PARAMAGNETIC RESONANCE OF ERBIUM IN $CaWO_4$*

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A study has been made of the paramagnetic resonance of Er^{3+} in single crystal $CaWO_4$, and the parameters of the spin-Hamiltonian determined.

The details of the paramagnetic resonance spectrum of Er^{3+} in $CaWO_4$ is the only one of the trivalent rare-earth ions which has not been reported to date.

We have observed the spectrum of Er^{3+} in a sample of $CaWO_4$ which contained only a trace amount of erbium. The spectrum consisted of an intense central line and eight hyperfine lines, the ratio of the intensities being approximately 1 : 25. This is the expected spectrum for erbium which has an isotope ^{167}Er with nuclear spin $I = \frac{7}{2}$ and 22.8% natural abundance. The spectrum can be described by an axially symmetric spin Hamiltonian with an effective spin $S = \frac{1}{2}$

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A I_z S_z + B(S_x I_x + S_y I_y)$$

The z axis of the spin Hamiltonian coincided with the c-axis of the crystal. The constants of the Hamiltonian were found to be

$$g_{\parallel} = 1.247 \mp 0.001 ,$$

$$g_{\perp} = 8.400 \mp 0.003 ,$$

$$A = (42.5 \mp 1) \times 10^{-4}\ \mathrm{cm}^{-1} ,$$

$$B = (289.6 \mp 1) \times 10^{-4}\ \mathrm{cm}^{-1} ,$$

$$Ag_{\perp}/Bg_{\parallel} = 0.99.$$

The corresponding g values reported by Kirton [1] were $g = 1.251$ and $g_{\perp} = 8.401$. The constants reported here are similar to the ones reported for Er^{3+} in $PbMoO_4$ [2].

The large arisotropy of the g-factor leads to the irregular spacing of the hyperfine lines. With the magnetic field perpendicular to the z-axis eight hyperfine lines of equal intensity are observed with the spacing between them increasing with increasing magnetic field. When the magnetic field is parallel with the z-axis the spectrum is not so simple and is shown in fig. 1. The positions of the $\Delta m = 0$, $\Delta m = \mp 1$ and $\Delta m = \mp 2$ lines calculated from the spin Hamiltonian are also shown. At the low field end of the spectrum the energy levels corresponding to the hyperfine transitions can no longer be described accurately by single high field quantum numbers. The subsequent appearance of additional lines in the spectrum corresponds to the "forbidden" transitions $\Delta m = \mp 1$, $\Delta m = \mp 2$ of the high field approximation.

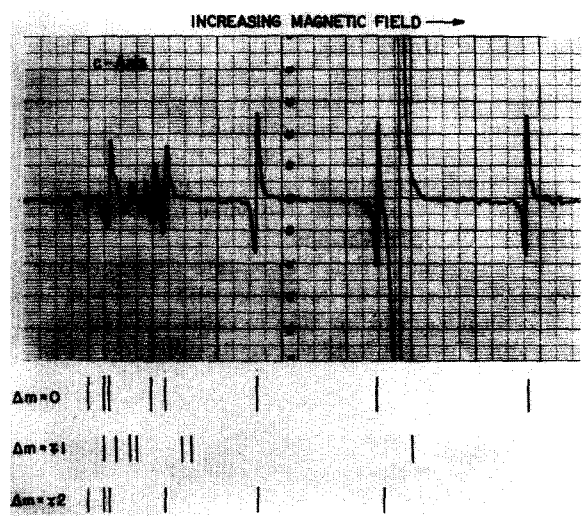

Fig. 1. EPR spectrum of Er^{3+} in $CaWO_4$, magnetic field parallel to the c-axis.

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The similarity in the form of this spectrum with the other trivalent rare earth ions leads us to conclude that the Er^{3+} ion occupies the calcium site in the lattice and experiences a crystal electric field of tetragonal symmetry.

The ground state of the Er^{3+} ion which has a $4f^{11}$ electron configuration is $^4I_{\frac{15}{2}}$. In a field of S_4 symmetry this level is split into eight Kramers doublets described by

$$D_{\frac{15}{2}} = 4\Gamma_{56} + 4\Gamma_{78}$$

The wavefunctions will be of the form

$$\Gamma_{56}: a_1|\mp\tfrac{13}{2}\rangle + a_2|\mp\tfrac{5}{2}\rangle + a_3|\pm\tfrac{3}{2}\rangle + a_4|\pm\tfrac{11}{2}\rangle$$

$$\Gamma_{78}: b_1|\mp\tfrac{9}{2}\rangle + b_2|\mp\tfrac{1}{2}\rangle + b_3|\pm\tfrac{7}{2}\rangle + b_4|\pm\tfrac{15}{2}\rangle$$

It is possible to choose a_i and b_i in such a way as to obtain the observed g-values, but this cannot be done uniquely. Crystal field calculations [3] indicate that the Γ_{56} doublet is most probably the lowest with a Γ_{78} doublet only a few tens of cm^{-1} above it. No additional resonance spectrum was observed that could be attributed to this upper doublet in the temperature range below $10^{\circ}K$, and we conclude that the separation of these doublets is probably greater than 15 cm^{-1}.

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References

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THRESHOLD MAGNETIC FIELDS AND TEMPERATURES FOR UNIAXIAL FERROMAGNETS WITH DOMAIN STRUCTURES

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It is shown that there exist a threshold magnetic field and temperature above which a magnetization antiparallel to the external magnetic field cannot occur in an uniaxial ferromagnet with domain structure.

Theoretical investigations of the influence of an external magnetic field on the domain structure [1,2] described satisfactorily the experimental data on the motion of interdomain walls. These calculations were restricted to zero temperature and made under the assumption that the magnitude of the average magnetization (σ) is independent of the external magnetic field and of the site in the domain structure. The hypothesis following from theoretical investigations, that in a ferromagnet with domain structure one can introduce local transition temperatures [3] dependent on the site in the structure, raised the question whether the assumption σ = const in sensible at high temperature. From the physical point of view the answer is apparently negative, as one can look at the external magnetic field as at an anisotropy changing with the magnetization direction.

Hence, for a sample with non-uniform magnetization being a consequence of the domain structure, one can anticipate two effects: 1. depending on the region, a temperature increase will lessen differently the average magnetization in the presence of the external magnetic field, 2. the critical temperature will depend on the magnetization direction in the region, and on the external magnetic field.