

Paramagnetic Resonance of V^{4+} in TiO_2 †H. J. GERRITSEN AND H. R. LEWIS
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The paramagnetic spectrum of vanadium in TiO_2 has been observed at 10.14 and 22.68 kMc/sec. An analysis of the data indicates that the spectrum is due to single d electrons of tetravalent vanadium ions located at titania sites in the lattice. The calculated values of the components of the g tensor and the hyperfine interaction constant are: $g_x=1.915$, $g_y=1.912^5$, $g_z=1.956^5$, $A_x=0.0031^5$ cm $^{-1}$, $A_y=0.0043$ cm $^{-1}$ and $A_z=0.0142$ cm $^{-1}$. The axes of the magnetic coordinate systems of the two nonequivalent ions per unit cell are: $[\bar{1},1,0]$, $[0,0,1]$, $[1,1,0]$ and $[\bar{1},\bar{1},0]$, $[0,0,1]$, $[\bar{1},1,0]$.

THE paramagnetic spectrum of vanadium, consisting of an eight line hyperfine structure due to a nuclear spin of $\frac{7}{2}$, has been observed in a single crystal of TiO_2 at frequencies of 10.14 and 22.68 kMc/sec. An analysis of the spectrum indicates that it arises from the single $3d$ electron of tetravalent vanadium. This ion should have a relatively short relaxation time in an approximately cubic crystalline field. Indeed, at 300°K, the spectrum of vanadium was not detected even though a weak spectrum of iron, present in this sample in very low concentration, was observed. At 78°K, however, the vanadium spectrum was thirty times as intense as the iron spectrum and at this temperature, the linewidth of the vanadium was about 3.5 gauss. The concentration of vanadium was nominally 0.1% in a crystal made by Linde Air Products.

The rutile form of TiO_2 is tetragonal. There are two Ti^{4+} ions in the unit cell and each of these has six neighboring oxygen atoms which produce an orthorhombic field at the position of the titanium ion. The crystal fields of the two nonequivalent titanium ions differ from one another by a 90° rotation around the c axis of the crystal. Thus when paramagnetic ions replace titanium ions in a single crystal of TiO_2 , the spectra of the two nonequivalent ions are identical when the magnetic field is along the c axis. As the orientation of the magnetic field is changed in the $(1,1,0)$ plane from the c axis to the $[\bar{1},1,0]$ direction, each absorption line splits into two components. This characteristic behavior is observed for vanadium in rutile (Fig. 1) indicating that it is located in the lattice at a titanium site. In addition, the spectrum in the plane perpendicular to the c axis has a 90° period with the two ions identical along the a axes.

The Hamiltonian describing the energy levels of the V^{4+} ion is¹:

$$\mathcal{H} = \beta [g_x S_x H_x + g_y S_y H_y + g_z S_z H_z] + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z + \frac{3}{2} P_z [I_z^2 - \frac{1}{3} I(I+1)] + \frac{1}{2} (P_x - P_y) (I_x^2 + I_y^2) - g_N \beta_N I_N.$$

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¹ K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. XVIII, p. 304.

To second order, the energy levels for a magnetic field along the Z axis are:

$$E_{\pm} = \pm \frac{g_z \beta H}{2} \pm \frac{m A_z}{2} \pm \frac{[I(I+1) - m^2]}{8 h \nu} (A_x^2 + A_y^2) - \frac{m}{4 h \nu} A_x A_y \pm m \{ 2 [I(I+1) - m^2] - 1 \} \times \frac{(P_x - P_y)^2}{4 (A_x - g_N \beta_N H_z)} + \frac{3}{2} P_z \{ m^2 - \frac{1}{3} I(I+1) \} - \gamma_N \beta_N H_z m. \quad (1)$$

The plus and minus signs refer to the two spin states of the electron and m is the magnetic quantum number of the nucleus. The energy differences of the $\Delta m=0$ transitions are then:

$$h \nu = g_z \beta H_z + m A_z + \frac{[I(I+1) - m^2]}{4 h \nu} (A_x^2 + A_y^2) + m \{ 2 [I(I+1) - m^2] - 1 \} \frac{(P_x - P_y)^2}{2 (A_x - g_N \beta_N H_z)}. \quad (2)$$

It is these transitions which produce the intense octet in the V^{4+} spectrum. Equations (1) and (2) can also be applied to magnetic fields along the X and Y axes by commuting the components of H , A , and P .

An analysis of data taken at 10 and 22 kMc/sec shows that the quadrupole term, $(P_i - P_j)^2 / 2 A_k$, in Eq. (2) can be neglected within the accuracy of this experiment. Then the calculated values of the components of the g tensor and hyperfine interaction constant are:

$$\begin{aligned} g_x &= 1.915, & A_x &= 0.0031^5 \text{ cm}^{-1}, \\ g_y &= 1.913^5, & A_y &= 0.0043 \text{ cm}^{-1}, \\ g_z &= 1.956^5, & A_z &= 0.0142 \text{ cm}^{-1}. \end{aligned}$$

The direction cosines of the magnetic axes relative to

TABLE I. A comparison of the observed and calculated resonant fields of V^{4+} in TiO_2 . All data were observed at 78°K. Linewidths are approximately $3\frac{1}{2}$ gauss.

Frequency	x axis		Frequency	y axis = c axis		Frequency	z axis	
	Observed	Calculated		Observed	Calculated		Observed	Calculated
22.685 kMc/sec	8336 gauss	8336 gauss	22.690	8634	8635	22.685	7737	7740
	8366	8367		8583	8583		7891	7894
	8396	8398		8531	8532		8046	8049
	8429	8431		8481	8482		8201	8203
	8465	8466		8433	8434		8357	8357
	8502	8504		8387	8388		8511	8513
	8541	8542		8341	8343		8668	8668
	8581	8582		8297	8299		8822	8824
10.140 kMc/sec	3899 gauss	3898	10.140	3951	3946	10.140	4249	4243
	3854	3854		3890	3889		4090	4087
	3814	3812		3837	3835		3932	3931
	3775	3770		3785	3783		3775	3775
	3738	3736		3735	3735		3620	3621
	3705	3706		3688	3691		3467	3467
	3677	3680		3647	3649		3313	3313
	3653	3652		3607	3610		3161	3159

the crystal axes are:

	a	a	c
x	$-\sqrt{2}/2$	$\pm\sqrt{2}/2$	0
y	0	0	1
z	$\pm\sqrt{2}/2$	$\sqrt{2}/2$	0

The z axis is the axis of nearly tetragonal symmetry of the local crystal field as is also shown by the spectra of trivalent chromium^{2,3} and iron⁴ in rutile. The above values may be compared to V^{4+} in sapphire⁵ where $g=1.97$ and $A=0.0132$ cm⁻¹. In this axial crystal, both are isotropic.

Table I is a comparison of the observed data with the calculated values of the magnetic field at resonance using the constants given above. The agreement is better than 0.2%. Moreover, the good agreement at two different frequencies eliminates the small possibility that the spectrum is due to V^{3+} .

At 78°K, a number of very weak resonances, attributed to $\Delta m=1$ or 2 transitions, were also observed. These were about as intense as the iron resonances and about 3% as intense as the principal vanadium spectrum. When the magnetic field is along the c axis of the crystal, one of these quadrupole resonances occurs just below the strong octet. This line is tentatively identified as a transition between $m=\frac{7}{2}$ and $m=\frac{3}{2}$ and on this basis it is estimated that $P_y=0.0015$ cm⁻¹. Further work with better sensitivity is required to verify this value and to determine the other components of P .

² H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. P. Wittke, Phys. Rev. Letters 2, 153 (1959).

³ I. Sierro, K. A. Muller, and R. Lacroix, Arch. sci. (Geneva) 12, 122 (1959).

⁴ A. Okaya, D. Carter, and F. Nash, Bull. Am. Phys. Soc. 3, 73 (1960).

⁵ J. Lambe and C. Kikuchi, technical memorandum, University of Michigan, November, 1959 (unpublished).

Since vanadium in rutile has a g tensor with very nearly axial symmetry, it seems reasonable to apply to this ion a theory of Abragam and Pryce for a single

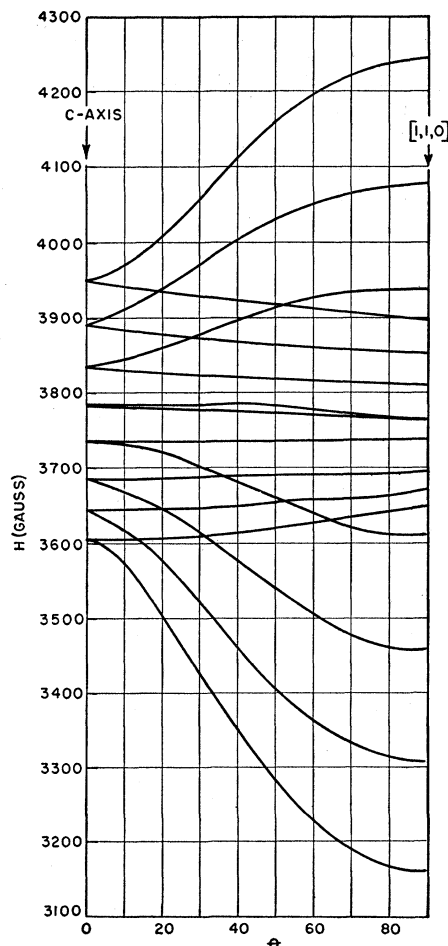


FIG. 1. The spectrum of V^{4+} in TiO_2 at 10.140 kMc/sec. $T=78^\circ K$.

d electron in axial crystal fields.⁶ Using this theory, it is possible to compute Δ , the splitting in the lower orbital triplet due to the axial field, from either $g_{||}$ or g_{\perp} . However, the values thus obtained differ by a factor of $2\frac{1}{2}$. This large discrepancy indicates that either the

⁶ A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

small orthorhombic component of the crystal field makes the theory inapplicable to this case, or that the theory requires some modification.

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Electron Wave Functions in Metallic Potassium

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Wave functions to order k^2 are presented for electrons in metallic potassium. The calculation is an application of the cellular method. The potential was derived from a self-consistent field and contains exchange effects.

INTRODUCTION

IN previous calculations, the cohesive energy of potassium was determined, and some features of the energy band system were studied.^{1,2} The present work presents wave functions determined according to the cellular method, together with an improved calculation of the cohesive energy.

The wave functions and energy of an electron of wave vector \mathbf{k} are expanded in powers of k according to the method of Silverman.³ We have:⁴

$$\psi_{\mathbf{k}} = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}; \quad u_{\mathbf{k}} = u_0 Y_{00} + i k u_1 Y_{10} + k^2 (u_2 Y_{20} + \phi_0 Y_{00}), \quad (1)$$

$$E(k) = E_0 + E_2 k^2 + E_4 k^4 + \dots \quad (2)$$

The Y_{lm} are normalized spherical harmonics.

$$Y_{00} = (4\pi)^{-\frac{1}{2}}; \quad Y_{10} = (3/4\pi)^{\frac{1}{2}} \cos\theta; \quad Y_{20} = (5/4\pi)^{\frac{1}{2}} (3 \cos^2\theta - 1)/2. \quad (3)$$

The equations determining the functions u_0 , u_1 , etc., and the energy parameters E_0 , E_2 , E_4 , are summarized in reference 4.

The functions which are tabulated are:

$$R_0 = r u_0; \quad R_1 = r u_1; \quad R_2 = r u_2; \quad Q_2 = r \phi_0. \quad (4)$$

The normalization integral for $\psi_{\mathbf{k}}$ is⁵

$$\int_{\Omega} |\psi_{\mathbf{k}}|^2 d\tau = \int_{\Omega} |u_{\mathbf{k}}|^2 d\tau = 1 + k^2 (J_1 + 2J_2), \quad (5)$$

in which

$$J_1 = \int_0^{r_s} R_1^2 dr; \quad J_2 = \int_0^{r_s} R_0 Q_2 dr.$$

In the original cohesive energy and band calculations, an attempt was made to take core valence exchange interactions into account by constructing separate exchange potentials for states of s , p , and d symmetry. The potentials given in reference 2 were used in this work for the basic s , p , and d functions incorporated in R_0 , R_1 , R_2 , and Q_2 . The exchange interaction is somewhat weaker for d functions than for s and p functions; this is the cause of the somewhat peculiar shape of the function R_2 .

All calculations were made for a sphere radius $r_s = 4.84$ (Bohr units), which is appropriate for 0°K .⁶

The band parameters computed in this way are $E_0 = -0.452$ ry; $E_2 = 1.160$; $E_4 = -0.85$. With the exception of E_4 , the results are in good agreement with those previously reported. The E_4 given in reference 2 is in error. The cohesive energy, computed in the standard way⁷ (but neglecting corrections due to core polarization) is 22.3 kcal/mole. A reasonable estimate of the core polarization effect is an increase of 2.6 kcal/mole in the cohesive energy. The experimental cohesive energy is 22.6 kcal/mole.

A quantity of interest in the theory of the Knight shift⁸ is $\xi = |\psi_f(0)|^2 / |\psi_A(0)|^2$ where $\psi_f(0)$ is the average over the Fermi surface of the value of the wave function

¹ S. Berman, J. Callaway, and R. D. Woods, Phys. Rev. **101**, 1467 (1956).

² J. Callaway, Phys. Rev. **103**, 1219 (1956).

³ R. A. Silverman, Phys. Rev. **85**, 227 (1952).

⁴ J. Callaway, Phys. Rev. **112**, 1061 (1958).

⁵ Use of the normalized spherical harmonics in (1) leads to a different normalization of $\psi_{\mathbf{k}}$ from that employed in reference 4.

⁶ C. A. Swenson, Phys. Rev. **99**, 423 (1955).

⁷ J. Callaway, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 99.

⁸ W. D. Knight, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 93.