

Paramagnetic Resonance of Mo^{5+} in TiO_2

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The paramagnetic resonance spectrum of molybdenum in rutile (TiO_2) has been studied. The crystal contained 0.05 molar percent molybdenum ions, and the experiments were mainly carried out at 77°K. The observed resonance lines were identified as due to molybdenum in a +5 valence state. The g values in the directions of the three orthorhombic crystal field axes are -1.7883 , -1.8117 , and -1.9125 . The effective orbital g factor, k , was calculated to be 0.8784, indicating partial covalent bonding. Hyperfine lines from Mo^{95} and Mo^{97} were also observed, and their hyperfine interaction constants were calculated.

The resonance lines broadened at helium temperature due to saturation of the sample. The spin-lattice relaxation time is very long at this temperature. It increased from 10 to 600 sec as the temperature decreased from 4.2 to 1.3°K.

THE paramagnetic resonance spectrum of rutile doped with molybdenum has been studied. A single intense line with six weak satellite lines, three on each side and nearly equally spaced, was observed at approximately 25 kMc/sec at 77°K.

The appearance of the absorption lines is shown in Fig. 1. The nearly equal spacing of the six weak lines indicates that the weak lines are the hyperfine structure due to isotopes with nuclear spin 5/2. The two odd isotopes Mo^{95} and Mo^{97} can be distinguished from the two outer lines and their relative magnetic moment can be calculated as $\mu_{\text{Mo}^{97}}/\mu_{\text{Mo}^{95}} = 1.03$.

The molar concentration of molybdenum in the TiO_2 crystal was approximately 0.05%. The crystal, obtained from the National Lead Company, appears dark violet.

The crystal structure of TiO_2 is tetrahedral D_{4h} . There are two nonequivalent titanium ions in a unit cell and each of these has six neighboring oxygen atoms which produce an orthorhombic field at the position of the titanium ion, Fig. 2. The three rhombic axes are related to the crystalline directions as:

| | Orthorhombic field axis | Direction in crystal |
|---------|----------------------------|-------------------------|
| Site I | I ₁ | [001] |
| | II ₁ | [110] |
| | III ₁ | [110] |
| Site II | I ₂ | [001] |
| | II ₂ | [110] |
| | III ₂ | [110] |

The crystalline field at the Ti(II) ions differs from that at the Ti(I) ions by a 90° rotation around the c axis, [001] direction, of the crystal. Thus, when a molybdenum ion replaces a Ti^{4+} ion, these two sites should be distinguishable in the resonance spectra except when the magnetic field is oriented along the c

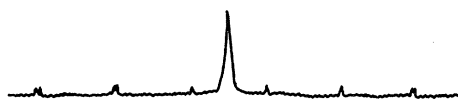


FIG. 1. Appearance of the resonance line.

¹ H. J. Gerritsen, S. E. Harrison, and H. R. Lewis, J. Appl. Phys. 31, 1566 (1960).

axis or either of the two a axes which make a 45° angle with the II, III axes.

Resonance spectra were taken with a double detection type microwave spectrometer at ~ 24 kMc/sec. The microwave cavity was excited in the TE_{01} mode and was connected to the waveguide by a variable coupling. A 12-in. Varian magnet with field strength up to 10.5 kG was used. The signals were displayed on a dual beam oscilloscope and recorded with a strip chart recorder. Precision field measurements of line positions were made with a nuclear resonance probe.

While no resonance absorption was observed at room temperature, an intense absorption was detected at 77°K. The absorption broadened at 4.2°K due to saturation of the sample; the relaxation time is very long (many seconds) at the last temperature. The result of the measurements of the relaxation time will be given in a separate paper. Only one intense line (i.e., no fine structure) was observed within the magnetic field range. It had an empirical g value of about 1.8.

As the valence state of molybdenum in the crystal, +5, +4, or +3, was unknown, various experiments were also done with resonance frequencies at M band

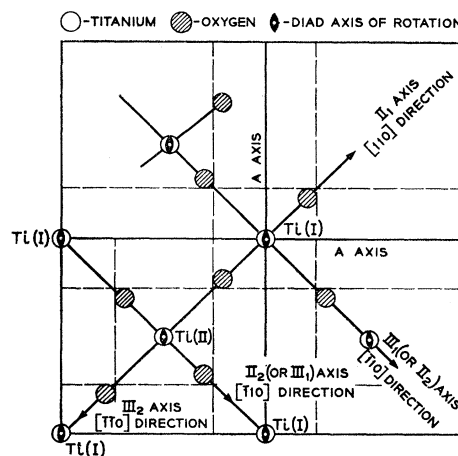


FIG. 2. Relation between two sites of titanium in the crystal. A projection in the (001) plane.

TABLE I. Experimental results.^a

| Magnetic field along | I axis | II axis | III axis |
|-------------------------------|--|--|--|
| Resonance frequency (kMc/sec) | 23.533 | 24.006 | 24.006 |
| Main line position (kG) | 9.4016 | 8.9683 | 9.4668 |
| Weak line positions (kG) | 9.3098 9.3449 9.3808 9.4175 9.4549 9.4915 | 8.7841 8.8572 8.9307 9.0066 9.0781 9.1520 | 9.3941 9.4208 9.4503 9.4794 9.5093 9.5391 |

^a The half-linewidth of the main line is 2.2 G.

and X band and with the crystalline axis 45° from the rf field, to see if there were additional lines due to either allowed or forbidden transitions. No additional lines were found. The conclusion is then that the observed lines are due to an ion with spin 1/2. Thus, the molybdenum valency is +5, as Mo⁺⁵ has a single *d* electron. Ru⁺³, having five 4*d* electrons and consisting approximately 30% of isotopes with nuclear spin 5/2, may give a similar spectrum. However, spectrochemical analysis did not show the presence of any Ru⁺³.

The long relaxation time and hyperfine structure, which shows odd isotopes only with spin 5/2, excludes the possibility of the observed line being due to Ti⁺³ ion. This ion should have a short relaxation time,² and also has an isotope with nuclear spin 7/2. In addition, an experiment on pure TiO₂ under the same conditions was done. The resonance did not appear.

The Hamiltonian for spin 1/2 and nuclear spin *I* in a crystalline field of rhombic symmetry is

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

For the main line, with even nuclei, the Hamiltonian is simply

$$\mathcal{H} = \beta[g_x S_x H_x + g_y S_y H_y + g_z S_z H_z]. \quad (2)$$

The energy levels for a magnetic field along the Z axis, calculated from (1) to second order, are³

$$E_{\pm} = \pm \frac{g_z \beta H_z}{2} \pm \frac{m A_z}{2} \pm \frac{[I(I+1) - m^2]}{8 h \nu} (A_x^2 + A_y^2) - \frac{m}{4 h \nu} A_x A_y \pm m \{ 2[I(I+1) - m^2] - 1 \} \times \frac{(P_x - P_y)^2}{4(A_z - g_n \beta_n H_z)} + \frac{3}{2} P_z [m^2 - \frac{1}{3} I(I+1)] - \gamma_n \beta_n H_z m, \quad (3)$$

where *m* is the magnetic quantum number of the nucleus.

The energy absorbed for a $\Delta m = 0$ transition is then

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

From (2) it is simply

$$h\nu = g_z \beta H_z. \quad (5)$$

For the magnetic field along the X and Y axes, equations similar to (3), (4), and (5) can be obtained by commuting components of *g*, *H*, *A*, and *P*.

The result of the experiments are shown in Table I.

We can obtain the *g* tensor from the main line immediately by Eq. (5).

$$g_I = 1.7884 \pm 0.0010, \\ g_{II} = 1.8117 \pm 0.0010, \\ g_{III} = 1.9125 \pm 0.0010.$$

The same *g* tensor as well as the mean hyperfine interaction constant of the odd isotopes can also be obtained from the six weak lines. The quadrupole term is negligible within the accuracy of the experiment.

$$g_I = 1.7883 \pm 0.0010, \\ g_{II} = 1.8117 \pm 0.0010, \\ g_{III} = 1.9125 \pm 0.0010, \\ A_I = 3.050 \pm 0.020 \times 10^{-3} \text{ cm}^{-1}, \\ A_{II} = 2.474 \pm 0.025 \times 10^{-3} \text{ cm}^{-1}, \\ A_{III} = 6.585 \pm 0.015 \times 10^{-3} \text{ cm}^{-1}.$$

The ground state of a 1*d* electron in a low-symmetry crystalline field may be written⁴ as

$$|1+m\rangle = [\sin\alpha |a^+\rangle + \cos\alpha |b_+^-\rangle] \cos\theta + \sin\theta |b_-^-\rangle, \\ |1+m\rangle = [\sin\alpha |a^-\rangle - \cos\alpha |b_+^+\rangle] \cos\theta + \sin\theta |b_+^+\rangle, \quad (6)$$

where

$$|b_+\rangle = |(b+ic)/\sqrt{2}\rangle, \quad |b_-\rangle = |(b-ic)/\sqrt{2}\rangle, \quad (7)$$

and *a*, *b*, *c* are the eigenstates of *V* on *dε* orbitals, i.e., they are linear combinations of the orbitals

$$|a\rangle = l_{xz} |xy\rangle + l_{zx} |yz\rangle + l_{yz} |zx\rangle, \\ |b\rangle = l_{xz} |xy\rangle + l_{zx} |yz\rangle + l_{xy} |zx\rangle, \\ |c\rangle = l_{yz} |xy\rangle + l_{yx} |yz\rangle + l_{yy} |zx\rangle, \quad (8)$$

and the superscripts + and - denote the sign of *S_z*. The matrices of the perturbation $\mathcal{H} = V + \zeta' \mathbf{L} \cdot \mathbf{S}$ on

² R. J. Blengie and A. H. Cooke, Proc. Roy. Soc. (London) **A209**, 269 (1951).

³ H. J. Gerritsen and H. R. Lewis, Phys. Rev. **119**, 1010 (1960).

⁴ B. Bleaney and M. C. M. O'Brien, Proc. Phys. Soc. (London) **B69**, 1216 (1956).

these states are then

| | a^+ | b_+^- | b_-^- | a^- | b_-^+ | b_+^+ |
|---------|-----------------|---------------------------|------------------------------------|------------------|------------------------------------|--------------------------------------|
| a^+ | A | $\xi'/\sqrt{2}$ | 0 | 0 | 0 | 0 |
| b_+^- | $\xi'/\sqrt{2}$ | $\frac{1}{2}(B+C)+\xi'/2$ | $\frac{1}{2}(B-C)$ | 0 | 0 | 0 |
| b_-^- | 0 | $\frac{1}{2}(B-C)$ | $\frac{1}{2}(B+C)-\frac{1}{2}\xi'$ | 0 | 0 | 0 |
| a^- | 0 | 0 | 0 | A | $-\xi'/\sqrt{2}$ | 0 |
| b_-^+ | 0 | 0 | 0 | $-\xi'/\sqrt{2}$ | $\frac{1}{2}(B+C)+\frac{1}{2}\xi'$ | $\frac{1}{2}(B-C)$ |
| b_+^+ | 0 | 0 | 0 | 0 | $\frac{1}{2}(B-C)$ | $\frac{1}{2}(B+C)-(\frac{1}{2})\xi'$ |

where A , B , and C are the eigenvalues of V . By solving the above matrix, α and θ of the ground state can be found.

The values of α and θ can be found from the experimental g values since the g values are obtained by operating $kL+2S$ on the ground state, where k is the effective orbital g factor due to π bonding.⁵

$$\begin{aligned} g_z &= 2 \cos^2 \theta [\sin^2 \alpha - (1+k) \cos^2 \alpha] + 2 \sin^2 \theta (k-1), \\ \frac{1}{2}(g_x + g_y) &= -2 \cos^2 \theta [\sin^2 \alpha + \sqrt{2}k \cos \alpha \sin \alpha], \\ \frac{1}{2}(g_x - g_y) &= 2 \sin 2\theta [\cos \alpha + (k/\sqrt{2}) \sin \alpha]. \end{aligned} \quad (9)$$

The observed g values of the ground states are then used to determine the three unknowns θ , α , and k .

By altering the identification of the three axes with the x , y , and z axes, solutions that correspond to the same physical ground state can be found with different values of θ and α , but the value of k should not vary with the choice of axes. The only reasonable k value is found by assuming the g values to be negative, and its value is 0.8784 ± 0.0001 . When the axes are chosen so that

$$g_x = -1.7883, \quad g_y = -1.9125, \quad g_z = -1.8117,$$

⁵ K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

the parameters θ and α are

$$\theta = 0.757^\circ, \quad \alpha = 35.538^\circ;$$

likewise, when

$$g_x = -1.8117, \quad g_y = -1.9125, \quad g_z = -1.7883,$$

then

$$\theta = 0.615^\circ, \quad \alpha = 35.795^\circ;$$

and when

$$g_x = -1.7883, \quad g_y = -1.8117, \quad g_z = -1.9125,$$

then

$$\theta = 0.143^\circ, \quad \alpha = 34.482^\circ.$$

Because of the high dielectric constant of TiO_2 an experimental determination of the sign of the g values is very difficult.

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