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ASPHERICAL COULOMB SCATTERING OF CONDUCTION ELECTRONS IN PrB$_6$ *

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The electrical resistivity of PrB$_6$ contains a term arising from the temperature dependent crystal field level populations by 4f electrons which our measurements indicate is equally made up of aspherical Coulomb and exchange scattering of conduction electrons.

The Hund's rule 4f ground state of a rare earth ion is generally split in a solid into a number of crystal field levels. The level populations change with temperature, and in a metal the transport properties reflect this temperature dependence through the interaction between 4f and conduction electrons. Conduction electrons interact with 4f electrons via exchange, the direct Coulomb interaction and interband mixing. This last interaction is most important for the case of a single 4f electron or hole and will not be considered here. The effect of exchange on the temperature dependence of transport properties has, in the past, usually been thought to dominate that of the direct Coulomb interaction. However, Fulde and coworkers[1,2] point out that in favorable cases the two should be of comparable magnitude, and that some properties of metals (particularly the superconducting behavior) will be affected by the direct Coulomb interaction in a way very different from that of exchange. We find that the temperature dependence of the electrical resistivity due to scattering from the 4f crystal field levels of Pr^{3+} in PrB$_6$ is sufficiently different for the two types of interaction for a separation of their contributions to be made, and that the two contributions to the resistivity in PrB$_6$ are equal in magnitude.

Hirst[3] and Anderson et al.[4] have computed the temperature dependent contribution to the electrical resistivity due to the exchange interaction. In the latter's notation, this contribution can be written $\rho = \rho_{ex} \, tr \, (PQ^{ex})$, where the trace is taken over the 2J+1 crystal field states $|i\rangle$ whose energies are E_i. The matrices P and Q^{ex} are:

$$P_{ij} = \frac{\exp(-E_i/k_B T)}{\displaystyle\sum_k \exp(-E_k/k_B T)} \cdot \frac{(E_i-E_j)/k_B T}{1 - \exp[-(E_i-E_j)/k_B T]}$$

and

$$Q_{ij}^{ex} = |\langle i|J_z|j\rangle|^2 + \frac{1}{2}|\langle i|J_+|j\rangle|^2 + \frac{1}{2}|\langle i|J_-|j\rangle|^2,$$

where k_B is Boltzmann's constant and ρ_{ex} is a constant which depends on the 4f-conduction electron interaction strength.

The direct Coulomb interaction is evaluated by making a multipole expansion of the Coulomb interaction energy of the 4f and conduction electrons. The L = 0 term is included in the lattice potential for a crystallographically ordered compound. The lowest order term which concerns us is the quadrupole term. This gives aspherical Coulomb scattering, first considered by Elliot.[5] Following Fulde et al.,[2] we have for the interaction Hamiltonian:

$$H_A = \sum_{k', k, s, \nu', \nu} \sum_{M=-2}^{+2} Q_2 I_2(k', \nu', k, \nu)$$
$$\times y_2^M(J) \, a_{k's\nu'}^\dagger \, a_{ks\nu} \; .$$

The y_2^M are operator equivalents (given in ref. 2) for L = 2. The operator $a_{ks\nu}$ destroys a conduction electron of momentum k and spin s in band ν. $I_2(k'\nu', k\nu)$ is an integral which we will assume to be a constant, an approximation also made in deriving the spin exchange

interaction $H_{ex} = -2\mathcal{J}(g-1) \underline{J} \cdot \underline{s}$. Q_2 is proportional to the quadrupole moment of the fully aligned 4f shell.

Hirst[3] points out that there are no cross terms between the direct and exchange interactions in the electrical resistivity. The contribution to the electrical resistivity from H_A calculated by second-order time-dependent perturbation theory is, therefore, similar to that due to exchange and of the form

$\rho = \rho_A \, tr(PQ^A)$, where P_{ij} has been given

above, and now $Q^A = \sum_{M=-2}^{+2} |\langle i | y_2^M | j \rangle|^2$. ρ_A is a constant which depends on the interaction strength. We expect the above formula to apply so long as each scattering event due to either spin or orbital disorder can be treated as isolated. The absolute resistivity (see below) indicates this to be the case for PrB_6.

We now turn to the experimental data. For our purposes, it is sufficient to know that PrB_6 is a cubic metal (with one conduction electron per Pr atom) with the Pr atoms situated on a primitive cubic lattice, each Pr site having full cubic symmetry. This cubic crystal field will split the Pr $J = 4$ f electron ground state into a Γ_1 singlet, a non-magnetic Γ_3 doublet and Γ_4 and Γ_5 triplets.[6]

PrB_6 orders antiferromagnetically at 6.9 K.[7] Specific heat measurements to 30 K give for the entropy of ordering $\sim R \log 3.3$,[8] where no subtraction of the small lattice term has been made. The phase transition is apparently second order.[8] Since Γ_4 cannot be the ground state in a cubic field, these data suggest a Γ_5 ground state.

Previous magnetic susceptibility measurements on Pr impurities in YB_6 suggested a Γ_1 singlet ground state.[9] We now believe these data may not be reliable; subsequent work has shown that sample preparation by arc melting causes segregation of mixed hexaborides.[10] We have re-investigated the magnetic susceptibility of dilute Pr in this structure by measurements on a sample of small single crystals of nominal $La_{0.977}Pr_{0.023}B_6$ grown[11] from molten Al, and the results are shown in Fig. 1. The low temperature data indicate that the ground state is Γ_5. The susceptibility of similarly grown LaB_6 crystals has been subtracted from the data in Fig. 1. We fitted these data to the magnetic susceptibility expression for Pr using fourth order fields only, an assumption which works well for NdB_6.[12,13] This is the case $x = 1$ in ref. 6. This fit involves the impurity concentration and an energy scale factor. The concentration of Pr in the sample was found to correspond to $La_{0.9819}Pr_{0.0181}B_6$, indicating that some fractionation occurred during crystallization. The solid line in Fig. 1 is the calculated sus-

ceptibility using this impurity concentration and the level scheme indicated, and the agreement with the data is within the experimental error. The fit is not improved for the case $x = +0.95$ in ref. 6, and the resistance fit (see below) is much worse.

We use this level scheme to separate the aspherical Coulomb and exchange contributions to the electrical resistivity; our measurements on single crystal specimens between 2 K and
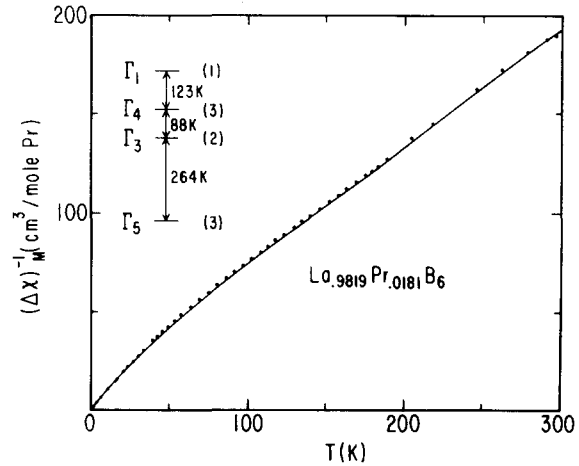

Fig. 1 Points are the reciprocal susceptibility of $La_{0.9819}Pr_{0.0181}B_6$, corrected for the host LaB_6 susceptibility. The crystal field level scheme and the Pr concentration were determined by a fitting (solid line) to the theoretical expression assuming fourth order crystal fields only.

295 K are shown in Fig. 2(a). We assume that the resistance of PrB_6 is the sum of a residual term ρ_0, a lattice term ρ_L which is given by the known lattice term of LaB_6, and the aspherical Coulomb and exchange scattering terms. We determine ρ_0 by extrapolating the low temperature PrB_6 data against T^2; this gives a good line. We require the magnitude and slope of the room temperature resistance to equal the theoretical expression. Our fit, then, depends on a geometrical factor for the PrB_6 sample and the ratio ρ_A / ρ_{ex}. We use this geometrical factor to give the absolute resistivity of PrB_6, since we cannot measure this value directly with enough accuracy for our purposes. Figure 2(b) shows the PrB_6 data with $\rho_L + \rho_0$ subtracted: the solid line gives the theoretical expression for aspherical Coulomb plus exchange scattering for $(\rho_A / \rho_{ex}) = 1$. Q^A and Q^{ex} are computed using the wave functions of ref. 6. For convenience we have chosen the normalization $\sum_{i,j} Q_{ij}^A = \sum_{i,j} Q_{ij}^{ex} = (2J+1) J(J+1)$.[14] The inset to Fig. 2(b) shows the sensitivity of the fit to the choice of

ρ_A/ρ_{ex}. For the correct value of this ratio, the plot of $\Delta\rho$ versus x tr(PQ^A) + (1-x) tr(PQ^{ex}) should extrapolate through the origin. We note that our analysis gives an absolute value for the room temperature resistivity of PrB$_6$ in agreement with the value reported in ref. 15.

At high temperature the exchange and aspherical Coulomb terms will each contribute 3.80 $\mu\Omega$-cm to the resistivity of PrB$_6$. If I_2 is the same in NdB$_6$, we expect, on the basis of tabulated values of Q_2 [16] and the sum rule for Q^A, [14] 0.55 $\mu\Omega$-cm for the aspherical term in NdB$_6$. The predicted exchange term in NdB$_6$, using the ratio of the appropriate deGennes factors, is 8.74 $\mu\Omega$-cm. Thus, in NdB$_6$ we predict that the aspherical term in the resistivity is only 6% of the exchange term. This explains why an earlier analysis of the resistivity of NdB$_6$ which neglected aspherical Coulomb scattering was successful. [8] The measured exchange term in NdB$_6$ is 6.85 $\mu\Omega$-cm, indicating an exchange coupling constant 13% larger in PrB$_6$.

Experimental estimates of the magnitude of the aspherical Coulomb interaction have previously been made by Fert and Friederick[17] using the anisotropy of the magnetoresistance of dilute heavy rare earths in silver and gold and by Keller and Holzer[18] using the depression of the superconducting transition temperature of LaSn$_3$ by Pr impurities. These agree in magnitude with our findings here on the relative importance of exchange and aspherical Coulomb scattering in PrB$_6$. The factor which makes the resistance measurement here so sensitive to the mixture of exchange and aspherical Coulomb scattering is that the ratio of scattering by the Γ_5 ground state compared to the high temperature scattering limit is 0.625 for exchange and 0.206 for aspherical Coulomb scattering.

The importance of our result is that we now have a quantitative determination of the aspherical Coulomb scattering contribution for one case. That the magnitude is so large means that aspherical Coulomb scattering cannot be neglected in the analysis of resistance data, and, more importantly, that other effects due to aspherical Coulomb scattering may be larger than expected.
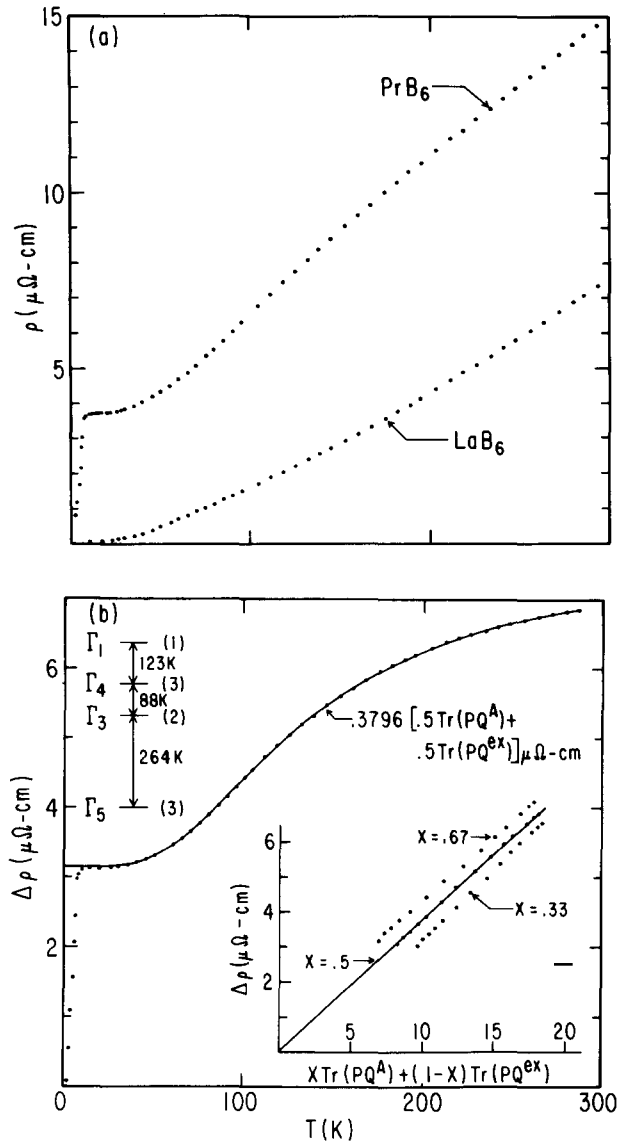
Fig. 2 (a) Absolute resistivities of PrB$_6$ and LaB$_6$. PrB$_6$ absolute value was determined as described in text. Residual terms are not subtracted here. Short range magnetic order effects are evident between the Neel temperature and 15K. (b) Excess resistivity of PrB$_6$ over lattice and residual term determined as described in text. Solid line is theoretical fit (using level scheme indicated) for equal amounts of aspherical Coulomb and exchange scattering. Inset indicates sensitivity of fit to the ratio ρ_A/ρ_{ex}.

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