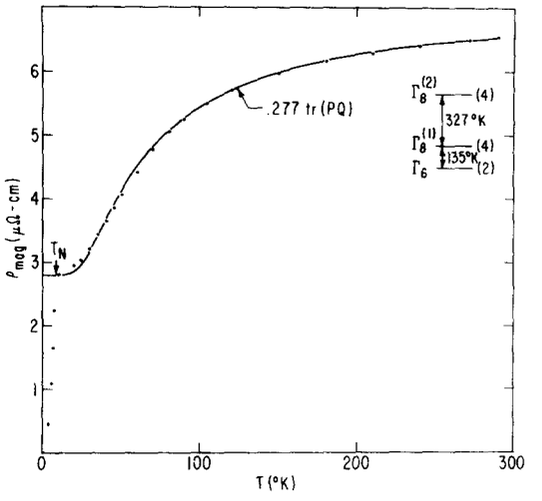

FIG. 2. ρ_{mag} as a function of temperature for NdB_6. Points are from experimental data analyzed as discussed in text. Curve is theoretical fit. The level scheme with splittings and degeneracies is shown.

NdB_6 is the sum of a temperature independent residual term, a lattice term and a magnetic term. We further assume that the lattice term is given by the lattice term of LaB_6 for which we have an absolute measurement. Our measured value of the resistance of NdB_6 depends, according to our assumptions, on three parameters: a geometrical factor for converting to absolute resistivity, ρ_0 and an energy scale factor for the crystal field splitting. Assuming a value for the energy scale factor, we have evaluated the resistivity at 294°K, as well as its temperature derivative in terms of the other two parameters. These two equations then uniquely determine these parameters for the assumed splitting. We have done this for several values of the splitting and find a reasonable fit for the quartets at 135 and 462°K above the ground state doublet. We show in Fig. 2 the magnetic term in the resistivity of NdB_6 determined in this way, as well as the theoretical prediction.

Hirst writes the exchange interaction between conduction and $4f$ core states as $H_{s-f} = -2J_{ex}(g_J - 1)\mathbf{J}\cdot\mathbf{s}$, where g_J is the gyromagnetic factor, **J** the total angular momentum of the Hund's Rule state and s the conduction electron spin. Using Hirst's expression for ρ_{mag} assuming effective mass 0.62 for LaB_6 from reference 2, we find $J_{ex} = 0.105$ eV using our value of ρ_0.

For a given splitting, the computed theoretical curve is completely determined by our requirement that it gives the experimental value at room temperature of the resistivity and its temperature derivative. Reasonable values of the splitting and ρ_0 are seen, in Fig. 2, to give the observed spin disorder resistance which is lost upon ordering. It is interesting that the theoretical expressions which are strictly applicable only to dilute alloys should work so well in this concentrated limit. It is possible, also, that in the region where the agreement is poorest, near T_N, $4f$–$4f$ interactions are important.

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