2.03 for CuPt (compared to 2.1 by Linde) and this does not effect our results.

Yamada and Shiotani[20] have tried to go a step further in the Kohn-Vosko expansion for $Q(R)$ in powers of $(1/R)$. This expression follows as successive integrations by part of the excess electron density with respect to the energy. The $1/R^3$ term contains the phase shift $\eta_l(E_F)$ at the Fermi energy; the following term in $1/R^4$ will contain the derivative of the phase shift $[d\eta_l(E)/dE]_{E=E_F}$ and might bring a correction to (1) in the case of a virtual d bound state which has a certain extent w in energy. But so far, w remains an adjustable parameter and should be determined by other experiments. For example, the specific heat can be expressed in terms of $[d\eta_l(E)/dE]$ as Daniel and Friedel[6] have shown. But as $[d\eta_l(E)/dE]$ itself is expressed in terms of η_l and w there still remains the same number of unknown quantities.

[20] K. Yamada and N. Shiotani (to be published). We are grateful to Dr. Yamada and Dr. Shiotani for giving us the opportunity to read their manuscript before publication.

IV. CONCLUSION

A nonmagnetic virtual bound state containing almost one d hole for Ni, Pd, and Pt in small concentration in Cu, allows satisfactory fit to the experimental resistivities and the electric field gradient of these alloys. There exist very few experimental data on dilute alloys of copper with nonmagnetic transition impurities. It could be interesting, especially in the case of CuPd [which requires absolutely the knowledge of (at least) 3-phase shifts] to study experimentally another property (specific heat, thermopower) in order to check our model of an incomplete d shell for Pd.

ACKNOWLEDGMENTS

Electron Paramagnetic Resonance of Gd³⁺ in YVO₄

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(Received 16 June 1967)

The EPR spectrum of Gd³⁺ in YVO₄ has been examined at room temperature with a K-band spectrometer. The results fit a tetragonal-spin Hamiltonian. The parameters are $g_{||} = g_{\perp} = 1.9916 \pm 0.0002$, $b_2^0 = -441.6 \pm 0.2$, $b_4^0 = -1.5 \pm 0.1$, $b_6^0 = 0.8 \pm 0.6$, $b_4^4 = 8.3 \pm 0.1$, and $b_6^4 = 0.0 \pm 0.2$ in units of 10^{-4} cm⁻¹. The signs of the parameters are relative.

I. INTRODUCTION

THE paramagnetic resonance study of S-state rare-earth ions (Gd³⁺, Eu²⁺) is basically motivated by two concerns: the character of the crystal field imposed by the host lattice and the mechanism which governs the zero-field splitting of the ground state. The latter problem has been a persistent one for some time. Recently, Wybourne[1] performed an extensive calculation to estimate the ionic contributions to the ground-state splitting of the trivalent gadolinium ion in a lanthanum ethyl-sulfate lattice. The poor correspondence between those results and experimental data suggests that the purely ionic model is inadequate, and that a correct explanation must include the detailed interaction of the ion with its ligands. Newman and Ellis[2] have considered the same ion in LaCl₃, and show that the observed order of magnitude of the ground-state splitting may be ex-plained on the basis of covalency induced by spin-orbit coupling. These authors also suggest that paramagnetic-resonance measurements of the Gd³⁺ ion provide the only direct means of probing the amount of covalency in host crystals.

The character of the crystal field in this vanadate has been investigated recently by Brecher *et al.*[3] in an analysis of the polarized spectra of Eu³⁺. The crystal has the zircon structure, and these authors find that the spectra are consistent with the D_{2d} site symmetry of the Eu³⁺ ion in this lattice. They show, that a simple electrostatic field approximation gives an adequate description of the structure of the ⁷F multiplet, with a proviso that a more refined treatment appears to be necessary.

We report here an analysis of the EPR spectrum of Gd³⁺ in YVO₄. This work is part of a larger program devoted to the examination of the resonance spectra of rare-earth ions in the zircon structure.

[1] B. G. Wybourne, Phys. Rev. **148**, 317 (1966).
[2] D. J. Newman and M. M. Ellis, Phys. Letters **23**, 46 (1966).
[3] C. Brecher, H. Samelson, A. Lempicki, R. Riley, and T. Peters, Phys. Rev. **155**, 178 (1967).

II. CRYSTAL STRUCTURE

Wyckoff[4] gives the generalized zircon structure. The lattice is tetragonal and belongs to the space group D_{4h}^{19} ($I\,4/amd$) with unit cell dimensions of $c=6.27$ Å and $a=7.10$ Å.[5] There are four molecules in the cell. The Gd^{3+} would be expected to enter the lattice substitutionally in the yttrium sites. The ions are then eightfold coordinated, a configuration which arises from the eight oxygens at the vertices of a tetragonal dodecahedron. The site symmetry is D_{2d}, and all yttrium sites are equivalent. For these reasons a single tetragonal spectrum is expected and, in fact, is found.

III. THEORY

The $(4f^7)\ ^8S_{7/2}$ ground state of Gd^{3+} in YVO_4 is split into four Kramers doublets. We assume, therefore, that the energies may be obtained from a diagonalization in the $^8S_{7/2}$ manifold of an effective-spin Hamiltonian.[6] This Hamiltonian, with a non-Zeeman term that reflects the tetragonal symmetry of the crystal field, has the form

$$\mathcal{H} = g_{||}\beta H_z S_z + g_\perp\beta(H_x S_x + H_y S_y)$$
$$+ B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4 \quad (1)$$

in the appropriate set of axes. The O_n^m are operators which have matrix elements in the above manifold proportional to those of the corresponding spherical harmonics, and the B_n^m are constants.

If the direction of the magnetic field is taken as the axis of quantization, the off-diagonal matrix elements of the spin Hamiltonian are considerably smaller than the diagonal ones for sufficiently high resonance frequency. When this is so, second-order perturbation theory may be adequate to fit results within experimental accuracy, or may provide good starting values for a trial-and-error exact diagonalization. The conditions for resonance in the z and x directions, to second order, are given by the following formulas[7]:

$$H_0 = H_{\pm 7/2} \pm 2(a-b) + \frac{P^2}{2[H_{\pm 7/2}\pm(a-c)]}$$
$$-\frac{Q^2}{2[H_{\pm 7/2}\pm(b-d)]} + \frac{E^2}{2[2H_{\pm 7/2}\pm(a-d)]}$$
$$-\frac{F^2}{2[2H_{\pm 7/2}\pm(b-c)]} + \frac{S^2}{2[3H_{\pm 7/2}\pm(a-b)]}$$
$$-\frac{S^2}{2[3H_{\pm 7/2}\pm(b-a)]}.$$

$$H_0 = H_{\pm 5/2} \pm 2(b-c) + \frac{Q^2}{2[H_{\pm 5/2}\pm(b-d)]}$$
$$+\frac{P^2}{2[H_{\pm 5/2}\pm(a-c)]} + \frac{F^2}{2[2H_{\pm 5/2}\pm(b-c)]}$$
$$-\frac{R^2}{2[H_{\pm 5/2}\pm(c-d)]} + \frac{S^2}{2[3H_{\pm 5/2}\pm(b-a)]}$$
$$-\frac{F^2}{2[2H_{\pm 5/2}\pm(c-b)]}.$$

$$H_0 = H_{\pm 3/2} \pm 2(c-d) - \frac{P^2}{2[H_{\pm 3/2}\pm(a-c)]}$$
$$+\tfrac{1}{2}R^2\{[H_{\pm 3/2}\pm(c-d)]^{-1}-[H_{\pm 3/2}\pm(d-c)]^{-1}\}$$
$$+\frac{Q^2}{2[H_{\pm 3/2}\pm(b-d)]} + \frac{F^2}{2[2H_{\pm 3/2}\pm(c-b)]}$$
$$-\frac{E^2}{2[2H_{\pm 3/2}\pm(d-a)]}.$$

$$H_0 = H_{1/2} - \tfrac{1}{2}Q^2\{[H_{1/2}-(d-b)]-[H_{1/2}+(d-b)]^{-1}\}$$
$$+\tfrac{1}{2}R^2\{[H_{1/2}+(d-c)]^{-1}+[H_{1/2}-(d-c)]^{-1}\}$$
$$+\tfrac{1}{2}E^2\{[2H_{1/2}+(d-a)]^{-1}+[2H_{1/2}-(d-a)]^{-1}\}. \quad (2)$$

The parameters in these formulas are:

	z axis	x axis
a	$(1/2g_{||}\beta)(7b_2^0+7b_4^0+b_6^0)$	$(1/32g_\perp\beta)(-56b_2^0+42b_4^0+70b_4^4-5b_6^0-21b_6^4)$
b	$(1/2g_{||}\beta)(b_2^0-13b_4^0-5b_6^0)$	$(1/32g_\perp\beta)(-8b_2^0-78b_4^0-130b_4^4+25b_6^0+105b_6^4)$
c	$(1/2g_{||}\beta)(-3b_2^0-3b_4^0+9b_6^0)$	$(1/32g_\perp\beta)(24b_2^0-18b_4^0-30b_4^4-45b_6^0-189b_6^4)$
d	$(1/2g_{||}\beta)(-5b_2^0+9b_4^0-5b_6^0)$	$(1/32g_\perp\beta)(40b_2^0+54b_4^0+90b_4^4+25b_6^0+105b_6^4)$
P	0	$[(21)^{1/2}/16g_\perp\beta](-8b_2^0+20b_4^0-20b_4^4-5b_6^0-5b_6^4)$
Q	0	$[(5)^{1/2}/16g_\perp\beta](-24b_2^0+4b_4^0-4b_4^4+21b_6^0+21b_6^4)$
R	0	$[(15)^{1/2}/16g_\perp\beta](-16b_2^0-16b_4^0+16b_4^4-7b_6^0-7b_6^4)$
E	$[(35)^{1/2}/g_{||}\beta](b_4^4+3b_6^4)$	$[(35)^{1/2}/16g_\perp\beta](14b_4^0+2b_4^4-9b_6^0+39b_6^4)$
F	$[(3)^{1/2}/g_{||}\beta](5b_4^4-7b_6^4)$	$[(3)^{1/2}/16g_\perp\beta](70b_4^0+10b_4^4+21b_6^0-91b_6^4)$
S	0	$-[33(7)^{1/2}/16g_\perp\beta](b_6^0+b_6^4)$
H_0	$h\nu/g_{||}\beta$	$h\nu/g_\perp\beta \hspace{4em} (3)$

[4] R. W. G. Wyckoff, *Crystal Strctures* (Interscience Publishers, Inc., New York, 1965) 2nd ed., Chap. VIII.

[5] See Ref. 3 and refs. cited therein.

[6] For a more extended discussion of these points, see J. Bronstein and V. Volterra, Phys. Rev. **137**, A1201 (1965); J. Bronstein and Maniv, *ibid.* **153**, 303 (1967).

[7] These formulas are given by Bronstein and Volterra (Ref. 6) but there are a sufficient number of errors to merit a restatement.

and $b_2{}^0 = 3B_2{}^0$; $b_4{}^0 = 60B_4{}^0$; $b_4{}^4 = 12B_4{}^4$; $b_6{}^0 = 1260B_6{}^0$; $b_6{}^4 = 60B_6{}^4$. [These are the usual definitions for the $b_n{}^m$ except for $b_4{}^4$, which most often is given as $b_4{}^4 = 60B_4{}^4$; the definition here facilitates the presentation of the parameters in Eqs. (2)]. Also, $H_{\pm M}$ signifies the $\pm M \leftrightarrow \pm M \mp 1$ transition.

IV. APPARATUS AND EXPERIMENTAL RESULTS

The single crystal used in this experiment was grown by the technique described in Ref. 3, and contained a nominal concentration of Gd^{3+} of approximately 0.5%. All measurements were made at room temperature using a conventional K band (24 kMc/sec) superheterodyne spectrometer. The spectral line positions were determined by proton resonance, and the microwave frequency was determined from the position of the diphenylpicrylhydrazl (DPPH) resonance.

The crystal habit was that of a rectangular prism with the unique axis (c axis) along the single long dimension, and with faces parallel to the (100) and (010) crystallographic planes. Hence, orientation was a simple matter. A single, seven-line tetragonal spectrum was observed with the c axis being the tetragonal axis. This defines the z axis in Eq. (1). The order of the lines reversed when passing from an orientation in which the static magnetic field was parallel to the c axis to the x-y plane. In this latter plane there are two inequivalent extrema which differ by 45°. One set occurs for the static field perpendicular to the crystallographic planes ($\pm 1°$), and these define our x or y axes. This is consistent with the zircon structure in which the oxygens lie in one or the other of two sets of perpendicular planes that are parallel to crystallographic planes.

The line assignments were made from relative intensities measured along the z axis. These followed fairly closely the theoretical ratios given by

$$H_{\pm 7/2}:H_{\pm 5/2}:H_{\pm 3/2}:H_{1/2},$$

$$7 \quad 12 \quad 15 \quad 16$$

and in this order. Since only room temperature measurements were made, the absolute signs of M could not be determined. Of course, this means that the absolute signs of the $b_n{}^m$ are also not known.

The values of $b_2{}^0$, $b_4{}^0$, and $b_6{}^0$ were calculated from the

TABLE I. Spin-Hamiltonian parameters for Gd^{3+} in YVO_4. Temperature is 300°K. Signs are relative. All $b_n{}^m$ s×10⁴ cm⁻¹.

$g_{\parallel}$	1.9916±0.0002
$g_{\perp}$	1.9916±0.0002
$b_2{}^0$	−441.6±0.2
$b_4{}^0$	−1.5±0.1
$b_6{}^0$	0.8±0.6
$b_4{}^4$	8.3±0.1
$b_6{}^4$	0.0±0.2

spacings between corresponding lines on either side of the central line, for the static field in the z direction, using Eqs. (2) to zero order. Measurements were then made along the x axis in order to determine $b_4{}^4$ and $b_6{}^4$. The second-order theory of Eqs. (2) did not give a fully satisfactory fit, and it was necessary to perform an exact diagonalization by computer. However, the second-order results were useful in providing input for the computer program which was used in a trial-and-error manner. With values of $b_4{}^4$ and $b_6{}^4$ at hand, second-order corrections to the $b_n{}^0$ were calculated and found to be outside experimental error. The results are shown in Table I. With these values, all but two lines were fit to within 2 G for the x spectrum, and the others to approximately 3 and 4 G each. No definite anisotropy in the g factor was observed within the quoted error.

Although hyperfine structure was discernible on some lines for certain orientations, no analysis was made because of the sizeable linewidths. With the magnetic field parallel to the z axis, linewidths (peak-to-peak of absorption derivative) ranging from 18 to 23 G were observed. From preliminary results on a $YAsO_4$ crystal with a more dilute Gd concentration, we suspect that some of this width arises from concentration broadening.