ESR Spectra of Er^{3+} in SmB_6 Single Crystals: Dynamic Jahn-Teller Effect in a Mixed-Valence Compound

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In an ESR study on the rare-earth ion Er^{3+} in the intermediate-valence single crystal SmB_6 a spectrum is found which is markedly different from those of comparable systems with integral valence. We analyze the unusual experimental results in terms of a dynamic Jahn-Teller effect in the Γ_8 cubic-crystal-field ground state. The characteristic features of our experimental data are well reproduced by the calculations, which suggest that the substitutional rare-earth ion Er^{3+} suffers enhanced electron-phonon coupling mediated by the valence-fluctuating host.

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During the past decade, the rare-earth compound SmB_6 has attracted intense interest because it belongs to the class of intermediate-valence (IV) systems.[1] It is widely accepted that the Sm ion can fluctuate between the $4f^6$ and $4f^5 5d^1$ configurations where the $5d$ electrons join the conduction band. These valence fluctuations give rise to various unusual electric, magnetic, elastic, and phonon properties which are the subject of current research.

To our knowledge we present in this Letter the first ESR spectrum on a non-S-ground-state rare-earth ion (Er^{3+}) in a matrix with valence fluctuations. Our extensive measurements in the temperature range 1.3–4.2 K were made at 9.25 GHz (X band), 23.8 GHz (K band), and 33.8 GHz (Q band), and for Er^{3+} concentrations in the range 1000–3000 ppm.

Our ESR spectra of Er^{3+} show an unusual multiline structure consisting of one nearly isotropic line and two doublets which cannot be explained by means of the conventional Zeeman effect within the $J=\frac{15}{2}$ manifold of Er^{3+} in a cubic crystal field.[2] The effective g factors associated with the observed transitions are shown in Fig. 1 for the external field in the [111], [011], and [001] directions, respectively. The remarkable features of the spectra are the weakly pronounced anisotropic g factors as compared to well-known ESR spectra of Er^{3+} with the Γ_8 ground state in cubic non-IV systems.[3] The angle-dependent splitting of the doublets is depicted for line (b) in Fig. 2. The centers of gravity of each pair become increasingly anisotropic as the resonance frequency is increased from the X to the Q band. The missing of one doublet in the X band seems peculiar. All detected angle-dependent transitions are of comparable intensity. From the temperature dependence of the intensity ratio of the almost isotropic line (a) to the doublet lines (b), one expects that the doublet transitions occur in a Γ_8 ground state and that the nearly isotropic line originates from an excited Kramers doublet which is at least 5 K above the Γ_8 ground state. No temperature variation of the effective g values between 1.3 and 4.2 K is observed. Especially, there are no indications for any motional narrowing effects in this temperature range.

All ESR lines show clearly resolved hyperfine splitting corresponding to the isotope ^{167}Er ($\approx 23\%$) with $I=\frac{7}{2}$. We find for the hyperfine constant the typical value for ^{167}Er: $A=75\pm1$ Oe. The linewidths ΔH of the ESR lines are frequency dependent. They amount to 17 ± 2 Oe and 28 ± 2 Oe for the X and Q bands, respectively, at 4.2 K.

Since intermediate valence is known to give rise to strong electron-phonon coupling, we interpret the unusual ESR spectra by a dynamic Jahn-Teller (JT) effect, i.e., we assume that the observed quartet ground state and the excited Kramers doublet result from an electronic Γ_8 cubic-field ground state of Er^{3+} subjected to a JT effect. In general, the Γ_8 state couples with JT-active lattice distortions of symmetry ϵ_g and t_{2g}. Our ESR data, however, give strong evidence of dominant $\Gamma_8 \otimes \epsilon_g$ coupling, in contrast to Er^{3+} in cubic single crystals of Pd where coupling to t_{2g} modes dominates.[4] As usual, we approximate the ϵ_g-multimode JT coupling in the crystal by an effective single-ϵ_g-mode, $q=(q_\theta, q_\epsilon)$, model.[5] We describe the dynamic JT effect in terms of the tunneling model which has been used successfully in the description of experimental observations in the case of $3d^n$ transition-metal ions.[6]

The electronic Γ_8 ground state is chosen to transform as the eigenstates $\{|\pm\frac{1}{2}\rangle, |\pm\frac{3}{2}\rangle\}$ of a fictitious spin $\tilde{J}=\frac{3}{2}$. In terms of the pseudospin operator $\tilde{J}=\frac{3}{2}$, the Zeeman interaction in a cubic crystal field is conveniently represented by[6]

$$\mathcal{H}^z = g\mu_B \mathbf{O}_1 \cdot \mathbf{H} + u\mu_B \mathbf{O}_2 \cdot \mathbf{H}, \quad (1)$$

where $O_{1\gamma}=\tilde{J}_\gamma$ and $O_{2\gamma}=\tilde{J}_\gamma^3 - \frac{41}{20}\tilde{J}_\gamma$, with $\gamma=x,y,z$. For a fixed JT distortion $\mathbf{q}$, the fourfold degenerate electronic ground state is split by the JT coupling into two Kramers doublets. For definiteness, we take as the lower split-off state the Kramers doublet

$$|\psi_{1/2}\rangle = \pm\cos(\phi/2)|\pm\tfrac{1}{2}\rangle \mp \sin(\phi/2)|\mp\tfrac{3}{2}\rangle. \quad (2)$$

In the spirit of the tunneling model[6] for the dynamic

JT effect, interactions between states associated with the upper split-off Kramers doublet are neglected and the Zeeman interaction Eq. (1) for an arbitrary configuration $\mathbf{q}=\rho(\cos\phi,\sin\phi)$ may appropriately be rewritten in the form

$$\mathscr{H}^{z}=-\tfrac{1}{2}(P-Q)\boldsymbol{\sigma}\cdot\mathbf{H}+\tfrac{1}{2}(P+Q)\{\cos\phi[\sigma_z H_z-\tfrac{1}{2}(\sigma_x H_x+\sigma_y H_y)]+\tfrac{1}{2}\sqrt{3}\sin\phi(\sigma_x H_x-\sigma_y H_y)\}. \quad (3)$$

Here, the σ_γ's are the usual Pauli spin operators acting in the subspace spanned by $\{|\psi_1\rangle, |\psi_2\rangle\}$ of Eq. (2). The Zeeman parameters P and Q, respectively, are related to $g\mu_B$ and $u\mu_B$ of Eq. (1) by $g\mu_B=(3P+Q)/5$ and $u\mu_B=(P-3Q)/3$.

Within the vibronic model, the JT tunneling Hamiltonian is represented by

$$\mathscr{H}^{T}=\begin{pmatrix}2\Delta & 0 & 0\\ 0 & -\Delta & 0\\ 0 & 0 & -\Delta\end{pmatrix}, \quad (4)$$

in the vibrational basis $\{|A\rangle, |E\rangle, |E'\rangle\}$.[7] Each energy level is degenerate with respect to the Kramers doublet $\{|\psi_1\rangle, |\psi_2\rangle\}$ of Eq. (2).

The Zeeman Hamiltonian Eq. (3) now operates within the low-lying vibronic Γ_8 quartet $\{|E\rangle|\psi_{1/2}\rangle, |E'\rangle|\psi_{1/2}\rangle\}$ and the high-lying vibronic doublet $\{|A\rangle|\psi_{1/2}\rangle\}$ separated by a tunneling energy 3Δ. The nonzero expectation values of $\cos\phi$ and $\sin\phi$ in the vibrational states are as usual parametrized by the constants c_1 and c_2, respectively.[7]

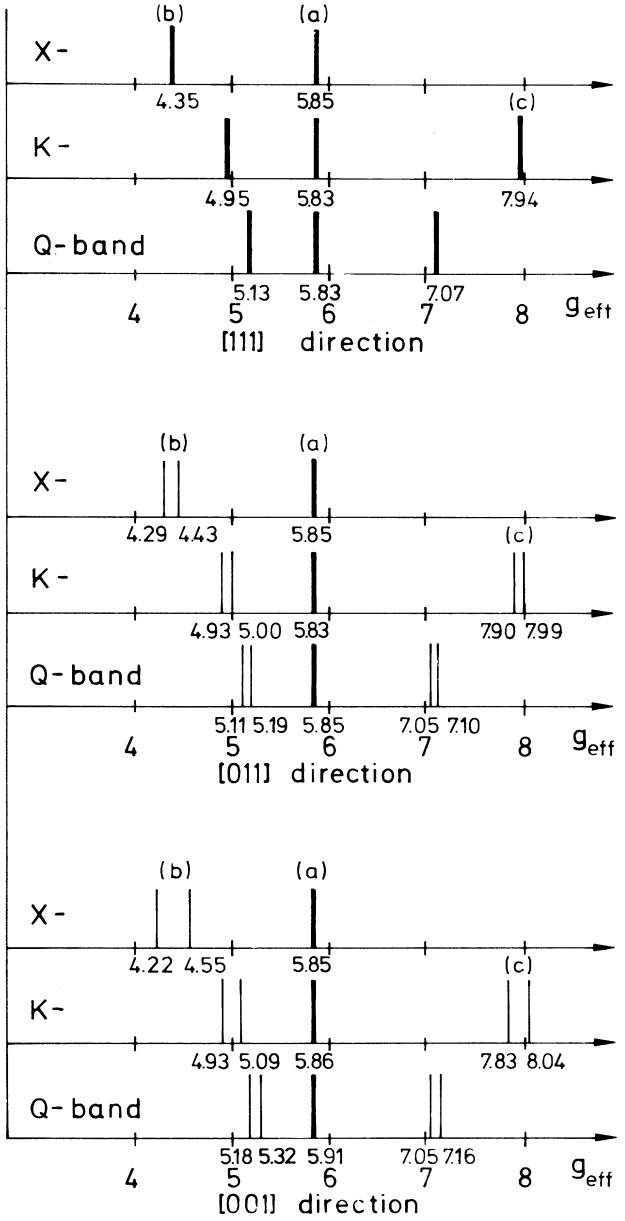

FIG. 1. Experimental g values for the [111], [011], and [001] directions at the X, K, and Q bands.

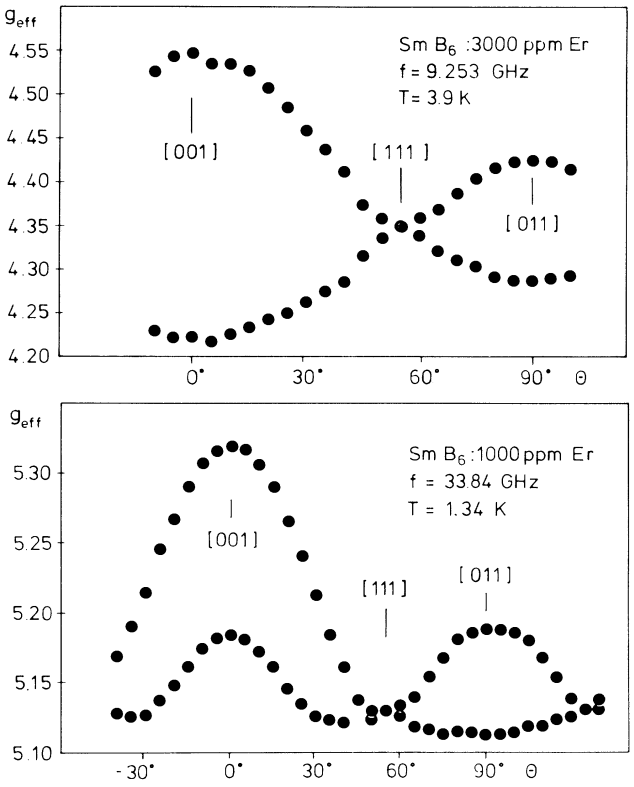

FIG. 2. Angular variation of the g values associated with line (b) for X- and Q-band measurements. θ is the angle between the [001] direction and the applied magnetic field, which is rotated in the (011) plane.

As an example, the Zeeman splitting of the low-lying vibronic quartet and the excited doublet resulting from Eqs. (3) and (4) is shown in Fig. 3 for the magnetic field parallel to the cubic z axis. For comparison with experiment, the parameter set (Δ,P,Q,c_1,c_2) entering in the model description is determined from a least-mean-squares fit using all measured ESR transitions detected for the selected X-, K-, and Q-band frequencies. These transitions are indicated by the bars in Fig. 3 at the various positions corresponding to fields of resonance as found from experiment. Fairly good agreement between experiment and theory is obtained especially in view of the fact that the same parameter set fits the experimental data for [011] and [111] directions as well. Moreover, it is to be noted that every measured transition corresponds to a transition allowed by the model and vice versa.

The fitting procedure provides for Δ the value 1.71 corresponding to a zero-field tunneling splitting of $3\Delta = 5.13$ K, which is in good agreement with the value of 5 K found from the temperature dependence of the intensity ratio of lines (a) and (b), as mentioned above.

The almost degenerate field variation of the lower split-off Zeeman levels of the vibronic quartet yields a spectrum in which the allowed resonance lines are arranged into two pairs of lines for the K band as well as for the Q band. In addition, the nonlinear field variation of the levels gives rise to a slight frequency-dependent splitting of each pair, as observed in the experiments. At X band only two angle-dependent lines could be resolved within experimental accuracy, unlike the K- and Q-band results. It is reasonable to consider these lines as two pairs of lines like the pairs appearing in the K and Q bands but with a splitting too small to be detected. This interpretation would qualitatively agree with the transitions expected from theory.

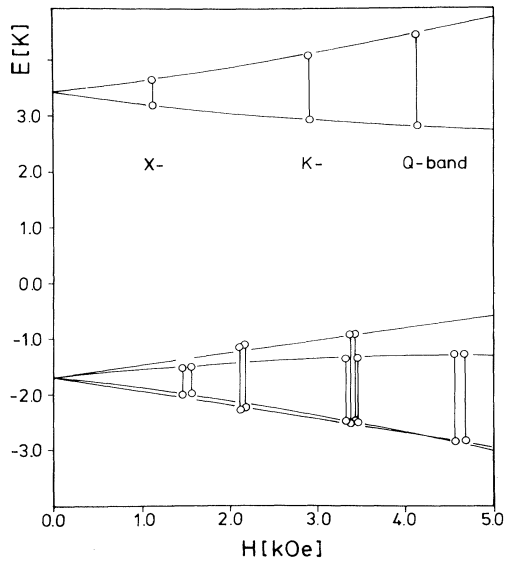

FIG. 3. Zeeman splitting of the low-lying vibronic states for magnetic field $H \parallel [001]$ as calculated from Eqs. (3) and (4) with $\Delta = 1.71$, $P = 0.63$, $Q = 0.23$, $c_1 = 0.70$, and $c_2 = 0.08$. The bars represent the measured ESR transitions at the X, K, and Q bands at the positions corresponding to the measured fields of resonance.

As seen from Fig. 3 allowed transitions from the low-lying vibronic quartet to the excited vibronic doublet may occur only at rather high fields of resonance. Below $H = 17$ kOe no such transitions were observed.

We agree that the successful interpretation of the resonance spectra of the rare-earth ion Er^{3+} in SmB_6 in terms of the tunneling model may appear to be fortuitous. The tunneling model implies at least moderately strong electron-phonon coupling which may be questioned to be realistic in the case of rare-earth ions, because the $4f$ electrons of the Er^{3+} probe are considered to be well localized within the Xe shell and thus relatively insensitive to lattice distortions. If electron-phonon coupling is important for the features of the ESR spectra at all, one should expect a weak JT effect to operate. But we know that a weak JT effect fails to explain our data. We emphasize that the Er^{3+} probe is substituted into a valence-fluctuating matrix. It is well established for a series of Sm chalcogenides that in valence-fluctuating materials electron-phonon coupling plays a dominant role, which leads to pronounced anomalies of some phonon branches.[8] Although only scarce experimental data are available at present for SmB_6, it seems rather likely that electron-lattice coupling plays a major role in this compound, too. Indeed, first indications for phonon anomalies are provided by recent Raman investigations.[9] A defect-induced, low-frequency Raman line is found in SmB_6, which is believed to result from a "soft" X-point phonon mode. Such a mode may induce large tetragonal modulations of the unit cell and thus enhance the $\Gamma_8 \otimes \epsilon_g$ JT effect at the Er^{3+} site. Our ESR results may thus stimulate further experimental and theoretical investigations of the problem of electron-phonon coupling in IV-SmB_6 compounds.

It should be noticed that in contrast to the unusual multiline spectra of Er^{3+} in SmB_6, X-band ESR spectra of Er^{3+} in the isostructural compounds LaB_6,[10] and our measurement on the semiconductors BaB_6, YbB_6, and CaB_6 do show only a single isotropic line, corresponding to a Γ_6 crystal-field ground state which is not JT active. The effective g factor associated with this line is given by $g = 5.87 \pm 0.02$ for LaB_6, $g = 5.89 \pm 0.05$ for BaB_6, $g = 5.90 \pm 0.05$ for YbB_6, and $g = 5.87 \pm 0.05$ for CaB_6.[11] The relatively large negative g shift from the nominal value of $g = 6$ for a Γ_6 crystal-field ground state probably results here from a

strong chemical shift of Er^{3+} in its boron environment.

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