

# PHYSICAL REVIEW B

## SOLID STATE

THIRD SERIES, VOL. 4, No. 1

1 JULY 1971

### Electron-Paramagnetic-Resonance Spectra of $\text{Nd}^{3+}$ , $\text{Dy}^{3+}$ , $\text{Er}^{3+}$ , and $\text{Yb}^{3+}$ in Lithium Yttrium Fluoride

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(Received 19 March 1971)

The electron-paramagnetic-resonance spectra have been obtained for trivalent neodymium, dysprosium, erbium, and ytterbium in single-crystal samples of the scheelite lithium yttrium fluoride. The measurements were made at X-band frequencies and at 4.2°K. The ions were found to have axial spectra which, together with chemical arguments, indicate that they occupy  $\text{Y}^{3+}$  sites with  $S_4$  point symmetry.  $g$  factors and hyperfine parameters were obtained by the complete diagonalization of the spin Hamiltonian and least-squares fitting to the observed spectra. The ground-state irreducible representations for  $\text{Yb}^{3+}$  and  $\text{Nd}^{3+}$  were determined to be  $\Gamma_{5,6}$  and  $\Gamma_{7,8}$ , respectively. Superhyperfine structure was observed in the  $\text{Yb}^{3+}$   $c$ -axis spectrum.

#### I. INTRODUCTION

There has been considerable interest in the electron paramagnetic resonance (EPR) and optical spectra of rare-earth ions in the tungstate and molybdate crystals with scheelite ( $\text{CaWO}_4$ ) structure.<sup>1-5</sup> These crystals vary approximately 30% in unit-cell volume, and may be grown with up to several percent rare-earth impurity. The rare-earth ions substitute for divalent cations which have tetragonal ( $S_4$ ) symmetry. By doping a series of scheelites with a rare-earth ion, the surroundings of the ionic impurity may be varied while preserving the tetragonal point symmetry. This family of crystals has therefore been recognized as useful for investigating the crystal-field model.

Lithium yttrium fluoride also possesses scheelite structure<sup>6</sup> and should prove to be an interesting host for the study of the spectra of rare-earth ions. On the basis of the similarity of ionic radii and the chemical properties of yttrium and rare-earth ions, it is expected that trivalent rare-earth ions will substitute for trivalent yttrium<sup>7,8</sup> ions which have tetragonal ( $S_4$ ) symmetry. This substitution of a rare-earth ion for an ion with the same valence is to be contrasted with the tungstate and molybdate scheelites where the rare-earth ion substitutes for the divalent cations of calcium, strontium, etc. The result should be less disruption of the host lattice by the impurity ion in  $\text{LiYF}_4$ . Comparison of

the optical spectra of neodymium in  $\text{CaWO}_4$  and  $\text{LiYF}_4$  appears to bear out this conjecture.<sup>7</sup> In addition, since  $\text{LiYF}_4$  is probably more nearly an ionic crystal than the tungstate and molybdate scheelites, it should allow a more realistic comparison of experimental crystal-field parameters with those calculated from a point-charge model.

In this paper we report on the EPR spectra of  $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$  in samples of single crystal  $\text{LiYF}_4$ . The results are compared with those previously published for these ions in tungstate and molybdate scheelites. An axial resonance spectrum was observed for each ion, and  $g$  factors and hyperfine parameters were obtained by fitting to an axial spin Hamiltonian. Superhyperfine structure (SHFS) was observed on the  $\text{Yb}^{3+}$  spectrum, when the external field was parallel to the crystal  $c$  axis. The similarity of the SHFS to that reported for  $\text{Yb}^{3+}$  in  $\text{CaF}_2$  suggests that the effect is due to the nuclear magnetic moments of the ligand fluorine ions.<sup>9</sup>

#### II. CRYSTAL STRUCTURE OF $\text{LiYF}_4$

The scheelite structure of  $\text{LiYF}_4$  was determined by Thoma *et al.*<sup>6</sup> using x-ray diffraction. One may take  $\text{CaWO}_4$  as the prototype crystal for the scheelite family which has the space group classification  $C_{4h}^6(I4_1/a)$ . With respect to the  $\text{CaWO}_4$  unit cell, in  $\text{LiYF}_4$ , yttrium is at the calcium site, lithium is at the tungsten site, and fluorine is at the oxygen

TABLE I. Lattice parameters for several crystals with scheelite structure.

| Crystal                      | $c(\text{\AA})$ | $a(\text{\AA})$ | $c/a$ |
|------------------------------|-----------------|-----------------|-------|
| LiYF <sub>4</sub> (Ref. 6)   | 10.94(3)        | 5.26(3)         | 2.08  |
| LiYF <sub>4</sub> (Ref. 10)  | 10.85(3)        | 5.16(1)         | 2.10  |
| CdMoO <sub>4</sub> (Ref. 11) | 11.194          | 5.1554          | 2.171 |
| CaWO <sub>4</sub> (Ref. 12)  | 11.376(3)       | 5.243(2)        | 2.170 |
| PbMoO <sub>4</sub> (Ref. 13) | 12.0165(39)     | 5.4312(16)      | 2.212 |
| BaWO <sub>4</sub> (Ref. 11)  | 12.720          | 5.6134          | 2.266 |

site. The lattice parameters for LiYF<sub>4</sub> and several other scheelites are shown in Table I. The tungstates and molybdates listed span the range of lattice sizes for scheelites that have been commonly used as hosts for rare-earth ions. The quantity  $c$  represents the length of the unique axis of the tetragonal body-centered unit cell, and  $a$  is the length of a base side. From the comparison with other scheelites, one sees that LiYF<sub>4</sub> has a smaller  $c$ -axis length, and a lower  $c/a$  ratio.

### III. EXPERIMENTAL DETAILS

The measurements were made at 4.2 °K with an X-band superheterodyne EPR spectrometer operating in the absorption mode. The rectangular sample cavity was designed so that crystals mounted in it could be rotated in a vertical plane while they were still immersed in liquid helium. Using this device, and a magnet mounted on a calibrated rotatable horizontal base, the angle between the  $c$  axis and the magnetic field could be determined to a tenth of a degree.

The crystal samples were grown by Linz and Gabbe of MIT, and Farrar of Harry Diamond Laboratories (HDL).

The LiYF<sub>4</sub>:Yb sample had a 0.1-at. % ytterbium doping and the LiYF<sub>4</sub>:Nd sample had a 2-at. % neodymium doping in the melt. A sample with a melt concentration of 2-at. % erbium had such a broad EPR line that the hyperfine structure could not be

distinguished. From this, one is tempted to conclude that erbium doping can be achieved more readily than neodymium doping.

The LiYF<sub>4</sub> crystals grown at this laboratory were pulled from the melt in an  $a$ -axis direction. The boule cross sections were elliptical in shape with the  $c$  axis parallel to the major axis. For CaWO<sub>4</sub> and other scheelites, the  $c$  axis was parallel to the minor axis.<sup>14</sup>

The EPR spectra of Er<sup>3+</sup> and Dy<sup>3+</sup> were first discovered and measured in a LiYF<sub>4</sub> sample which had been grown without intentional rare-earth doping. The trace amounts of Er<sup>3+</sup> and Dy<sup>3+</sup> had probably been present as impurities in the yttrium fluoride starting material. These ions were identified from their hyperfine structure. The identification was checked by measuring spectra in intentionally doped crystals. It was found that the resolution of the hyperfine lines was better in the "undoped" LiYF<sub>4</sub>, so this crystal was used to measure the hyperfine parameters.

Several other resonance lines have been noted in every LiYF<sub>4</sub> sample so far examined, but these lines have not yet been identified.

### IV. ANALYSIS

The spin Hamiltonian used to fit the data was

$$\mathcal{H} = g_{\parallel} \mu_B H_z S_z + g_{\perp} \mu_B (H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y) + P [I_z^2 - \frac{1}{3} I(I+1)]. \quad (1)$$

Here  $S = \frac{1}{2}$  for these Kramers ions, and the quantity  $I$  takes on appropriate values for the various isotopes. Least-squares fit spin-Hamiltonian parameters were calculated by computer using an iterative procedure which included complete diagonalization of the spin Hamiltonian. The results are given in Table II. Also listed are the measured peak-to-trough derivative linewidths  $\Delta H_{\parallel}$  and  $\Delta H_{\perp}$  for the parallel and perpendicular spectra. (The quantity  $\Delta H_{\perp}$  is not necessarily constant for every perpendicular direction.)

TABLE II. Spin-Hamiltonian parameters for rare-earth ions in LiYF<sub>4</sub>.

| Ion              | $g_{\parallel}$      | $g_{\perp}$          | $\Delta H_{\parallel}$<br>(G) | $\Delta H_{\perp}$<br>(G) | Isotope | $A$<br>(10 <sup>-4</sup> cm <sup>-1</sup> ) | $B$<br>(10 <sup>-4</sup> cm <sup>-1</sup> ) | $P$<br>(10 <sup>-4</sup> cm <sup>-1</sup> ) |
|------------------|----------------------|----------------------|-------------------------------|---------------------------|---------|---|---|---|
| Nd <sup>3+</sup> | 1.987(2)             | 2.554(3)             | 18.8                          | 25.1                      | 143     | 197(6)                                      | 263(9)                                      | ...   |
|                  |                      |                      |                               |                           | 145     | 124(4)                                      | 164(6)                                      | ...   |
| Dy <sup>3+</sup> | 1.112(2)             | 9.219(15)            | 8.2                           | 10.9                      | 161     | 31.6(8)                                     | 263(5)                                      | <30   |
|                  |                      |                      |                               |                           | 163     | 41.5(10)                                    | 366(3)                                      | <40   |
| Er <sup>3+</sup> | 3.137(3)             | 8.105(12)            | 13.2                          | 11.3                      | 167     | 108.6(6)                                    | 280(3)                                      | ...   |
|                  | 3.32(1) <sup>a</sup> | 8.09(5) <sup>a</sup> |                               |                           |         |   |   |   |
| Yb <sup>3+</sup> | 1.3308(6)            | 3.917(3)             | 19.7                          | 13.9                      | 171     | 338(2)                                      | 1028(4)                                     | ...   |
|                  |                      |                      |                               |                           | 173     | 92.5(5)                                     | 284(1)                                      | ...   |

<sup>a</sup>Reference 8.

The rms deviation between a measured and calculated line position was less than one-fifth of a linewidth for all spectra except the parallel spectrum of  $\text{Dy}^{3+}$ . The rms deviation was just slightly less than the average measured linewidth for  $\text{Dy}^{3+}$ . It is not known why the fit was not better, but it may be that a spin Hamiltonian with higher terms than those in Eq. (1) is required to describe adequately the spectrum. A quadrupole term was needed only for  $\text{Dy}^{3+}$ .

The difference between the value of  $g_{\parallel}$  for  $\text{Er}^{3+}$  reported here and in Ref. 8 may be due in part to the higher concentration of erbium in the samples used in Ref. 8.

#### V. DISCUSSION

Arguments have been presented which indicate that trivalent rare-earth ions substitute for the divalent cations in the tungstate and molybdate scheelites.<sup>4,14,15</sup> Similar considerations of crystal structure, valence, ionic size, and the axial symmetry of the EPR resonances indicate that the rare-earth ions are located at the yttrium site of  $S_4$  point symmetry in  $\text{LiYF}_4$ . These arguments are strengthened by the fact that no charge compensation is necessary in this case. The crystal structure is too compact<sup>16</sup> for interstitial sites which, moreover, would not have axial resonance spectra. The lithium and yttrium sites alone have tetragonal symmetry. Trivalent rare earths, with ionic radii ranging from 1.28 to 1.12 Å would be expected to substitute for the trivalent yttrium ion of radius 1.115 Å rather than the smaller univalent lithium ion of radius 0.73 Å.<sup>17</sup>

The EPR data may be used to determine the  $S_4$  irreducible representations of the ground states for  $\text{Yb}^{3+}$  and  $\text{Nd}^{3+}$ . As discussed in Ref. 4, the ground-state  $g$  factors for  $\text{Yb}^{3+}$  are related by

$$4g_{\perp}^2 = -3g_{\parallel}^2 + 6\Lambda g_{\parallel} + 45\Lambda^2,$$

if the state is characterized by  $J = \frac{7}{2}$  with Kramers components

$$\begin{aligned} |\Gamma_5\rangle &= a \left| \frac{7}{2}, \frac{5}{2} \right\rangle + b \left| \frac{7}{2}, -\frac{3}{2} \right\rangle, \\ |\Gamma_6\rangle &= -a^* \left| \frac{7}{2}, -\frac{5}{2} \right\rangle - b^* \left| \frac{7}{2}, \frac{3}{2} \right\rangle. \end{aligned}$$

Here the states are expressed in  $|JM\rangle$  notation and  $\Lambda = \frac{8}{7}$  is the Landé factor for the  ${}^2F_{7/2}$  multiplet of  $\text{Yb}^{3+}$ . The corresponding relationship is

$$4g_{\perp}^2 = g_{\parallel}^2 + 14\Lambda g_{\parallel} + 49\Lambda^2$$

for a pure  $J = \frac{7}{2}$ ,  $\Gamma_{7,8}$  state with components

$$\begin{aligned} |\Gamma_7\rangle &= c \left| \frac{7}{2}, \frac{1}{2} \right\rangle + d \left| \frac{7}{2}, -\frac{7}{2} \right\rangle, \\ |\Gamma_8\rangle &= -c^* \left| \frac{7}{2}, -\frac{1}{2} \right\rangle - d^* \left| \frac{7}{2}, \frac{7}{2} \right\rangle. \end{aligned}$$

The degree of  $J$  mixing is small<sup>18</sup> and can be neglected for the purpose of determining the ground state. This is also evident from the fact that the Elliott-Stevens parameter<sup>19</sup>  $\alpha = Ag_{\perp}/Bg_{\parallel}$  is approximately unity. The measured  $g$  factors fit the relation for the  $\Gamma_{5,6}$  state more closely, and so we make this assignment for the ground state of  $\text{Yb}^{3+}$ . This is consistent with the optical analysis of  $\text{LiYF}_4:\text{Yb}^{3+}$ .<sup>18</sup>

The ground state for the  ${}^4I_{9/2}$  multiplet of  $\text{Nd}^{3+}$  may have the components

$$\begin{aligned} |\Gamma_5\rangle &= a \left| \frac{9}{2}, \frac{5}{2} \right\rangle + b \left| \frac{9}{2}, -\frac{3}{2} \right\rangle, \\ |\Gamma_6\rangle &= -a^* \left| \frac{9}{2}, -\frac{5}{2} \right\rangle - b^* \left| \frac{9}{2}, \frac{3}{2} \right\rangle \end{aligned}$$

or the components

$$\begin{aligned} |\Gamma_7\rangle &= a \left| \frac{9}{2}, \frac{9}{2} \right\rangle + b \left| \frac{9}{2}, \frac{1}{2} \right\rangle + c \left| \frac{9}{2}, -\frac{7}{2} \right\rangle, \\ |\Gamma_8\rangle &= -a^* \left| \frac{9}{2}, -\frac{9}{2} \right\rangle - b^* \left| \frac{9}{2}, -\frac{1}{2} \right\rangle - c^* \left| \frac{9}{2}, \frac{7}{2} \right\rangle, \end{aligned}$$

if the effects of  $J$  mixing are neglected. The Elliott-Stevens parameter  $\alpha$  is about 0.96 for  $\text{LiYF}_4:\text{Nd}$ , so we shall neglect  $J$  mixing. It may be readily shown that the  $g$  factors are related by

$$16g_{\perp}^2 = 21(-g_{\parallel}^2 + 2\Lambda g_{\parallel} + 15\Lambda^2),$$

if the ground state is a  $\Gamma_{5,6}$ . Here  $\Lambda = \frac{8}{11}$  is the Landé factor for the  $J = \frac{9}{2}$  multiplet of  $\text{Nd}^{3+}$ . Since the measured  $g$  factors do not satisfy this equation, the ground state is assigned as a  $\Gamma_{7,8}$ , even though the EPR data are not enough to determine the wave function uniquely. This assignment is consistent with the optical analysis.<sup>20</sup>

TABLE III.  $g$  factors for rare-earth ions in scheelite crystals.

| Crystals         | $\text{Nd}^{3+}$   |                    | $\text{Dy}^{3+}$   |                    | $\text{Er}^{3+}$   |                    | $\text{Yb}^{3+}$    |                    |
|------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|--------------------|
|                  | $g_{\parallel}$    | $g_{\perp}$        | $g_{\parallel}$    | $g_{\perp}$        | $g_{\parallel}$    | $g_{\perp}$        | $g_{\parallel}$     | $g_{\perp}$        |
| $\text{LiYF}_4$  | 1.987 <sup>a</sup> | 2.554 <sup>a</sup> | 1.112 <sup>a</sup> | 9.219 <sup>a</sup> | 3.137 <sup>a</sup> | 8.105 <sup>a</sup> | 1.3308 <sup>a</sup> | 3.917 <sup>a</sup> |
| $\text{CdMoO}_4$ | 2.302 <sup>b</sup> | 2.492 <sup>b</sup> | ...                | ...                | ...                | ...                | 1.2393 <sup>c</sup> | 3.917 <sup>c</sup> |
| $\text{CaWO}_4$  | 2.035 <sup>b</sup> | 2.537 <sup>b</sup> | 7.5 <sup>d</sup>   | 5.5 <sup>d</sup>   | 1.247 <sup>e</sup> | 8.38 <sup>e</sup>  | 1.0530 <sup>c</sup> | 3.916 <sup>c</sup> |
| $\text{PbMoO}_4$ | 1.351 <sup>b</sup> | 2.592 <sup>b</sup> | ...                | ...                | 1.195 <sup>e</sup> | 8.45 <sup>e</sup>  | 0.6622 <sup>c</sup> | 3.883 <sup>c</sup> |
| $\text{BaWO}_4$  | 0.820 <sup>b</sup> | 2.563 <sup>b</sup> | ...                | ...                | 1.164 <sup>e</sup> | 8.62 <sup>e</sup>  | 0.234 <sup>c</sup>  | 3.822 <sup>c</sup> |

<sup>a</sup>Present results. <sup>b</sup>Reference 22.

<sup>c</sup>Reference 4. <sup>d</sup>Reference 23.

<sup>e</sup>Reference 21.

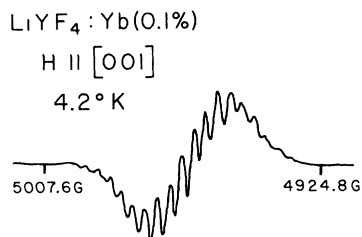


FIG. 1. Superhyperfine structure on EPR resonance line of  $I=0$   $\text{Yb}^{3+}$  in  $\text{LiYF}_4$ .

The irreducible representations of the ground states of  $\text{Dy}^{3+}$  and  $\text{Er}^{3+}$  could not be determined from the EPR results. Both ions have ground multiplets with  $J = \frac{15}{2}$  and therefore have four projections possible in each of the Kramers components of either the  $\Gamma_{5,6}$  or the  $\Gamma_{7,8}$  ground states for  $H$  parallel to  $c$ . Hence the values of  $g_{\parallel}$  and  $g_{\perp}$  alone are insufficient, in general, to allow one to distinguish between the two possible irreducible representations.

It is instructive to compare the  $g$  factors for these ions in several scheelite crystals. Table III gives the ground-state  $g$  factors in  $\text{LiYF}_4$ ,  $\text{CdMoO}_4$ ,  $\text{CaWO}_4$ ,  $\text{PbMoO}_4$ , and  $\text{BaWO}_4$  for the rare-earth ions  $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$ . Previous studies<sup>4,21,22</sup> of the tungstate and molybdate scheelites have noted that an approximately linear relationship between the  $g$  factors and  $c$ -axis lattice parameter holds for the ions  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Nd}^{3+}$ . The reason for this dependence has not yet been demonstrated. The  $g$  factors depend on wave-function coefficients which may be evaluated explicitly in terms of the crystal-field parameters, which themselves depend on sums over the ions in the lattice. There is no *a priori* reason why the  $g$  factors should have a linear dependence on the  $c$ -axis lattice parameter, and breakdown of this empirical relationship should not be regarded as surprising, particularly if one goes from oxygen to fluorine coordination. Using the data in Tables I and III, one can show that this linear relationship holds for  $\text{LiYF}_4:\text{Yb}$ , begins to break down for  $\text{LiYF}_4:\text{Nd}$ , and breaks down entirely for  $\text{LiYF}_4:\text{Er}$ . The EPR of  $\text{Dy}^{3+}$  has been reported previously in scheelites for only  $\text{CaWO}_4:\text{Dy}$ ,<sup>23</sup> and so one cannot establish a trend for this ion. It is apparent, however, that the  $g$  factors of  $\text{Dy}^{3+}$  in  $\text{CaWO}_4$  and  $\text{LiYF}_4$  are very different. Karayianis has pointed out that for two levels of the same representation, the sensitivity

of the  $g$  factors to changes in the crystal-field parameters increases as their energy separation decreases.<sup>24</sup> The two lowest levels with the same irreducible representations are separated by about  $132\text{ cm}^{-1}$  for  $\text{Nd}^{3+}$  in  $\text{LiYF}_4$ ,<sup>7</sup> about  $17\text{ cm}^{-1}$  for  $\text{Er}^{3+}$  in  $\text{LiYF}_4$ ,<sup>8</sup> and about  $425\text{ cm}^{-1}$  for  $\text{Yb}^{3+}$  in  $\text{LiYF}_4$ .<sup>18</sup> The separations are not significantly different for these ions in  $\text{CaWO}_4$ . The spectrum of  $\text{Dy}^{3+}$  in scheelites has been obtained only in  $\text{CaWO}_4$ , and there are two excited levels within less than  $10\text{ cm}^{-1}$  of the ground state.<sup>25</sup> Thus, one could expect the changes in  $g$  factors of these ions in  $\text{CaWO}_4$  and  $\text{LiYF}_4$  to be greatest for  $\text{Dy}^{3+}$ , next greatest for  $\text{Er}^{3+}$ , lesser for  $\text{Nd}^{3+}$ , and least for  $\text{Yb}^{3+}$ . This indeed is the case.

A strong superhyperfine structure (SHFS) was found on all the resonances of the  $c$ -axis spectrum for  $\text{Yb}^{3+}$ . The SHFS died out if the angle between the external magnetic field and the  $c$  axis exceeded  $2^\circ$ , and the SHFS did not reappear in the plane perpendicular to the  $c$  axis. The  $c$ -axis SHFS on the  $I=0$  line is displayed in Fig. 1. The 17-line spectrum is similar to the  $[100]$  SHFS spectrum seen for  $\text{CaF}_2$ .<sup>9</sup> In that case the SHFS was attributed to the interaction of the magnetic moments of the nearest-neighbor fluorine nuclei with the paramagnetic electrons of  $\text{Yb}^{3+}$ . The same mechanism may be responsible for the SHFS of  $\text{LiYF}_4:\text{Yb}^{3+}$ .

## VI. CONCLUSIONS

The EPR spectra of  $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$  have been observed in  $\text{LiYF}_4$ . The spectra are attributed to ions substituting for  $\text{Y}^{3+}$  which has tetragonal ( $S_4$ ) point symmetry in this scheelite crystal. The axial spin Hamiltonian was diagonalized and least-squares fit parameters were obtained. The  $g$  factors were used to determine that the ground states of  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  were  $\Gamma_{7,8}$  and  $\Gamma_{5,6}$ , respectively. Superhyperfine structure was observed on the  $c$ -axis spectrum of  $\text{Yb}^{3+}$ .

## ACKNOWLEDGMENTS

We would like to thank Dr. A. Linz and Dr. D. Gabbe of MIT and R. T. Farrar of HDL for the crystals used in this work. Some of the samples from MIT were kindly made available by Dr. E. Sharp of the Night Vision Laboratory, Fort Belvoir. We would also like to thank Dr. N. Karayianis and Dr. D. E. Wortman for making available their results prior to publication and also for helpful conversations.

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## Hyperfine Splitting of Er and Yb Resonances in Au: A Separation between the Atomic and Covalent Contributions to the Exchange Integral\*

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(Received 2 February 1971)

The hyperfine splitting has been observed in the magnetic resonance spectrum of dilute Au:Er and Au:Yb alloys. In both cases, the observed hyperfine coupling constant was larger (more positive) than in cubic nonmetallic hosts. Attributing this increase to conduction-electron polarization, and utilizing independent estimates of the 6s contribution to the hyperfine coupling constant, the atomic and covalent contributions to the localized-conduction-electron exchange integral are separated. It is found that the latter increases by an order of magnitude from Er to Yb in Au. This increase is attributed to the nearness of the  $4f^{14}$  level to the Fermi surface in Au:Yb alloys, noting that Ag:Yb is diamagnetic.

### I. INTRODUCTION

We report the first observation of the hyperfine splitting in the magnetic resonance spectrum of dilute Au:Yb and Au:Er alloys. In both cases the hyperfine coupling constant  $A$  is larger (more positive) than in nonmetallic hosts with the same local symmetry. This increase is attributed to the spin-polarized conduction electrons. The temperature dependence of the resonance linewidth yields values for the localized-conduction-electron exchange coupling constant  $J$ . Knowing the increase in  $A$  and  $J$  over the insulator value, and using the estimate of Gossard *et al.*<sup>1</sup> of the value of the 6s contribution to the hyperfine coupling constant, we are able to separate out the two contributions to  $J$ , commonly referred to as "atomic" ( $J_{at}$ ) and "covalent mixing"

( $J_{cm}$ ), for both alloys. We find the ratio of ( $J_{cm}$ )<sub>Au:Yb</sub> to ( $J_{cm}$ )<sub>Au:Er</sub> to be approximately 20, much larger than expected from simple theoretical estimates.<sup>2</sup> We speculate, knowing that the isomorphous alloy Ag:Yb is diamagnetic,<sup>3</sup> that this is caused by a close proximity of the  $4f^{14}$  virtual level in Au:Yb to the Fermi level, allowing a strong "absorption" contribution<sup>2</sup> to  $J_{cm}$  to obtain for that alloy.

### II. EXPERIMENTAL RESULTS

#### A. Au:Er

The magnetic resonance spectra of powdered samples of Au:Er for Er concentrations of 50, 100, 500, 1000, and 5000 ppm was obtained as a function of temperature. The measurements were conducted at 3-cm wavelength, the apparatus having been described elsewhere.<sup>4</sup> The spectrum of a 50-ppm