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Paramagnetic-Resonance Spectrum of W^{5+} in Rutile (TiO_2)†

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The paramagnetic-resonance spectrum of W^{5+} substitutional in TiO_2 was measured and analyzed. Both hyperfine lines and superhyperfine lines are observed. In the superhyperfine spectrum there is one group of relatively weak lines that is probably due to "forbidden" transitions. The g factors are: $g_c=1.4431$, $g_{1\bar{1}0}=1.5944$, $g_{110}=1.4725$. The hyperfine coupling constants are $A_c=63.7\times10^{-4}$ cm^{-1}, $A_{1\bar{1}0}=92.5\times10^{-4}$ cm^{-1}, $A_{110}=40.8\times10^{-4}$ cm^{-1}.

INTRODUCTION

THE electron paramagnetic resonance of W^{5+} in ionic complexes and as an impurity in glass has been reported by several authors.[1-4] This paper deals with the paramagnetic-resonance spectrum of W^{5+} ions substituted for the cation in single-crystal TiO_2 (rutile). The W^{5+} ion has one $5d$ electron outside the closed shell. It should play the same role in the $5d^n$ configuration as V^{4+} in the $3d^n$ and Mo^{5+} in the $4d^n$ configurations. A comparison between results obtained on these three ions is interesting. The host lattice of rutile was chosen because its structure is well known. The high dielectric constant of rutile makes it advantageous to use the crystal as its own microwave cavity.

The spectrum shows not only the hyperfine structure but also the superhyperfine structure arising from the interaction of the W^{5+} electronic magnetic moment with the nuclear magnetic moment of some of the surrounding Ti ions.

EXPERIMENTAL ASPECTS

The spectrum was observed with an X-band spectrometer and a 12-in. electromagnet. The magnetic field was measured with a proton nuclear-magnetic-resonance gaussmeter, while the microwave frequency was determined with a transfer oscillator and an electronic frequency counter. The signal was observed visually on an oscilloscope as well as recorded with a strip-chart recorder.

The sample was grown by the flame-fusion method at this laboratory. Tungsten was added to the TiO_2 powder as WO_3 at a nominal concentration of 0.01 mole percent. Because of the high vapor pressure of WO_3 at about 1700°C, the final concentration of tungsten in TiO_2 was less than 10^{-4} mole percent as indicated by spectrochemical analysis. Considering that the atmosphere of the flame is somewhat reducing, it is believed that W ions go into the lattice in different valence states. A rectangular piece about the size of 2×6×10 mm was cut from the boule and was fully oxidized. This piece was ground by hand with carborundum paper until a moderately shiny surface was obtained. When this piece was used as a dielectric microwave cavity,[5] the Q was estimated to be about 200 000 at 20°K. No attempt was made to measure Q exactly. The automatic-frequency-control system of the spectrometer was not fast enough to lock the klystron frequency to that of the rutile cavity; hence the frequency stabilization was operated with a conventional cavity of much lower Q. This method provided a fairly stable microwave frequency and low noise.

The experiment was performed at 20°K (liquid H_2), where the linewidth is about 0.5 Oe. At 4°K the resonance line is easily saturated. The crystal was oriented with polarized light and x ray. Further alignment was done by rotating the magnet during the experiment.

THE SPECTRUM

A typical recorder trace of the derivative curve of the resonance spectrum is shown in Fig. 1. The spectrum consists of two sets of lines. Each set consists of a strong center line, two hyperfine lines, and superhyperfine lines clustered around the center line and around each of the hyperfine lines. When the external magnetic field is parallel to the crystalline c axis or to either a axis, the two sets of lines collapse into one set. Maximum separation of the two sets of lines occurs when the external magnetic field is perpendicular to the c axis and at 45° with the a axis. This means the magnetic axes are along a 110 direction (x axis), an 001 direction (y axis), and a $1\bar{1}0$ direction (z axis). The regular sites of Ti ions in rutile show the same type of symmetry.[6] So we conclude that the impurity ions responsible for the spectrum are substituted in regular Ti positions.

The number of hyperfine lines suggests that the nuclear spin is $\frac{1}{2}$, and the relative strength of the hyperfine lines to the center line matches the natural abundance of W^{183}. Other known impurities in this rutile

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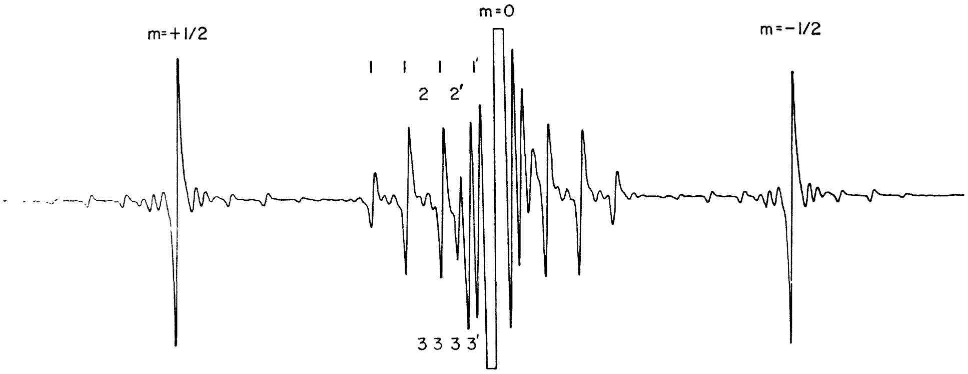

FIG. 1. EPR spectrum of W^{5+} in TiO$_2$ at X-band frequency, and 20°K (liquid-H$_2$ temperature) $H_0 \parallel$ (c axis). (For clarity, not all of the superhyperfine lines are labeled.)

sample are iron and vanadium, whose resonance spectra could be readily identified. However, lines of the latter kind have been observed only in a different spectral region; the spectrum under consideration is unambiguously identified as originating from W ions. Since only one resonance spectrum was observed, the effective spin apparently has the value $\frac{1}{2}$, corresponding to a valence state 5+.

The following Hamiltonian can be adopted to explain the results[7]:

$$\mathcal{H}=g\beta\mathbf{A}\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}+\sum_{\mathrm{Ti}}\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}. \tag{1}$$

The symbols have the usual meaning. Since $S=\frac{1}{2}$, the crystalline field term is omitted and the quadrupole term is zero. The third term is added to explain the superhyperfine lines. The summation refers to the neighboring Ti nuclei. It does not include the oxygen nuclei because ^{17}O—the only oxygen isotope with $I\neq 0$—has a very low natural abundance. The Hamiltonian of Eq. (1) explains most of the spectrum, but it is inadequate to explain all the fine details, as will be discussed below. Nevertheless, the spectrum will be analyzed in terms of Eq. (1). The solution of the above Hamiltonian along the z axis is

$$H_z=H_{0z}-\frac{A_z}{g\beta}m_{\mathrm{W}}$$

$$-\frac{I(I+1)-m_{\mathrm{W}}^2}{4H_z}\frac{(A_x^2+A_y^2)}{(g\beta)^2}-\frac{A_z^{\mathrm{Ti}}}{g\beta}\sum_{\mathrm{Ti}}m_{\mathrm{Ti}}. \tag{2}$$

The solution along other axes can be obtained by permuting x, y, and z. $H_{0z}=h\nu/g\beta$, where ν is the microwave frequency. The terms in formula (2) have been transposed to give the position of the resonance lines in magnetic field at fixed microwave frequencies. For $I=0$ (i.e., $m_{\mathrm{W}}=0$), the second and the third terms are always zero; if Σm_{Ti} is zero too, the transition should occur at $H_z=H_{0z}$. This is the observed center line (marked $m=0$ in Fig. 1). If $\Sigma m_{\mathrm{Ti}}\neq 0$, the center line will be surrounded by superhyperfine lines. In the case of $I=\frac{1}{2}$, or $m=\pm\frac{1}{2}$, the spectrum shows two hyperfine lines (marked $m=\frac{1}{2}$, and $m=-\frac{1}{2}$ in Fig. 1), also accompanied by a superhyperfine structure.

The superhyperfine lines surrounding the center line and the groups that surround the hyperfine lines appear to be the same; they follow the same general pattern as the spectrum of the Ti complex observed by Waters and Maki.[8] Hence the neighboring Ti ions are responsible for the superhyperfine lines. There are ten Ti neighbors (see Fig. 2), but the largest contribution comes from the two neighbors along the c axis,[9,10] which are directly above and below the ion concerned. These two are the nearest ones among the ten, and the d-like electron wave function of the center ion has a high density in those directions. There is an appreciable probability (23%) that one of the two nearest-neighbor Ti ions will have a nuclear spin (^{47}Ti, $I=\frac{5}{2}$, natural abundance 7.75%, or ^{49}Ti, $I=\frac{7}{2}$, natural abundance 5.52%). This situation will produce a superhyperfine spectrum consisting of 8 lines, 6 strong lines on the inside and 2 lines further out having about one-half the strength of the inner 6. These lines are marked "1" in Fig. 1.

There is also a (smaller) chance that both nearest-neighbor sites be occupied by Ti ions with nuclear spin. The latter case will give rise to Σm_{Ti} being an integer

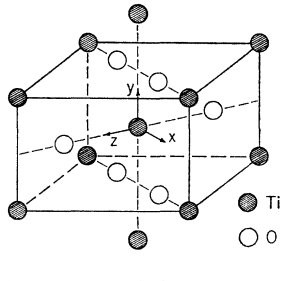

FIG. 2. Crystal structure of TiO$_2$.

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[7] See, for example, H. J. Gerritsen and H. R. Lewis, Phys. Rev. **119**, 1010 (1960).

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

[9] C. Kikuchi, I. Chen, W. H. From, and P. B. Dorain, J. Chem. Phys. **42**, 181 (1965).

[10] T. Chang, Phys. Rev. **136**, A1413 (1964).

(while Σm_{Ti} will be a half-integer in the former case). These lines are marked by "2"; they are halfway between the lines of group 1. The two inner members of the group-1 lines, and those of the group-2 lines, as marked by 1′ and 2′, are much more intense, and their positions are shifted. The reason is not clear. There are also lines marked "3"; this group is so far unexplained and will be discussed in the next section.

SUPERHYPERFINE LINES, GROUP 3

The group-3 lines appear to be associated with the superhyperfine structure. The origin is not clearly understood.

This group of lines is positioned very nearly halfway between group 1 and group 2. They are well resolved in the spectrum when $H \| (c$ axis). For magnetic field parallel to the 110 or $1\bar{1}0$ axes, the group-3 lines are somewhat masked by the wings of lines 1 and 2, but can still be observed. There are two shoulders on either side of the center line and of the two hyperfine lines. These are members of group 3 also. The strength of the two center members (marked 3′) rises very high. With regard to the origin of the group-3 lines, we offer the following suggestions.

(1) Since the lines are narrow, the first thought is that group-3 lines may be the modulation side bands from the klystron frequency stabilization. However, the modulation frequency is 10 kHz and this corresponds to about 4 or 5 m-Oe. This is too small to account for the observed shift, which is about 1 Oe.

(2) There may be clusters of W ions. Such clustering, however, only broadens the resonance lines, and does not introduce new lines. Furthermore, since the concentration of W ions is extremely low, clustering is not likely.

(3) W ions may be in other valence states than 5^+. In this case both the g factor and the energy spacings would be entirely different.

(4) The observed lines may be due to "forbidden" transitions. Usually the terms expressing the interaction of the nuclear moments and the external magnetic field are omitted in the Hamiltonian [Eq. (1)]. The reason is that in most cases the transitions between the nuclear levels concurrent with the electronic transitions are forbidden. And even if the transitions become allowed (because of some perturbation) the energies involved are usually negligible compared with the electronic transition energies. Occasionally the perturbation is sufficient to invalidate the selection rule and render the transition allowable. This can be caused either by mixing of states at low magnetic field or by quadrupole interactions.[11]

In this experiment two species of nuclei are involved: the tungsten and the titanium nuclei. The transitions of the tungsten nuclei will remain forbidden, because (a) the magnetic field is so high that the different nuclear quantum states do not mix, and (b) the tungsten nucleus ($I=\frac{1}{2}$ or 0) does not possess a quadrupole moment.

For the Ti nuclei the situation is different. In this case the nuclear quadrupole moment is not zero, and there is an electric-field gradient at the regular Ti site. The quadrupole interaction will produce an allowed nuclear transition and this line is sharp enough to be observable. In the Hamiltonian [Eq. (1)], a term $-\gamma_{\mathrm{Ti}}\beta_N H . I_{\mathrm{Ti}}$ should be added, changing the resonance field H_z to

$$H_z = H_{0z} - \frac{A_z}{g\beta} m_{\mathrm{W}} + \frac{I(I+1)-m_{\mathrm{W}}^2}{4H_z} \frac{A_x^2+A_y^2}{(g\beta)^2} - \frac{A_z^{\mathrm{Ti}}}{g\beta}\Big[\sum_{\mathrm{Ti}} m_{\mathrm{Ti}} \mp \tfrac{1}{2}\Big] \pm \frac{\gamma_{\mathrm{Ti}}\beta_N H_z}{g\beta}, \qquad (2')$$

for $\Delta m_{\mathrm{Ti}} = \pm 1$. The effect of this modification is to move some lines of group 1 to the corresponding position of the group-2 lines (or vice versa), and then to shift them by an amount of $\gamma_{\mathrm{Ti}}\beta_N H_z/g\beta$, which is about 0.5 Oe at 4.5 kOe. This change of field is comparable to the observed shift of 1 Oe. To prove this point an experiment at a different frequency (hence at a different magnetic field) may produce the desired evidence. A double-resonance experiment would be helpful, too.

(5) Only the two next-nearest neighbors—the two Ti ions along the c axis—were considered so far in the superhyperfine interaction. The other Ti ions, especially those four which are co-planar with the four oxygen ions forming the rectangle of the octahedron—i.e., in the x-y plane, see Fig. 2—contribute a small but not negligible amount. Because they are further away from the central ion, and the lower density of the electron wave function of the central ions in that direction, the superhyperfine interaction is expected to be lower. Kikuchi *et al.* had observed this interaction in their spin-resonance work on $\mathrm{SnO_2}$:V.[9] Their theoretical calculation[12] agrees well with their experimental finding. Unfortunately, the nuclear magnetic moment of Ti is too small to render the superhyperfine splitting large enough to be determined explicitly.

(6) Since the abundance of $^{17}\mathrm{O}$ is low, the superhyperfine interaction with those ions is usually not observable. However, the proximity of the O ions to the W ions concerned, and the strong chemical bonding are favorable factors for a measurable effect. If the sensitivity of the spectrometer is high enough, the $^{17}\mathrm{O}$ superhyperfine line may be seen. A $^{17}\mathrm{O}$-enriched sample may help to resolve this point.

(7) Although the rutile structure is well known, the position of many defects and foreign ions is still a matter

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[11] See, for example, Sec. 3.3 of B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. **16**, 108 (1953).

[12] I. Chen, C. Kikuchi, and H. Watanabe, J. Chem. Phys. **42**, 186 (1965).

of speculation. The possibility of association of the W ion and other "impurities" should be considered. It is known, for instance, that the rutile lattice often contains OH^- radicals. Such a radical could be located in a position of the nearest neighbor to a W^{5+} ion. The large nuclear magnetic moment of the proton may then produce some superhyperfine lines. Infrared-absorption measurements and double-resonance experiments could be helpful in this situation.

The above list of suggestions with regard to the origin of the "group-3" lines is certainly not exhaustive. None of the explanations mentioned is completely satisfactory. We believe, however, that the "group-3" lines most likely are due to the "forbidden" transition, or the superhyperfine interaction due to the other Ti nuclei, or both. Hence further investigation is recommended.

DISCUSSION

In Table I, the measured values of the g factors, the hyperfine coupling constant, and the superhyperfine coupling constant of W^{5+}, V^{4+} (from Yamake[13]), and Mo^{5+} (from Chang[10]) are listed. All of the ions have one d electron outside a closed shell, and are in about the same crystalline environment.

In general the g factor will deviate from the free-electron value of 2.0023 by an amount[14]

$$\Delta g_{ii} = -2\lambda \sum_j \frac{|\langle 0|L_i|j\rangle|^2}{E_j - E_0},$$

where λ = spin-orbit coupling constant, E_0 = energy of the ground state, E_j = energy of the higher states determined by the crystalline field. The summation should be over all the higher states. "i" stands for x, y, z, which are the principal axes as determined by the crystalline field. It is clear that in a low-symmetry environment like the one under discussion, Δg will be anisotropic.

TABLE I. The g factors, the hyperfine coupling constants, and the superhyperfine coupling constants of V^{4+}, Mo^{5+}, and W^{5+} in TiO_2.

		y (c axis)	z $[1\bar{1}0]$	x $[110]$	Ref.
$V^{4+}(3d^1)$	g	1.913	1.956	1.915	(13)
	A	43×10^{-4} cm^{-1}	142	31	
	A^{Ti}	2.1×10^{-4} cm^{-1}	1.8	1.8	
$Mo^{5+}(4d^1)$	g	1.7923	1.9167	1.8155	(10)
	A	30.5×10^{-4} cm^{-1}	65.1	24.5	
		31.1×10^{-4} cm^{-1}	66.4	25.0	
	A^{Ti}	3.4×10^{-4} cm^{-1}	3.1	2.8	
$W^{5+}(5d^1)$	g	1.4431	1.5944	1.4725	Present work
	A	63.7×10^{-4} cm^{-1}	92.5	40.8	
	A^{Ti}	3.5×10^{-4} cm^{-1}	2.6	2.6	

The constant λ can be calculated from the spacing of the $^2D_{5/2}$ and $^2D_{3/2}$ states. For the free ions V^{4+} and Mo^{5+}, these values are available,[15] i.e., 248 cm^{-1} and 1031.2 cm^{-1}, respectively. A rough guess of λ for W^{5+} may be obtained from an extrapolation of the λ values for Lu (71), Hf (72), and Ta (73).[16] The result is ≈ 5000 cm^{-1}.

The energy differences $E_j - E_0$ are usually of the order of 2000 to 20 000 cm^{-1}. Occasionally these splittings show up as reasonably sharp bands in the visible or near infrared range of the spectrum.[17] However, in most cases of d^1 configuration, the bands are very broad and shallow and identification is out of the question. The optical spectra of the ions under study, V^{4+}, Mo^{5+}, and W^{5+} in rutile, have never been observed. Furthermore, the effect of covalency would be to reduce the effective value of λ.

The above discussion shows that predicting the magnitude of the g factor is still an unsolved problem, even on a comparative basis.

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[15] C. G. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Publishing and Printing Office, Washington, D. C., 1949).

[16] We appreciate very much the kindness of Mrs. C. G. Moore Sitterly of the National Bureau of Standards for unpublished experimental results.

[17] J. R. O'Connor and J. H. Chen, J. Phys. Chem. Solids **24**, 1382 (1963).