Distorted $4f$-$5d$ Hybridization as a Jahn-Teller Phenomenon

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Stimulated by ESR measurements in SmB_6:Er^{3+} we have ascribed the unusual g-factor behavior of the Er^{3+} ground state, which is extraordinarily isotropic, to a new kind of Jahn-Teller-type phenomenon. The $4f$-$5d$ hybridization deformations of the Sm neighborhood adopt the role which in conventional Jahn-Teller systems is played by nuclear distortions. Arguments for this proposition and numerical results are given.

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This work has been stimulated by ESR measurements (Sturm and co-workers[1,2]) at an Er^{3+} defect which is embedded in a crystalline surrounding of BaB_6, CaB_6, YbB_6, or SmB_6. It turned out that Er^{3+} behaved differently in a valence-mixing neighborhood (SmB_6) than in others, although the crystal symmetry was the same. Specifically, in the SmB_6 surrounding the ground state of Er^{3+} is a Γ_8 state in contrast to the Γ_6 nature of the Er^{3+} ground state in the other crystals. Thus in SmB_6 one must have an additional interaction which allows a Γ_8 state to move below the Γ_6 state. A further hint for such an interaction is the untypically isotropic nature of the Γ_8 state ESR spectrum.

If a central degenerate electronic state interacts with the excitations of a surrounding subsystem, the total ground state is lowered. This lowering is especially pronounced if the surrounding is a "soft" one (i.e., one with low-energetic excitations). If the coupled system has the same point-symmetry group as the two subsystems, the symmetry species (e.g., Γ_8) of the lowered ground state (as well as that of the excited states) will remain unchanged.

There seem to be only two interaction options which allow a Γ_8 state to relax in a "soft" surrounding. One is the conventional vibronic interaction, as considered by Jahn and Teller [1937, "Jahn-Teller (JT) distortion"] and the other would be the interaction with the very low-energetic excitations of the $4f$-$5d$ hybridization sequence of the Sm cores. Since experimentally the effect is only observed in a "mixed valence" surrounding, we believe that the latter option is the only possible mechanism. A review of the intermediate-valence description is given by Jefferson and Stevens.[3]

Our model is a "minimal model" in the sense that we incorporate in it only the lowest flexibility of the surrounding which one could think of. The Sm ions collectively establish a multiple sequence of states ordered in accordance with the point symmetry of the Er^{3+} center. In our model, however, we assume that this Hilbert space is built up by only one A_{1g} and one E_g state (three-level model). The A_{1g}-E_g excitation then is coupled to the Γ_8 state of the central Er^{3+} ion as governed by group theory.

Our model bears some similarities to the conventional JT situation. The role which there is played by the motion of the lattice nuclei is adopted in our model by valency-mixing excitations. Therefore the general electronic state of Er^{3+} gives rise to a distortion within the Sm core clouds rather than in the nuclear position. Hence one can denote our model as a "mixed-valence JT effect."

To derive our Hamiltonian we first consider the neighborhood established by the six Sm ions. For any single Sm^{2+} ion the basic hybridization process will be one which transmits an electron from a $4f$ shell to a $5d$ shell either at the same Sm^{2+} ion or at one of the five neighboring Sm^{2+} ions. We need not specify this further. Combined, all these elementary processes establish a reducible high-dimensional representation of the central point group. If we disentangle this representation into its irreducible components, a sequence of collective states evolves. Since the basic $4f$-$5d$ hybridization process is low-energetic (~ 30 K),[4] the distance between these collective states also will remain low-energetic. Any transition between two of these states the product of which has representations contained in $\Gamma_8\times\Gamma_8$ may couple to the Γ_8 states of the central Er^{3+} ion. In our minimal model we assume the lowest collective Sm state to be of A_{1g} type and take a single E_g state as a representation of the higher states. In the Er^{3+} subsystem we consider a single Γ_8 state. We then end up with a product Hilbert space of $(A_{1g}+E_g)\times\Gamma_8$ nature.

The Hamiltonian of the Er-Sm system reads

$$H=\epsilon(c_1^\dagger c_1+c_2^\dagger c_2)+\kappa[(a_1^\dagger a_1-a_2^\dagger a_2-a_3^\dagger a_3+a_4^\dagger a_4)(c_0^\dagger c_1+c_1^\dagger c_0)+(a_1^\dagger a_3+a_3^\dagger a_1+a_2^\dagger a_4+a_4^\dagger a_2)(c_0^\dagger c_2+c_2^\dagger c_0)]. \quad (1)$$

Here the electronic operators c_0, c_1, and c_2 act in the $\{A_{1g},E_g\}$ valency mixing subspace, whereas a_1, a_2, a_3, and a_4 refer to the Γ_8 state of the Er^{3+} ion. The interaction part has been chosen according to group theory.

The Hamiltonian (1) can be diagonalized exactly. This can be done easily with an *Ansatz* for the wave functions of the form

$$|\Phi_{\pm 3/2}\rangle = (1+2\alpha^2)^{-1/2}[|\pm\tfrac{3}{2},c_0^\dagger\rangle - \alpha(|\pm\tfrac{3}{2},c_1^\dagger\rangle + |\mp\tfrac{1}{2},c_2^\dagger\rangle)],$$
$$|\Phi_{\pm 1/2}\rangle = (1+2\alpha^2)^{-1/2}[|\pm\tfrac{1}{2},c_0^\dagger\rangle + \alpha(|\pm\tfrac{1}{2},c_1^\dagger\rangle - |\mp\tfrac{3}{2},c_2^\dagger\rangle)]. \quad (2)$$

These functions constitute a basic set of Γ_8 type and their structure is given by group theory. $|\pm\frac{1}{2}\rangle$ and $|\pm\frac{3}{2}\rangle$ are eigenstates of the angular momentum $J=\frac{3}{2}$ which describes the Γ_8 Er^{3+} ground state. The parameter α is a measure of the hybridization of the new ground state, which would be absent ($\alpha=0$) if the interaction is switched off. The energy expectation value calculated with the functions (2) is

$$E(\alpha) = \epsilon(2\alpha^2 - 4\alpha\kappa/\epsilon)(1+2\alpha^2)^{-1}. \quad (3)$$

This is depicted in Fig. 1. $E(\alpha)$ is minimal for

$$\alpha = \alpha(\kappa) = -\epsilon[1-(1+8\kappa^2/\epsilon^2)^{1/2}]/4\kappa. \quad (4)$$

In this case the functions (2) are exact eigenfunctions with the eigenvalue

$$E(\kappa) = \epsilon[1-(1+8\kappa^2/\epsilon^2)^{1/2}]/2, \quad (5)$$

which is seen to decrease monotonically with rising coupling parameter κ.

The $4f$-$5d$ collective hybridization of the six Sm^{2+} ions surrounding Er^{3+} may be characterized by quadrupole moments. It turns out that only the two E components of the quadrupole, which we denote by Q_1 and Q_2, are involved. We may evaluate these components as the expectation values of quadrupole operators given in the electronic operators c_0, c_1, and c_2, but we do not write down these expressions here. Using the basic functions (2) we then may define dimensionless quadrupole coordinates by means of $Q_1^2 + Q_2^2 = [2\alpha/(1+2\alpha^2)]^2 \leq \frac{1}{2}$. Since the hybridization parameter α also measures the energy [via Eq. (3)], the ground-state energy may be expressed as a function of the quadrupole components:

$$E(Q_1,Q_2) = \tfrac{1}{2}\{1-[1-2(Q_1^2+Q_2^2)^{1/2}]\} - 2\kappa(Q_1^2+Q_2^2)^{1/2}. \quad (6)$$

It is very illustrative to draw this function in a two-dimensional picture. This is done in Fig. 2. It is this figure which may be conceived as the analogy to the famous "Mexican hat" known from the conventional work on the $E\times e$ (or the isomorphic $\Gamma_8\times e$) JT problem.

The coupling to the magnetic field is given by[5]

$$H(\Gamma_8) = g_J\mu_B[a\mathbf{H}\cdot\mathbf{J} + b(H_xJ_x^3 + H_yJ_y^3 + H_zJ_z^3)], \quad (7)$$

where the parameters a and b are defined by

$$\tfrac{1}{2}a + \tfrac{1}{8}b = Q = \langle\tfrac{1}{2}|J_z|\tfrac{1}{2}\rangle, \quad \tfrac{3}{2}a + \tfrac{27}{8}b = P = \langle\tfrac{3}{2}|J_z|\tfrac{3}{2}\rangle. \quad (8)$$

With the eigenfunctions (2) the matrix elements of the interaction Hamiltonian (7), which are nonvanishing between the Er Γ_8 states only, can be calculated. The eigenvalues read

$$\mu_{1,2}^2 = 0.5(\bar{P}^2+\bar{Q}^2) \pm [(\bar{P}^2-\bar{Q}^2)^2 - \tfrac{3}{4}(\bar{P}+\bar{Q})^2(\bar{P}-3\bar{Q})(3\bar{P}-\bar{Q})(n_1^2n_2^2 + n_1^2n_3^2 + n_2^2n_3^2)]^{1/2}, \quad (9)$$

where n_1, n_2, and n_3 are the direction cosines of the magnetic field and

$$\bar{P} = [P-\alpha^2(Q-P)]/(1+2\alpha^2),$$
$$\bar{Q} = [Q+\alpha^2(Q-P)]/(1+2\alpha^2). \quad (10)$$

One can see that the Zeeman parameters P and Q are changed because of the Er^{3+}-Sm interaction (1) described by the hybridization parameter α. From the eigenvalues (9) we can calculate the ESR spectrum of this ground state which involves the valency mixing in the six Sm neighbors. In Fig. 3 the g values of the pure uncoupled Γ_8 Er ground state (dotted lines) and the g values of the coupled system (1) (full lines) are shown. It turns out that this mixed ground state displays a remarkably isotropic ESR spectrum, which is

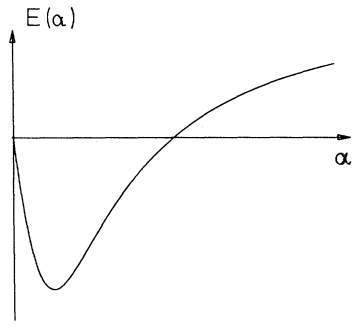

FIG. 1. Er^{3+} ground-state lowering by $4f$-$5d$ hybridization of the Sm^{2+} neighborhood. α is the hybridization parameter (see text).

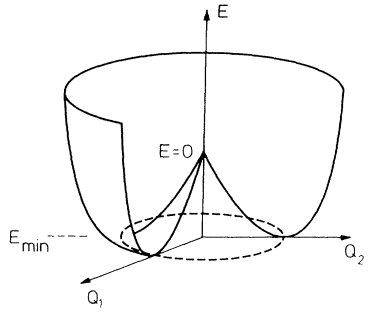

FIG. 2. Er^{3+} ground-state dependence on the Sm^{2+} hybridization quadrupole. Q_1 and Q_2 are the quadrupole variables of E_g species. Q_1 and Q_2 are dimensionless quantities such that $Q_1^2 + Q_2^2 \leq \frac{1}{2}$. $E_{min} = E(\kappa) = \epsilon[1 - (1 + 8\kappa^2/\epsilon^2)^{1/2}]/2$.

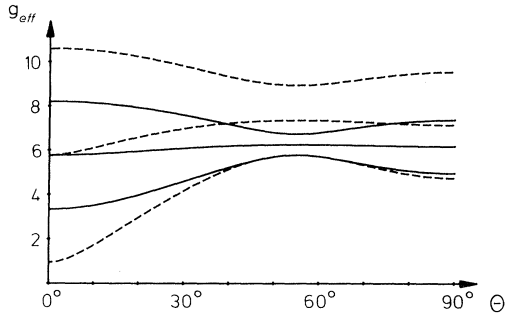

FIG. 3. Calculated ESR spectrum of a Γ_8 state from our distorted hybridization model. Zeeman parameter $P = -0.4$, $Q = 4.4$, coupling parameter $\kappa = 3\epsilon$. The dashed lines result from a pure Er^{3+} state of Γ_8 nature.

much more isotropic than one evolving from a pure Γ_8 crystal-field state.

To explain the experimental results we have to consider in addition the neighboring Γ_6 state, which mixes with the Γ_8 state via the magnetic field. The experimental results, as found by Sturm and Elschner,[1] are given in Figs. 4 and 5. The results of our calculation are shown in Fig. 6, where the coupling parameter is chosen as $\kappa = 3\epsilon$. Furthermore, we have employed the two Zeeman parameters $P = -0.4$ and $Q = 4.4$. The Γ_8-Γ_6 distance we have taken from experiments[1] ($\Delta = 5$ K). Comparing the results in Fig. 3 and Fig. 6 one can see that the Γ_6 admixing separates two transitions and we end up with four lines. The anisotropy of the lines, however, is nearly unchanged.

We want to emphasize that our model is of "minimal" nature, involving only a single coupling constant. Nevertheless it explains the experimental data quite well. If we extend our "minimal model" to a more realistic one by adding a second pure electronic Er^{3+} Γ_8 state the anisotropy can be removed further. Then a more quantitative comparison with the experimental data may be possible.

We propose in this paper a new coupling mechanism which seems to play the dominant role, when a localized degenerate electronic state interacts with the mixed-valence state of the surrounding host crystal. In view of the analogy to the conventional Jahn-Teller situation we call this model a "valency-mixing" Jahn-Teller model. We strongly believe that our model is physically preferable to a conventional Jahn-Teller model for the following reasons:

(1) To explain the experimental data by vibronic interactions, on the one hand, one must postulate a very strong linear electron-phonon coupling. But in addition to that a strong nonlinear coupling must also be assumed. Both assumptions do not seem to make physical sense, since the $4f$ orbitals of the Er ions are strongly localized and do not provide any appreciable direct electron-phonon interaction, as seen also from the experiments in the other crystals (CaB_6, BaB_6, and YbB_6).[1]

(2) The linewidths ΔH of the ESR lines are relatively small.[1,2] This is an additional hint that relaxations due to lattice vibrations are unimportant.

(3) If we adopt a three-cornered-hat JT model with both a strong linear and a strong third-order nonlinear coupling parameter, a numerical trial to fit the experimental results reveals that even the best fit is less satisfactory than in the valency-mixing option. This is seen if one tries to verify the measured isotropic ESR result. In the vibronic case one then has to resort to a P,Q choice which introduces the isotropy already in the pure Er Γ_8 state [see Eq. (6) for[2] $\alpha = 0$, $P \simeq 3Q$].

(4) From the calculation done with the conventional JT model it is found that the anharmonic terms are necessary to describe the behavior of the experimental results. To illuminate this aspect, we also introduce a kind of "anharmonic" description in our model. This

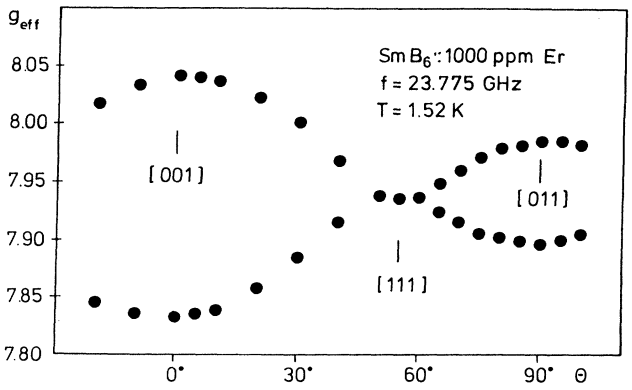

FIG. 4. ESR measurements of the Er^{3+} in the SmB_6 (see Ref. 1). Upper two lines of the Γ_8 ground-state quartet.

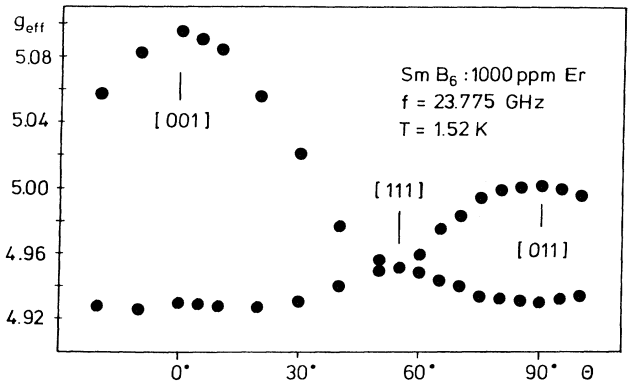

FIG. 5. ESR measurements of the Er^{3+} in the SmB_6 (see Ref. 1). Lower two lines of the Γ_8 ground-state quartet.

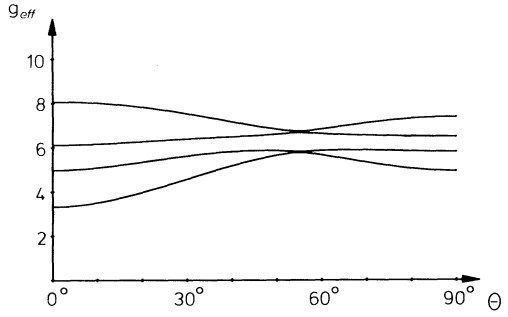

FIG. 6. Calculated ESR spectrum of a Γ_8 state from our distorted hybridization model including the Γ_6 admixing. Zeeman parameter $P=-0.4$, $Q=4.4$, coupling parameter $\kappa=3\epsilon$, $\Delta=5$ K (experimental distance between the lowest Γ_6 and Γ_8 states).

can be achieved by application of an extended Holstein-Primakoff transformation,[6]

$$\begin{aligned}
&\tau_+ = c_1^\dagger c_0 = b_1^\dagger [1-(b_1^\dagger b_1 + b_2^\dagger b_2)]^{1/2},\\
&\tau_- = c_0^\dagger c_1 = [1-(b_1^\dagger b_1 + b_2^\dagger b_2)]^{1/2} b_1,\\
&\beta_+ = c_2^\dagger c_0 = b_2^\dagger [1-(b_1^\dagger b_1 + b_2^\dagger b_2)]^{1/2},\\
&\beta_- = c_0^\dagger c_2 = [1-(b_1^\dagger b_1 + b_2^\dagger b_2)]^{1/2} b_2,\\
&\tau_0 = b_1^\dagger b_1 + \tfrac{1}{2}(b_2^\dagger b_2 - 1), \quad \Gamma = \tfrac{1}{3} - b_2^\dagger b_2,\\
&\tau_0 = \tfrac{1}{2}(c_1^\dagger c_1 - c_0^\dagger c_0), \quad \Gamma = \tfrac{1}{3}(c_0^\dagger c_0 + c_1^\dagger c_1 - 2c_2^\dagger c_2),
\end{aligned} \tag{11}$$

to Hamiltonian (1). Expanding the square roots, one ends up with a Hamiltonian which involves anharmonic terms of all orders in the operators. If we interpret

$$q_{1,2} = (b_{1,2} + b_{1,2}^\dagger)/\sqrt{2},$$
$$p_{1,2} = (b_{1,2} - b_{1,2}^\dagger)/i\sqrt{2}$$

as vibrational coordinates and take only the terms up to the third order, the Hamiltonian (1) has the same structural form as the conventional electron-phonon JT Hamiltonian. In contrast, however, to a conventional JT system, the linear and nonlinear coupling constants cannot be independently chosen, but are rigidly fixed by means of the Holstein-Primakoff derivation.

Finally, we want to stress that the basic $4f$-$5d$ process of the Sm ions themselves can couple to the nuclear motion of the lattice. So, beyond the direct coupling of Er^{3+} to the valence fluctuations, there may be an indirect one to the lattice motion, which is mediated by the Sm-phonon coupling. In our opinion this, however, is a higher-order effect and therefore of minor importance with regard to the Er spectroscopy.

We want to thank Professor Elschner and Dr. Sturm for valuable and stimulating discussions and for the permission to reproduce their measurements (Figs. 3 and 4).

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