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f-electron–band-electron hybridization and the anomalous crystal-field splitting in cerium monopnictides

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We demonstrate the common physical origin, lying in *f*-electron–band-electron hybridization, of the anomalous crystal-field-splitting reduction and of the two-ion interaction giving magnetic ordering, for cerium systems with moderately delocalized *f* electrons.

In CeBi and CeSb, which show unusual magnetic behavior[1] in their magnetically ordered states, the observed crystal-field splitting in the paramagnetic phase is very much reduced[2] from the value expected on extrapolation from corresponding monopnictides of the other rare earths. The crystal-field splitting (between the Γ_7 and Γ_8 states of Ce^{3+}, $J=\frac{5}{2}$) in CeBi and CeSb is 8 and 37 K, compared to 247 and 264 K, expected from the extrapolation.[2] Takahashi, Takegahara, Yanase, and Kasuya[3] have explained this reduction as being caused by the mixing of the localized *f* level with the holes in the *p* band (of anion *p*-state parentage). As discussed here, such a reduction can also be explained starting from the Anderson model,[4] through the hybridization between the *f* levels and the band. This, we believe, is in principle the same as the effect modeled by Takahashi *et al*;[3] and the present exposition makes clear the common physical origin of the anomalous crystal-field effects as treated by Takahashi *et al.*[3] and the hybridization-mediated two-ion interaction developed by Coqblin and Schrieffer[5] and by ourselves.[6–8]

The reduction in crystal-field splitting is expected to be important when large hybridization exists between the localized ionic *f* states and the band. Previously,[6–8] we have explained the behavior of the cerium monopnictides in the magnetically ordered phase by using a two-ion coupling which arises from hybridization between moderately delocalized *f* levels and the band. In such calculations, we have introduced[7] a phenomenological crystal-field parameter, equal to the observed crystal-field splitting in the paramagnetic phase of these compounds, in order to obtain agreement with experimental results. We shall show here that the two-ion interaction as was previously treated[6–8] does not influence the crystal-field splitting observed in the paramagnetic phase. The suppression of the crystal-field splitting from the value expected from the point-charge model is an independent effect, which arises from single-site-hybridization interaction, and which had been omitted in our previous work (which concentrated on explaining magnetic ordering effects, and hence treated only the two-ion coupling). Thus, both these effects—suppression of the crystal-field splitting, and the magnetic ordering—occur when band-electron–*f*-electron hybridization interaction dominates the magnetic behavior of the system, and the physical origins of both can be developed starting from the same (Anderson) Hamiltonian.

We have successfully modeled the equilibrium[6] and excitation[8] behavior of CeBi in the ordered states, by using a hybridization-mediated interionic coupling of the Coqblin-Schrieffer[5] (CS) type. However, in a system which contains only two-ion interactions, the mean-field states obtained above the ordering temperature are degenerate (i.e., have sixfold degeneracy for Ce^{3+} with $J=\frac{5}{2}$). In order to reproduce the experimental paramagnetic behavior in CeBi and CeSb, which show evidence of crystal-field splitting, in our past calculations[6–8] we have added a phenomenological cubic crystal-field Hamiltonian to the hybridization-mediated two-ion interaction. Using an effective-field treatment of the two-ion interaction, such calculations above the ordering temperature, yield a characteristic crystal-field splitting as would be obtained in the absence of two-ion interactions. Even just above the ordering temperature, the change (from the point-charge value) in the crystal-field splitting due to the presence of two-ion interactions is small, and the change goes to zero as the temperature is increased. This shows that the hybridization-mediated two-ion interaction does not contribute to the crystal-field splitting in the paramagnetic region in any important measure.

The reduction in the observed crystal-field splitting (below the extrapolated point-charge value[2]) in the paramagnetic region is an effect which has so far not been included in our theory (which in turn is based on the Anderson[4] and Coqblin-Schrieffer[5] models for the band-electron–*f*-electron single-site hybridization effects). The reduction is a consequence of the hybridization at a single site, and here we develop the theory of such an effect for the paramagnetic state of the compound. We shall show that the single-site interaction does substantially modify the crystal-field splitting in the paramagnetic phase, as well as introduce a temperature dependence of this crystal-field splitting.

We have used the Anderson model[4] as the starting point in describing the hybridization between the localized *f* and the band electrons. The Hamiltonian is

$$H=H_0+H_1\ , \tag{1}$$

$$H_0=\sum_{k,M}\epsilon_k n_{kM}+\sum_{M}E_M n_M+(U/2)\sum_{M,M'}n_M n_{M'}\ , \tag{2}$$

$$H_1=\sum_{k,M}(V_k c_{kM}^{\dagger}c_M+V_k^{*}c_M^{\dagger}c_{kM})\ , \tag{3}$$

where M labels the f levels by appropriate quantum numbers, ϵ_k denotes the energy of a band state of wave vector k, E_M denotes the energy of the localized state $|M\rangle$, n_M denotes the number operator for the state $|M\rangle$, and U is the Coulomb correction energy of the localized levels. The Hamiltonian H_1 describes the mixing between the ionic states and the band. The mixing takes place between states of the same symmetry about the mixing site. In the original treatment of Anderson[4] (and of Coqblin and Schrieffer[5]), M denoted the magnetic quantum number of the localized level, and the spherical mixing potential V_k mixed only states of the same M about the mixing site. This idea has to be extended somewhat in our treatment described below.

On treating H_1 as a perturbation on H_0, and using the Schrieffer-Wolff transformation, Cornut and Coqblin[9] replace H_1 approximately by an interaction $H'+H_{\rm eff}$ where

$$H' = -\sum_{k,M} |V_k|^2 \frac{(\epsilon_k - E_M) - U\langle n_M\rangle}{(\epsilon_k - E_M)(\epsilon_k - E_M - U)} c_M^\dagger c_M \ , \tag{4}$$

$$H_{\rm eff} = -\sum_{\substack{k,\ k'\\ M,\ M'}} J(k,k')\, c^\dagger_{k'M'} c_{kM} c^\dagger_M c_{M'} \ , \tag{5}$$

with

$$J(k,k') = \frac{V_k V^*_{k'} U}{2} \left[\frac{1}{(\epsilon_k - E_M)(\epsilon_k - E_M - U)} + \frac{1}{(\epsilon_{k'} - E_M)(\epsilon_{k'} - E_M - U)} \right] . \tag{6}$$

Equations (4), (5), and (6) can easily be obtained from Ref. 9, by specifying to the case of f^1. The Hamiltonian H' describes an energy shift of the f levels. Clearly there is a relative shift between the different levels denoted by M, if either E_M are different, or the populations $\langle n_M\rangle$ are different, or both. The Hamiltonian $H_{\rm eff}$ describes the effective interaction between localized spins and the band, and it is important only for f levels close to the Fermi energy (i.e., $k,\ k' \approx k_F$). In this region, the interaction constant can be approximated by

$$J \approx \frac{|V_{k_F}|^2 U}{(E_F - E_M)(E_F - E_M - U)} \ . \tag{7}$$

Here E_F and k_F represent the Fermi energy and the Fermi wave vector, respectively. The interaction given by $H_{\rm eff}$ is large when E_M is close to E_F, as can be seen from Eq. (7); also, since U is large compared to $E_F - E_M$, J, is negative[10] and approximately equal to $-|V_k|^2/(E_F - E_M)$. The interionic interaction is obtained[5-7] by treating $H_{\rm eff}$ in second-order perturbation theory, and performing an integration over band states as in Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange. The interionic interaction strength depends on $|J|^2$, the density of band states at the Fermi energy, and the distance between ions (compared to the inverse of a pertinent Fermi surface dimension).

We shall now show that the anomalous decrease in crystal-field splitting[2] is caused by the hybridization as given by the same quantity strength J. We take the basis states denoted by M in Eqs. (2) and (3) as the eigenstates of the point charge crystal-field Hamiltonian. Then V_k mixes these crystal-field states with band states of the same (cubic) symmetry about the mixing site. For an octahedron of negative point charges (i.e., located on nearest-neighbor anion sites in a NaCl lattice), the crystal-field ground state of Ce^{3+} is the Γ_7 doublet. In the paramagnetic phase, following the model of Takahashi *et al.*,[3] we assume that predominant interaction with the band occurs for the excited crystal-field Γ_8 quartet. (This follows from the symmetry of the mixing states; in the theory of Ref. 3, the f levels mix with the p states of the pnictogens, which at the center of the Brillouin zone split into Γ_8 and Γ_6 states when spin-orbit coupling is taken into account.) We assume that no mixing occurs with the Γ_7 levels.

In Eq. (4), since the Coulomb correlation energy U is much larger than $\epsilon_k - E_M$, we neglect $\epsilon_k - E_M$ in the numerator, compared to $U\langle n_M\rangle$, and on using Eq. (6), we obtain

$$H' = \sum_k J(k,k)\langle n_M\rangle c_M^\dagger c_M \ . \tag{8}$$

From Eq. (8), the shift of the Γ_8 level (from the point-charge value) is seen to be

$$\Delta\epsilon \approx \sum_k J(k,k)\langle n_{\Gamma_8}\rangle^2 \ . \tag{9}$$

As discussed above, the interaction strength $J(k,k)$ is assumed constant when k is close to the Fermi wave vector k_F, and zero far from k_F. We approximate the summation of $J(k,k)$ over k by the constant J [its value at k_F, given in Eq. (7)] times the number of band states N with which the localized level interacts. From Eq. (9) it is seen that the Γ_8 crystal-field level is pushed down in energy if J is negative. Further, the band states in the vicinity of the Γ_8 state are pushed up in energy. This will affect the summation $\sum_k J(k,k)$ in Eq. (8). However, the relative shift of the band states will not be directly taken into account in our theory, and we shall only assume that the shift does not drastically affect the product JN. In the theory of Takahashi *et al.*,[3] the band shift and the associated change in the N are included.[11] This makes the reduction of the crystal field in their theory even more pronounced (as the interaction itself varies with the relative positions of the band states and the Γ_8 level), than the result which we shall describe below.

Using Eq. (9), the splitting Δ between the crystal-field states is related to the bare point-charge crystal-field splitting Δ_0 by

$$\Delta = \Delta_0 - |J|N\langle n_{\Gamma_8}\rangle^2 \ . \tag{10}$$

Since at zero temperature, the population of the Γ_8 level is zero, Δ_0 is also the crystal-field splitting at $T=0$. The population of the Γ_8 level is related to the crystal-field splitting itself, and, at a temperature T, it is given by

$$\langle n_{\Gamma_8}\rangle = \frac{2e^{-\Delta/kT}}{1+2e^{-\Delta/kT}} \ . \tag{11}$$

If Δ_0 and the crystal-field splitting at infinite temperature Δ_∞ are known, the product $|J|N$ is found from Eqs. (10) and (11), as

$$|J|N = \tfrac{9}{4}(\Delta_0 - \Delta_\infty) \ . \tag{12}$$

Then, the crystal-field splitting at any intermediate temperature can easily be found by solving Eqs. (10)-(12). Figure 1 gives the results thus obtained, for the cases (1) $\Delta_0 = 250$ K and $\Delta_\infty = 10$ K, and (2) $\Delta_0 = 100$ K, $\Delta_\infty = 10$ K. For the former case, where Δ_0 and Δ_∞ are close to the values for CeBi, one obtains a value for $|J|N$ of 540 K. We expect this to be a reasonable number as J is expected[5] to be of the order of a tenth of an eV. It is seen from Fig. 1 that there is a marked increase in the crystal-field splitting at temperatures below $|J|N$. At much lower temperatures, magnetic ordering may occur, as in CeBi and CeSb, and this

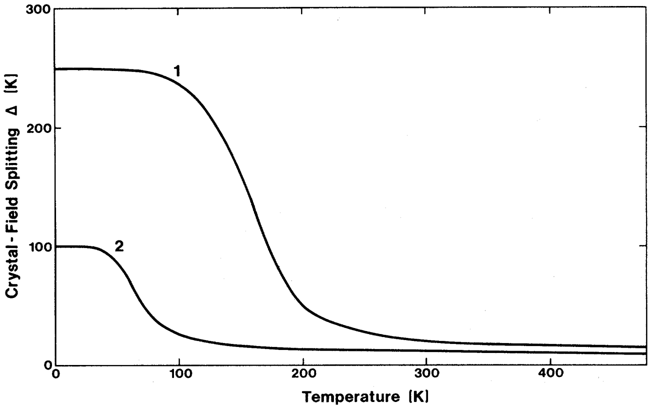

FIG. 1. Calculated variation of the crystal-field splitting Δ (in K) with temperature. Curve 1 shows the case for $\Delta_0 = 250$ K, $\Delta_\infty = 10$ K, and curve 2 shows the case for $\Delta_0 = 100$ K, $\Delta_\infty = 10$ K. Δ_0 and Δ_∞ are the crystal-field splittings at zero and infinite temperatures, respectively.

theory for the crystal-field splitting does not apply.

The results of Fig. 1 for the temperature variation of Δ show that the crystal-field splitting just above the ordering temperature of CeBi and CeSb (about 20 K), is almost as large as the bare crystal-field splitting. Experimentally, such a large value of crystal-field splitting is not observed. This discrepancy may be a consequence of assuming a constant value for $|J|N$, since it is to be expected that as the Γ_8 level moves with respect to the band, the hybridization strength would change. To obtain a large suppression of the bare crystal field at low temperatures in our model, $|J|N$ should increase with decreasing temperature.

The above calculations are strictly valid for the system only in a paramagnetic state. However, the cerium systems which show this hybridization-induced crystal-field reduction also order magnetically at low temperatures because of the hybridization-mediated two-ion interaction.[6–8] A complete calculation which incorporates both the single-ion effects and the two-ion coupling can, in principle, be carried out. The model will then provide a way of looking at the region where there are "interference" effects between the one- and two-ion effects. Such effects may be evident in the magnetically ordered state of the system. One interesting example is CeSb, which, with increasing temperature in the magnetically-ordered state, exhibits phases containing {001} planes which have a zero moment, along with {001} planes having nonzero-ordered moments. Following the work of Siemann and Cooper,[12] such structures are feasible, on introducing a small phenomenological crystal-field interaction, together with the hybridization-mediated (CS) two-ion interaction. Some evidence may also exist[13] that the ions in the paramagnetic planes possess crystal-field-like excitations, with a crystal-field splitting equal to the high-temperature paramagnetic value. (Thus the temperature at which the crystal-field splitting Δ rises sharply in Fig. 1 is probably exaggerated, and the rise probably does not occur with decreasing temperature until a much lower temperature is reached). Thus, it appears likely that the crystal-field splitting is decreased even in the magnetically ordered phases, much more so than is indicated by the temperature at which the drop in Δ occurs in Fig. 1.

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[1] J. Rossat-Mignod, J. Burlet, P. Quezel, and O. Vogt, Physica B **102**, 237 (1980).

[2] R. J. Birgeneau, E. Bucher, J. P. Maita, L. Passel, and K. C. Turberfield, Phys. Rev. B **8**, 5345 (1973).

[3] H. Takahashi, K. Takegahara, A. Yanase, and T. Kasuya, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), pp. 379–382.

[4] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[5] B. Coqblin and J. R. Schrieffer, Phys. Rev. **185**, 847 (1969).

[6] R. Siemann and B. R. Cooper, Phys. Rev. Lett. **44**, 1015 (1980).

[7] B. R. Cooper, J. Magn. Magn. Mater. **29**, 230 (1982).

[8] P. Thayamballi, B. R. Cooper, and D. Yang, Phys. Rev. B **29**, 4049 (1984).

[9] B. Cornut and B. Coqblin, Phys. Rev. B **5**, 4541 (1972).

[10] Evidence for *J* being negative is obtained from the presence of Kondo effect in diluted Ce compounds. See Ref. 5.

[11] K. Takegahara, H. Takahashi, A. Yanase, and T. Kasuya, Solid State Commun. **39**, 857 (1981).

[12] Result reported in Ref. 6.

[13] Experimental report on magnetic excitations in CeSb of J. M. Effantin, J. Rossat-Mignod, O. Vogt, and C. Vettier, Institut Laue-Langeuin Report No. 4-03 243, 1983 (unpublished).