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Crystal field levels and hybridization effects in Pr skutterudites

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We investigate theoretically fomation of the crystalline electric field (CEF) level structure in Pr skutterudites. Although 4f electrons in Pr seem localized in skutterdudites, neutron scattering often fails to detect clear CEF levels, and a broad quasi-elastic peak is found [1]. Thus interaction of 4f electrons with conduction electrons should be taken into account for proper understanding of dynamics. Especially, the continued softening of an elastic constant down to very low temperature [2] may not exclude the singlet CEF ground state. In this talk, however, we shall address only to the level structure, postponing the broadening of levels for future study.

In the filled skutterudite structure, each trivalent Pr is surrounded by 8 transition metal ions which form a cube, and 12 pnictogens which form an icosahedron deformed slightly from the regular one. In addition to the Coulomb potential from ligands, hybridization between 4f electrons and pnictogen p electrons seems important. It is known that the positive point charge on the surrounding cube stabilizes the Γ_1 (singlet) level. Explicit calculation [3] shows that negative charges on the icosahedron also favor Γ_1. The absence of the four-fold rotation axis does not play an important role in the point-charge potential. In the notation of the point group O_h, the level sequence from the bottom is $\Gamma_1 - \Gamma_4 - \Gamma_3 - \Gamma_5$. This sequence shows that the sixth-order CEF potential is small [4]. The magnetic excitation from the Γ_1 state is possible only to the Γ_4 level.

The actual symmetry T_h mixes Γ_4 and Γ_5. The resultant levels are written as $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$, the latter of which gains finite matrix element for magnetic excitations. Experimentally, neutron scattering and magnetization measurements [5] on $PrOs_4Sb_{12}$ suggest that $\Gamma_4^{(2)}$ is within 1 meV above Γ_1, and $\Gamma_4^{(1)}$ is separated by the order of 10 meV. Recent neutron results on $PrRu_4P_{12}$ below 60 K [1] seem to show the same sequence of levels. The position of Γ_{23}, which corresponds to Γ_3 in O_h, cannot be seen by neutron scattering.

We have derived the CEF levels formed by virtural hybridization taking the Slater-Koster parameters $(pf\sigma)$ and $(pf\pi)$, and assuming the following intermediates states:
(i) $4f^1$ and an extra electron in vacant states, and
(ii) $4f^3$ and an extra hole in filled states.
The large Coulomb repulsion makes it reasonable to neglect the width of the bands in the first approximation, but the matrix elements should faithfully be taken into account. It turns out the intermediate states (i) and (ii) have opposite tendency to determine the level sequence. In the case where (i) is dominant and $|(pf\pi)/(pf\sigma)| \ll 1$, the $\Gamma_4^{(2)}$ level is much more stabilized than the others. Thus a competition between the point charge potential and the p-f hybridization can lead to the experimentally proposed sequence, $\Gamma_1 - \Gamma_4^{(2)} - \Gamma_4^{(1)}$, with a reversal of levels $\Gamma_4^{(2)}$ and $\Gamma_4^{(1)}$ from the point charge model.

[1] K. Iwasa et al., Talk at Physical Society of Japan Meeting (September, 2003).
[2] T. Goto et al., Talk at Physical Society of Japan Meeting (September, 2003).
[3] H. Harima and K. Takegahara, Talk at ASR2002, Tokai, Japan.
[4] K.R. Lea, M.J.M. Leask and W.P. Wolf, J. Phys. Chem. Solids **23** (1962) 1381.
[5] M. Kohgi et al., J.Phys.Soc.Jpn, **72** (2003) 1002; T. Tayama et al., J.Phys.Soc.Jpn, **72** (2003) 1516.