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Effective Crystal Fields in the Rare Earth Pnictides

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Various contributions to the effective 4f electron crystal fields in the rare earth pnictides are estimated and compared. These include the direct interaction with the ligand electrostatic field and effects associated with the 5d band electrons.

The 4f electron crystal field levels of the rare earth pnictides (ReX, X=P, As, Sb, Bi) have been parameterized extraordinarily well with a simple point charge model [1]. There are certain deviations from the point charge picture, however; the model does not account for the Ce compounds, and the effective charges for the heavy rare earth pnictides are substantially greater than those for the lighter lanthanide compounds. Consequently, it is of interest to study other contributions to the effective field. Here we consider two obvious mechanisms which influence the crystal field splittings in addition to the direct interaction with

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the ligand field. First, the 5d band electrons can generate a 4f-5d interaction having cubic symmetry. Second, the electrostatic field polarizes the 5d shell, and this polarization can in turn affect the 4f shell.

Through the use of 4f and 5d wave functions obtained in relativistic Hartree-Fock calculations of 4f excitation energies [2] we have computed the $F^4(4f,5d)$ Slater integrals and $\langle r^4 \rangle_{4f}$ and $\langle r^4 \rangle_{5d}$ radial matrix elements for the entire rare earth series. With these quantities we estimate the different component of the effective crystal field and intercompare them. Recently reported 5d level splittings [3] will be contrasted with the 4f splittings in an effort to disentangle the various terms.

The fourth-order potential energy due to the electrostatic field (which is much larger than the sixth-order term) is proportional to $A = A_4 \langle r^4 \rangle_{4f}$. In the point charge model $A_4 = (7/16)Ze^2 a_{nn}^{-5}$, where a_{nn} is the rare earth-ligand separation and Ze is the effective ligand charge. Values of A for the P and Sb series have been plotted in Fig. 1 assuming $Z = -1.2$, the choice used in [1]. The discrepancies for the heavy rare earth compounds are evident.

The cubic term in the Coulomb interaction between the 4f and the 5d electrons involves

$$F^4(4f,5d) = \iint P_{4f}^2(r_1) \frac{r_1^4}{r_2^5} P_{5d}^2(r_2) r_1^2 dr_1 r_2^2 dr_2 ,$$

where P_{4f} and P_{5d} are the 4f and 5d radial wave functions, respectively. Neglecting exchange, N 5d- e_g electrons contribute $(1/48)N F^4(4f,5d)$ to the effective crystal field energy; the dot-dash curve of Fig. 1 shows

values for $N=0.1$. t_{2g} states contribute terms of opposite sign. The 5d nature of the band electrons has two origins. First, there is 5d character hybridized into the filled ligand valence bands; we expect e_g mixing to predominate since e_g orbitals point towards the ligand atoms. Second, the rare earth 5d bands are slightly occupied; an occupation number of 0.05 electrons per rare earth atom has recently been estimated [4] for these bands. In addition to affecting the 4f electrons, the electrostatic field leads to a splitting energy of $(5/3)Ze^2 \langle r^4 \rangle_{5d} a_{nn}^{-5}$ for the 5d states in the point charge model. With Z negative, the t_{2g} electrons are of lower energy; hence, the occupied 5d bands are expected to be t_{2g} -like. Hybridization and band filling are thus competitive effects. In view of the small 5d band occupancy, we expect the e_g character resulting from hybridization to dominate. This can be tested. A 5d splitting of $\sim 1.8\text{eV}$ has been reported [3] for GdP. Using the above expression, this implies $Z \sim -0.65$, a value half that inferred from the 4f splittings. If we assume that the 5d splitting is a better measure of ligand field effects, then half of the 4f splitting must stem from other sources. The sign and magnitude of the remainder is consistent with the 0.1 5d- e_g contribution displayed in Fig. 1. A net e_g occupancy of this magnitude is plausible.

5d polarization may be a third component of the effective 4f field. A polarization energy proportional to $\langle r^4 \rangle_{5d} a_{nn}^{-5}$ is induced by the electrostatic field, and the 4f shell responds to the polarization via the $k^4(4f,5d)$ Slater integral. The product $\langle r^4 \rangle_{5d} F^4(4f,5d) a_{nn}^{-5}$ for the ReP compounds is shown by the dashed line in the figure. The energy associated with the polarization effect can be of the order of the electrostatic component. It is not expected to be important here since the 5d

occupancy is so small (the contribution to the f crystal field involves the above product divided by an energy of the order of the $5d$ bandwidth). We have included the shielding product in the figure because it can be of experimental significance in metallic rare earth compounds for which there are approximately two $5d$ electrons per lanthanide atom in the occupied bands.

We can clearly improve the fit to experiment by suitably combining the above-mentioned components. The improvement, however, would be neither significant nor conclusive. We believe that the larger splittings for the heavy rare earth compounds are indicative of changing band effects; Z and $e_g - t_{2g}$ counts apparently vary across the rare earth row. Comparison of the $5d$ and $4f$ splittings suggests that the point charge model, even with varying Z , does not suffice. $5d$ contributions of the kind described here are almost certainly of experimental significance.

We emphasize that our estimates are not restricted to the pnictides. The mechanisms we have considered are probably quite important for systems with larger $5d$ electron concentration. We hope that our results will be helpful in interpreting other rare earth materials.

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FIGURE CAPTION

Fig. 1 Effective fourth order crystal fields in the rare-earth pnictides.