PHYSICAL REVIEW VOLUME 136, NUMBER 5A 30 NOVEMBER 1964

# Electron Spin Resonance of $Mo^{5+}$ in Rutile*

TE–TSE CHANG
*National Bureau of Standards, Washington, D. C.*

(Received 24 January 1964; revised manuscript received 30 July 1964)

The electron-spin-resonance spectrum of $Mo^{5+}$ in the host lattice of $TiO_2$ was determined. Both the hyperfine lines due to the coupling with Mo nuclei, and the superhyperfine lines due to the coupling with the next nearest neighbors, Ti nuclei, were observed. The sign of the $g$ factor of $Mo^{5+}$ was found to be positive by observing the resonance with circularly polarized microwave radiation. The theory of Bleaney and O'Brien cannot be applied in this case, probably because the crystalline field is not strong enough and/or covalent bonding is appreciable.

## I. INTRODUCTION

THE spin resonance of molybdenum in rutile has been reported recently by Kyi.[1] Her experimental results indicated that Mo ions are substitutional in the host lattice, and are in the 5+ valence state, where $S=\frac{1}{2}$. The hyperfine lines of Mo were observed, and the isotope effect was partially resolved. The $g$ factor had to be negative if Bleaney's and O'Brien's theoretical expression of the $g$ factor[2] was used to explain the result.

Considering the unusual conclusion of a negative $g$ factor, which is unlikely for light and medium elements, it was then considered worthwhile to repeat the experiment and determine experimentally the sign of the $g$ factor of $Mo^{5+}$ ions in rutile.

A piece of rutile was used as its own microwave cavity, resulting in a very high $Q$ factor and 100% filling factor. This technique made it possible to resolve the isotope effect of the hyperfine lines, and in addition, to observe the *super*hyperfine lines. Those results will be reported in Sec. II.

A special cavity was designed and constructed which enabled us to observe the absorption spectrum of $Mo^{5+}$ with circularly polarized microwaves. An unambiguous experimental determination of the sign of the $g$ factor was then possible. This part of the experiment will be presented in Sec. III.

A short discussion of the reason for the failure of the Bleaney and O'Brien theory for this case can be found in Sec. IV.

## II. HYPERFINE LINES AND SUPERHYPERFINE LINES

The resonance spectra of Mo-doped $TiO_2$ at liquid-nitrogen temperature were observed with a Varian X-band EPR spectrometer and a 12-in. Harvey-Wells electromagnet. The signals were observed visually on an oscilloscope and were also recorded with a strip chart recorder. The magnetic field was measured with a proton nuclear resonance probe, while the microwave frequency was determined with a transfer oscillator and an electronic frequency counter.

The sample was grown by the flame fusion method at this laboratory. Mo was added to the $TiO_2$ powder as $MoO_3$ at nominal concentration of 0.05 mole percent. After growth, a piece about 2×5×9 mm was cut from the boule, and was then fully oxidized. Since the dielectric constant[3,4] of rutile is high, this piece of rutile was used as its own microwave cavity.[5] The $Q$ factor was about 47 000 at liquid-nitrogen temperature for this specific sample. A polished and clean surface of the rutile cavity is essential for a high $Q$. The sample was held inside the waveguide with a polystyrene holder and nylon screws which can be adjusted from outside the Dewar to orient the sample.

The macroscopic symmetry of rutile[6] is tetragonal, but the local symmetry of each Ti ion is orthorhombic; there are two distinguishable local sites. The nearest neighbors of each Ti ion are six oxygen ions forming an octahedron around the Ti ions. The next-nearest neighbors are ten Ti ions, two of them are along the $c$ axis and eight of them are at the corners of the unit cell.

With this crystal structure in mind, one can readily interpret the experimental observations. An angular dependence study of the spectrum confirmed that the Mo ions go into the host lattice substitutionally. A typical trace of the derivative curve of the absorption lines is shown in Fig. 1. Two sets of lines were observed. The linewidth is about 0.6 to 1.0 G. When the external magnetic field is along the [110] direction, the two sets of lines have the largest separation from each other. When the external magnetic field is either at 45° with the [110] direction or along the $c$ axis, the two sets of lines coincide.

Each set of lines consists of a strong center line and six hyperfine lines. The center line is due to the resonance absorption of the Mo ions with zero nuclear spin, and the hyperfine lines are due to the resonance absorption of Mo ions with nonzero nuclear spin. The odd

---

* Research supported in part by the Advanced Research Projects Agency.

[1] R. Kyi, Phys. Rev. 128, 151 (1962).

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

[3] Rebecca A. Parker, Phys. Rev. **124**, 1719 (1961).

[4] E. S. Sabisky and H. J. Gerritsen, J. Appl. Phys. **33**, 1450 (1962).

[5] A. Okaya, Proc. IRE **48** ,1921 (1960).

[6] F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).

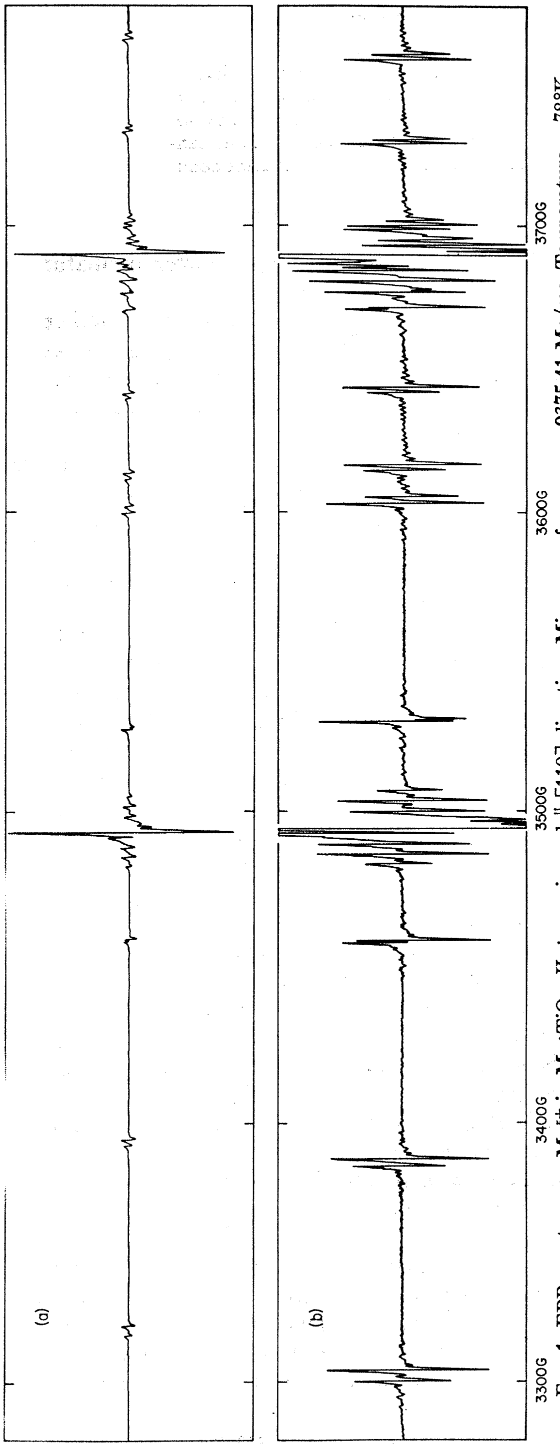

FIG. 1. EPR spectrum or $Mo^{5+}$ in Mo:$TiO_2$. $H_0 \perp c$ axis, and ∥ [110] direction. Microwave frequency = 9375.41 Mc/sec. Temperature = 78°K. Curve (b) was traced with higher gain in lock-in amplifier.

isotopes[7] are $Mo^{95}$ and $Mo^{97}$ which have natural abundances of 15.70% and 9.60%, respectively, and nuclear magnetic moments of $-0.9099$ and $-0.9290$ nuclear magneton, respectively. The nuclear spin is $\frac{5}{2}$ for both. Each hyperfine line is split into two components because of the difference of nuclear magnetic moments. The measured hyperfine coupling constants of those two components have the same ratio as the nuclear magnetic moments of the two isotopes, and the relative intensity of the two components corresponds correctly to the natural abundance.

The eight-line structure around the center line is the superhyperfine structure. In the high gain recorder traces, the superhyperfine lines of each hyperfine line can be seen also. The pattern of the superhyperfine lines appears to be the same as the hyperfine structure of $Ti^{47}$ $(I=\frac{5}{2})$ and $Ti^{49}$ $(I=\frac{7}{2})$ complex in solution as observed by Waters and Maki.[8] As there are no other nuclei present in the crystal that could contribute to the observed superhyperfine structure, the next-nearest-neighbor Ti ions are assumed to be the origin of the superhyperfine structure.

The following Hamiltonian is then adopted to explain the spectrum:

$$\mathcal{H}=\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}+\sum_{\mathrm{Ti}}\mathbf{S}\cdot\mathbf{A}^{\mathrm{Ti}}\cdot\mathbf{I}^{\mathrm{Ti}}. \qquad (1)$$

The symbols have their usual meanings. The quadrupole terms are neglected. The last term is added to represent the superhyperfine structure. The superscript "Ti" indicates that the summation is carried out over the neighboring titanium ions. The solution of the above Hamiltonian along the $z$ axis (110 axis of the crystal) up to the second order of $A$ and the first order of $A^{\mathrm{Ti}}$ is

$$h\nu=g_z\beta H_z+A_z m+\frac{I(I+1)-m^2}{4h\nu}(A_x^2+A_y^2)+A_z^{\mathrm{Ti}}\sum m^{\mathrm{Ti}}. \qquad (2)$$

The solution along other axes can be obtained by permuting $x$ (crystalline $1\bar{1}0$), $y$ (crystalline $c$ axis), and $z$.

The total natural abundance of $Ti^{47}$ and $Ti^{49}$ is 13.26%. If only one neighboring Ti ion of the $Mo^{5+}$ site has nuclear spin, $\sum m^{\mathrm{Ti}}$ may take a maximum value of $\frac{7}{2}$ or $\frac{5}{2}$. But the hyperfine coupling constants are almost exactly the same[8] for $Ti^{47}$ and $Ti^{49}$, so that the six superhyperfine lines from $Ti^{47}$ can be expected to overlap the inner six lines from $Ti^{49}$. The lines should thus arrange themselves in the sequence of $-\frac{7}{2}A^{\mathrm{Ti}}$, $-\frac{5}{2}A^{\mathrm{Ti}}, \cdots, \frac{5}{2}A^{\mathrm{Ti}}, \frac{7}{2}A^{\mathrm{Ti}}$ about the center. The relative intensity among them should be about 1:2:2:2:2:2:2:1 if the difference of natural abundance between $Ti^{47}$ and $Ti^{49}$ is ignored to get an order of magnitude estimation.

---

[7] *Handbook of Chemistry and Physics* (The Chemical Rubber Publishing Company, Cleveland, Ohio, 1962–1963) 44th ed., p. 2650.

[8] E. L. Waters and A. H. Maki, Phys. Rev. **125**, 233 (1962).

If two neighboring Ti ions have nuclear spins, they may occur in the combination of $\frac{7}{2}$, $\frac{7}{2}$; $\frac{7}{2}$, $\frac{5}{2}$; or $\frac{5}{2}$, $\frac{5}{2}$. $\sum m^{\mathrm{Ti}}$ may take maximum value of 7, 6, or 5. The superhyperfine lines should arrange themselves in the sequence $-7A^{\mathrm{Ti}}$, $-6A^{\mathrm{Ti}}$, $-5A^{\mathrm{Ti}}$, $\cdots$, $5A^{\mathrm{Ti}}$, $6A^{\mathrm{Ti}}$, $7A^{\mathrm{Ti}}$. The relative intensity should be about 1:4:8:12:16:20:24:28:24:20:16:12:8:4:1. Both series of lines were observed, but the two-spin lines were very weak and only a few were observed. If the ten neighboring Ti ions perturb the Mo electron wave function equally, the two-spin lines should not be so weak. The ratio of the probability of finding one spin or two spins is 1.74:1.17. The intensity ratio of $m=-\frac{5}{2}$ line to $m=-2$ line should be about $[1.74(2/14)]/[1.17(20/198)]\approx 2$. But this is not the case. If only the two Ti ions along the $c$ axis are effective, following the same considerations, the intensity ratio should be about 20:1 which is about the correct order of magnitude. This could be explained by noting that the two Ti ions along the $c$ axis are closer, and the $d$ electron wave function has a large density in this direction also. This conclusion agrees well with Kikuchi's work[9] on $SnO_2$:V and Yamaka's work[10] on $TiO_2$ doped with iron group elements.

The results of the measurements are summarized in Table I. The $g$ factors are a little higher than Kyi's values. The hyperfine coupling constants agree very well with Kyi's results. The largest components of both the $g$ factor and the hyperfine coupling constant are along the $z$ direction which is the [110] direction of the crystal and the orthorhombic axis of the local site. The superhyperfine coupling is nearly spherically symmetric. The $y$ component of the superhyperfine coupling constant, i.e., the component along the crystal $c$ axis, is the largest. The reason may be that the two Ti ions along the $c$ axis contribute most to the superhyperfine coupling. The same effect was observed by Yamaka and Barnes.[10]

### III. THE SIGN OF THE $g$ FACTOR

Equation (2) does not allow determination of the sign of the $g$ factor. The resonance signal of the dispersion mode could be obtained with a Varian microwave bridge and could be used to give a clue to the sign of the $g$ factor. But an experiment with circularly polarized microwave radiation will give an unambiguous determination. This kind of polarized radiation requires a circular cylindrical cavity. An attempt to fabricate a piece of rutile into a circular cylindrical cavity was not successful. A conventional silver-plated copper cavity was used. The design follows Hutchison's work[11] on Np, and is shown in Fig. 2. The probe at the end of the waveguide was used to detect the signal, and was fabricated to be a matched load so that there would be no reflected microwave power. This produces a traveling microwave in the waveguide. The loaded $Q$ of this cavity was about 9000. The cavity and the attached waveguide were filled with helium at slightly higher than atmospheric pressure to keep liquid nitrogen out of the cavity and the waveguide during the experiment. The rutile sample was shaped in the form of a circular disk of about 5 mm o.d. and 0.5 mm thick. A dot of diphenylpicrylhydrazyl (DPPH) was glued to the center of the sample, and the sample was glued on the bottom of the cavity. It was found that the shape and the size of the sample and the position of the sample in the cavity were very critical.

TABLE I. The $g$ factors and hyperfine and superhyperfine coupling constants of Mo in $TiO_2$. All $A$'s in $10^{-4}$ cm$^{-1}$.

| | $x$ | | $y$ ($c$ axis) | | $z$ | |
|---|---|---|---|---|---|---|
| $g$ | $1.8155\pm0.0005$ | | $1.7923\pm0.0005$ | | $1.9167\pm0.0005$ | |
| $A^{95}$ | 24.32 | $\pm0.15$ | 30.48 | $\pm0.15$ | 65.08 | $\pm0.15$ |
| $A^{97}$ | 25.00 | $\pm0.15$ | 31.13 | $\pm0.15$ | 66.38 | $\pm0.15$ |
| $A^{47,49}$ | 2.8 | $\pm0.8$ | 3.4 | $\pm0.8$ | 3.1 | $\pm0.8$ |

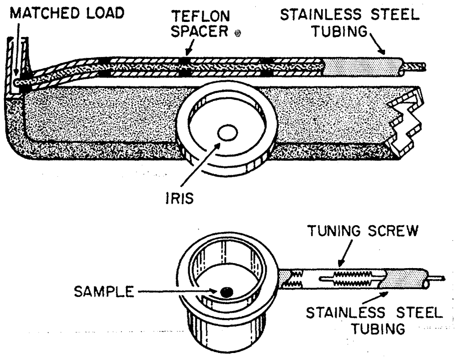

FIG. 2. The circularly polarized cavity.

The results are shown in Fig. 3. Since the DPPH signal is strong, lower gain of the lock-in amplifier was used for DPPH, and higher gain was used for the Mo signal. However, the gain was kept the same during the recording of both curves (a) and (b). Only the two center lines of the Mo signal could be observed. Those two lines were verified to be the Mo signal by gluing this sample on a pure rutile cavity and placing it in the magnetic field at approximately the same orientation; the characteristic spectrum of Mo was observed. The external magnetic field was parallel to the axis of the circular cavity, but the field for curve (a) is opposite in direction to the field for curve (b). Reversal of the magnetic field has the same effect as reversal of the sense of rotation of the circularly polarized microwaves. The small DPPH signal in (b) indicates that the polarization of the microwave in the cavity was about 95%. The ratio of DPPH signal in (a) and (b) is about 20:1. If the $g$ factor of $Mo^{5+}$ has the same sign as that

---

[9] W. H. From, C. Kikuchi, and P. Dorian (to be published); see also Bull. Am. Phys. Soc. **9**, 37 (1964).

[10] E. Yamaka and R. G. Barnes, Phys. Rev. **135**, A144 (1964).

[11] C. A. Hutchison, Jr., and B. Weinstock, J. Chem. Phys. **32**, 56 (1960).

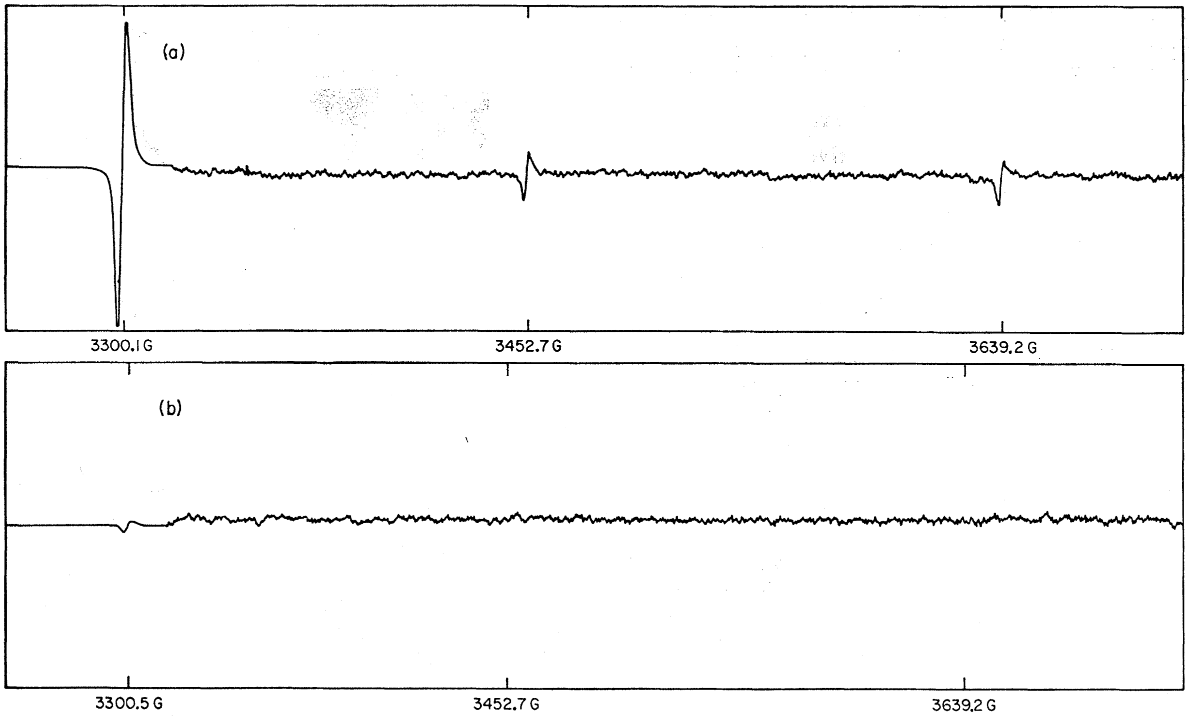

FIG. 3. The EPR spectrum of DPPH and $Mo^{5+}$ in Mo:$TiO_2$ with circularly polarized microwave. Temperature = 78°K. Microwave frequency = 9257.86 Mc/sec. The magnetic fields for curves (a) and (b) were in opposite directions.

of DPPH, the Mo signal should be reduced in the same ratio in (b) and therefore could not be observed. If the signs of the $g$ factors were opposite, the Mo signal in (b) should be 20 times as large as that in (a) and should be off scale and easily observed. From the above reasoning, the sign of the $g$ factor of $Mo^{5+}$ in $TiO_2$ is positive as in DPPH.

## IV. CONCLUSIONS

It is clear, from the above described experimental result, that $Mo^{5+}$ in $TiO_2$ has positive $g$ factors. However, the Bleaney and O'Brien theory yields a negative sign. These two conclusions are in contradiction.

In Bleaney and O'Brien's article,[2] the following assumptions were made: The fivefold degenerate $d$ state was split by crystalline cubic fields into a doublet and a triplet. The crystalline field was assumed *very strong* so that the doublet state was far above the triplet and its effects could be neglected. The triplet state was further split by a crystalline field of lower symmetry and $L$-$S$ coupling. The assumption of very strong crystalline field may not be true in the case of $TiO_2$.

The presence of the superhyperfine structure indicates that the $Mo^{5+}$ electron wave functions are partially shared by neighboring ions. This means that the covalent bonding may be appreciable. A theoretical calculation of the $g$ factor should take the covalent bonding into consideration, not only over the nearest neighbors, but also up to at least the next-nearest neighbors.

Finally, Bleaney and O'Brien had tried to fit their experimental results on $K_3Fe(CN)_6$ into their theory. The best fit obtained required that the $g$ factor of $Fe^{3+}$ be negative. Their statement, "··· that the observed $g$ values cannot be fitted using the strong field model without any $\pi$ bonding," clearly predicted our conclusion for $TiO_2$:Mo.

## ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. H. P. R. Frederikse, Dr. J. H. Becker, and Dr. A. H. Kahn for their constant encouragement and interesting discussions about this work. He also owes thanks to D. E. Roberts for growing the crystal, to Dr. B. Mangum for suggesting the circularly polarized cavity, and to R. Stone for helping to fabricate the cavity.