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Paramagnetic Resonance of Vanadium in Amorphous and Polycrystalline GeO_2

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The *X*-band electron paramagnetic resonance absorption spectra of vanadium-doped amorphous and polycrystalline tetragonal GeO_2 have been observed at room temperature. The spectrum of the amorphous GeO_2, attributed to VO^{++}, can be described by $g_{\parallel}=1.929\pm0.001$, $g_{\perp}=1.976\pm0.001$, $|A_{\parallel}|=(175.5\pm0.1)\times10^{-4}$ cm^{-1}, and $|A_{\perp}|=(68.2\pm0.1)\times10^{-4}$ cm^{-1}. In the tetragonal GeO_2, the vanadium appears as V^{4+} with spectrum constants $g_z=1.963_2\pm0.0003$, $g_x=1.921_3\pm0.0006$, $g_y=1.921_3\pm0.0001$, $|A_z|=(134.36\pm0.02)\times10^{-4}$ cm^{-1}, $|A_x|=(36.69\pm0.01)\times10^{-4}$ cm^{-1}, and $|A_y|=(37.54\pm0.01)\times10^{-4}$ cm^{-1}. The spectrum of vanadium-doped polycrystalline hexagonal GeO_2 was not observable at 300 or at 77°K.

I. INTRODUCTION

THE electron paramagnetic resonance (EPR) spectra of transition-metal ions in glasses was first investigated by Sands.[1] Subsequent measurements of ions doped into amorphous solids have been reported.[2] In practically all cases, the glassy host structures have been complicated multicomponent systems. GeO_2 does not seem to have received any attention as a host material for EPR studies of transition-metal ions. Despite this apparent neglect, GeO_2 appears to be a particularly interesting system since it exists in the amorphous form and in two different crystalline modifications[3]—the tetragonal form (the rutile structure) and the hexagonal form (the structure of α quartz). Furthermore, GeO_2 is available commercially in very pure form so that doping this system with paramagnetic ions is feasible. Unfortunately, doped single crystals of GeO_2 have apparently not yet been synthesized. Therefore, EPR work on this substance is limited at the present time to amorphous and polycrystalline samples. Parallel studies on the different structural forms of GeO_2 might ultimately lead to a better understanding of the amorphous state of matter, an aim which would be facilitated by the relatively simple one-component glass system used.

Vanadium was incorporated into all samples studied in this investigation because of its isotopic purity and large nuclear spin value (V^{51}, $I=7/2$, 99.76% isotopic abundance). The spectra possess a rich hyperfine structure which serves as a characteristic "signature" of vanadium signals. Furthermore, the fact that vanadium forms paramagnetic ions in several different valence states makes this element an interesting one to examine.[4] The amorphous and tetragonal GeO_2 systems gave spectra at 300°K which, although poorly resolved, could be analyzed. No absorption signal was observed for the hexagonal sample at room temperature or at 77°K.

II. EXPERIMENTAL DETAILS

All samples were prepared from Eagle-Picher electronic grade hexagonal GeO_2 powder having a nominal purity of 99.999+%. Approximately 0.05 wt% of reagent-grade V_2O_5 was added to the starting material. The amorphous sample was made by melting a treated GeO_2-V_2O_5 mixture in a Pt crucible at 1540°C for about one hour. The polycrystalline tetragonal specimen was prepared by hydrothermal synthesis from the doped GeO_2 glass. Finally, the polycrystalline hexagonal sample was made by devitrifying the doped amorphous GeO_2. The three structural forms of the doped GeO_2 materials were verified by x-ray diffraction analyses.

The spectrometer used in this work was a Varian V-4500 unit with a 12-in. electromagnet and 100-kc/sec field modulation. A TE_{102} rectangular cavity resonated at approximately 9500 Mc/sec when loaded with quartz tubes containing the powder specimens. Incident microwave power levels used were approximately 0.3 mW.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Amorphous GeO_2

The structure of amorphous GeO_2 has been investigated by Warren.[5] The x-ray diffraction pattern indicated that glassy GeO_2 is built up of randomly oriented GeO_2 tetrahedra with a Ge-O interatomic spacing of 1.65 Å.

The EPR spectrum observed for amorphous GeO_2 containing 0.05 wt.% V_2O_5 is shown in Fig. 1 and, upon analysis, is attributed to the presence of the vanadyl ion, VO^{++}. The VO^{++} ion ($3d^1$ electronic configuration) is formed when a V^{4+} ion is bound to a ligand oxide ion by a strong, double covalent bond. Such bonding is commonly found for the higher valence states of transition-metal ions near the beginning of a transition series,[6] (e.g., MoO^{3+}, CrO^{3+}, UO_2^{++}). Although anhydrous vanadyl bisacetylacetonate has been reported[7] to contain the ion in fivefold coordination, VO^{++} usually has a

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[1] R. H. Sands, Phys. Rev. **99**, 1222 (1955).

[2] See, e.g., T. Castner, G. S. Newell, W. C. Holton, and C. P. Slichter, J. Chem. Phys. **32**, 668 (1960).

[3] W. Zachariasen, Z. Krist. **67**, 226 (1928); A. W. Laubengayer and D. S. Morton, J. Am. Chem. Soc. **54**, 2303 (1932); R. Schwarz and E. Haschke, Z. Anorg. Allgem. Chem. **252**, 170 (1943).

[4] J. Lambe and C. Kikuchi, Phys. Rev. **118**, 71 (1960).

[5] B. E. Warren, Phys. Rev. **45**, 657 (1934).

[6] J. Selbin and L. H. Holmes, Jr., J. Inorg. Nucl. Chem. **24**, 1111 (1962).

[7] R. P. Dodge, D. H. Templeton, and A. Zalkin, J. Chem. Phys. **35**, 55 (1961).

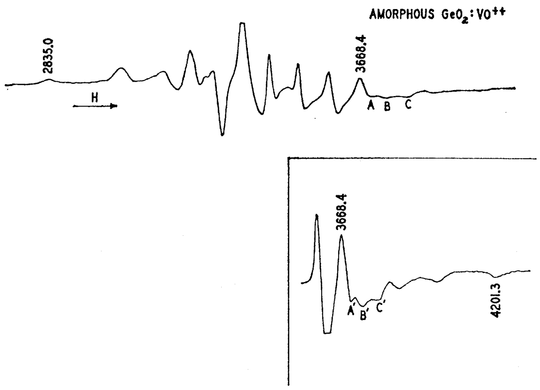

FIG. 1. First derivative recorder tracing of the EPR spectrum of VO^{++} in amorphous GeO_2. The inset shows the extreme high-field portion of the spectrum with increased amplification. The peaks labeled A, B, and C in the spectrum appear in the inset as A′, B′, and C′, respectively. The magnetic-field scale is indicated by the values 2835.0 and 4201.3 G for the $H_{\|}(\pm 7/2)$ derivative peaks at the extreme ends of the spectrum.

coordination number of six when incorporated chemically into solids or solutions.[8] The octahedral vanadyl complexes are tetragonally distorted[9] since one of the axial V-O bonds (due to its strong covalent nature), is shorter than any of the remaining five bonds. The V^{4+} ion itself presumably lies in the plane of the four nonaxial oxygen ions.

There is no spin Hamiltonian expression for paramagnetic ions incorporated into an amorphous solid. Therefore, EPR spectra for glasses are interpreted using the simpler model of a random array[1] of polycrystals which contain magnetic ions. The following spin Hamiltonian[10] for a system with axial symmetry was used to interpret the spectrum of vanadium in amorphous GeO_2:

$$\mathcal{H}=g_{\|}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+AI_zS_z+B(I_xS_x+I_yS_y), \quad (1)$$

where

$$g=(g_{\|}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2},$$
$$K^2g^2=A^2g_{\|}^2\cos^2\theta+B^2g_{\perp}^2\sin^2\theta, \quad (2)$$

and where the other terms have their usual[1,10] significance. The crystalline-field z axis is taken parallel to the external magnetic field H. For a $3d^1$ configuration, all fine-structure terms are absent in Eq. (1). Also, the quadrupole term and the term expressing the direct interaction between the external field and the V^{51} nuclear magnetic moment have been neglected. The spectrum for VO^{++} ($S=1/2$, $I=7/2$) is expected to show a single absorption line split into eight $(2I+1)$ hyperfine components. Due to g-factor anisotropy and the relatively broad absorption lines a considerable degree of overlapping is evident in the observed spectrum.

The analysis of the amorphous spectrum was based on the line positions corresponding to the $\theta=0°$ and $\theta=90°$ orientations. For convenience, Eq. (1) may be rearranged to give the line positions in magnetic field units. Using Eq. (2), we have

$$H(m)=H_0-Km-\frac{B^2}{4H_0}\,\frac{A^2+K^2}{K^2}[I(I+1)-m^2], \quad (3)$$

where $H_0=h\nu_0/\beta g$, and where K, A, and B (now in units of gauss) are equal to those used in Eq. (1) but divided by βg. Analysis of the spectrum using Eq. (3) yields

$$g_{\|}=1.929\pm0.001 \quad |A|=(175.5\pm0.1)\times10^{-4}\ \text{cm}^{-1}$$
$$g_{\perp}=1.976\pm0.001 \quad |B|=(\ 68.2\pm0.1)\times10^{-4}\ \text{cm}^{-1}.$$

The observable spectrum at 300°K, the absence of fine structure, and the general agreement of these results with published[11] and unpublished[12] values for VO^{++} serve to identify this ion as the source of the observed resonance. This conclusion is supported further by an optical absorption spectrum obtained for the amorphous GeO_2 sample (see Sec. IV).

The signs of A and B cannot be determined from the spectrum of a $3d^1$ ion because of the absence of fine structure.[13] However, a better fit between the observed spectrum and that calculated from Eq. (3) and the values given above is obtained with A and B having the same, rather than opposite signs. From their work, Faber and Rogers[11] concluded that A and B were both negative.

B. Tetragonal GeO_2

The EPR spectrum of V^{4+} in single crystal TiO_2 (rutile) has been studied at 77°K by Gerritsen and Lewis[14] and by Zverev and Prokhorov.[15] The spectrum given by GL was used as an approximate model in the analysis of our polycrystalline tetragonal GeO_2 spectrum. This approach turned out to be extremely useful because of the complicated nature of our spectrum (*vide infra*). This procedure seemed reasonable because of the analogous structures of the host crystals. Moreover, considerations based on valence and the similar ionic radii of Ge^{4+} and V^{4+} seemed to further justify this procedure. It was therefore assumed that, in tetragonal GeO_2, the vanadium (as V^{4+}) appears substitutionally at Ge^{4+} sites. As a result, the pattern of line positions for the V^{4+} spectrum in polycrystalline GeO_2 might be expected to resemble the line pattern observed for this ion in single crystal TiO_2.

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[8] In this paper, we shall assume the vanadyl vanadium ion in amorphous GeO_2 to be octahedrally coordinated.

[9] C. J. Ballhausen and H. B. Gray, Inorg. Chem. **1**, 111 (1962).

[10] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951); B. Bleaney, Phil. Mag. **42**, 441 (1951).

[11] See, for example, R. J. Faber and M. T. Rogers, J. Am. Chem. Soc. **81**, 1849 (1959).

[12] R. H. Borcherts, Ph.D. thesis, University of Michigan, 1963 (unpublished).

[13] See, for example, W. Low in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

[14] H. J. Gerritsen and H. R. Lewis, Phys. Rev. **119**, 1010 (1960), hereafter referred to as GL.

[15] G. M. Zverev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **39**, 222 (1960) [English transl.: Soviet Phys.—JETP **12**, 160 (1961)].

Tetragonal GeO_2 crystallizes in the rutile structure (site symmetry D_{2h}), the unit cell dimensions being $c=2.859$ Å and $a=4.390$ Å.[16] The unit cell contains two nonequivalent ions, each of which is surrounded by six oxygens forming a distorted octahedron. This arrangement produces a crystalline field of predominantly octahedral symmetry with slight orthorhombic distortion. The z axes for the two ions are parallel to the plane aa and lie in the [110] and [$1\bar{1}0$] directions. The z axes thus differ from one another by a 90° rotation about the tetragonal c axis (taken as the magnetic y axis). The magnetic x and z axes for one nonequivalent ion have the same directions as the z and x axes, respectively, of the other ion.

The spectrum for polycrystalline tetragonal GeO_2 containing 0.05 wt% V_2O_5 is shown in Fig. 2 and is attributed to V^{4+} located substitutionally in Ge sites. V^{4+} ($3d^1$ configuration) is expected to give a single absorption line split into eight hyperfine components. Because of the rhombic field symmetry at the V^{4+} sites, both the g tensor and hyperfine splitting tensor are characterized by three distinct principal values. From the spectrum alone, however, it is impossible to distinguish unequivocally the sets of lines $H_x(m)$, $H_y(m)$ and $H_z(m)$ because of the random orientation of magnetic axes in the sample. The situation is further complicated by the partial overlapping of lines and by the presence of several apparently extraneous derivative peaks (see Sec. IV).

Because of the above circumstances, the following procedure was used to decompose the tetragonal GeO_2 spectrum. Assuming the presence of V^{4+} substituting for Ge^{4+}, the situation should be analogous to that for V^{4+} in single crystal TiO_2. In particular, it should then be possible to establish a *one-to-one correspondence* between the respective line positions for these two samples so long as the linewidths in the polycrystalline GeO_2 specimen are not sufficiently great to obviate this procedure.

Examination of GL's spectrum shows that the $H_z(m)$ positions are well separated and extend to the extreme ends of the spectrum. This was also found for the GeO_2 specimen so that the line positions for this orientation were found readily. The positions $H_x(m)$ and $H_y(m)$ for a given m value fall close together in the TiO_2 spectrum. Examination of the TiO_2 spectrum shows, however, that $H_x(m)>H_y(m)$ for the four lowest field hyperfine components and that $H_y(m)>H_x(m)$ for the three highest field components. [The remaining component in the TiO_2 spectrum is anomalous in this respect in that $H_x(m)=H_z(m)<H_y(m)$.] Using this line pattern as an approximate model, we find line positions in the GeO_2 spectrum such that $H_x(m)>H_y(m)$ for the five low-field components and $H_y(m)>H_x(m)$ for the remaining three lines. Thus, for each of the eight components in the GeO_2 spectrum, the positions $H_x(m)$ and $H_z(m)$ are extremes, while the corresponding $H_y(m)$ have intermediate positions. This result allows us to distinguish between the $H_x(m)$ and $H_y(m)$ positions in the polycrystalline GeO_2 spectrum. All eight $H_x(m)$ correspond to derivative extrema while all of the $H_y(m)$ correspond to zeros of the spectrum.[17] [For each m value, the extrema corresponding to $H_x(m)$ and $H_z(m)$ will, of course, have opposite signs.]

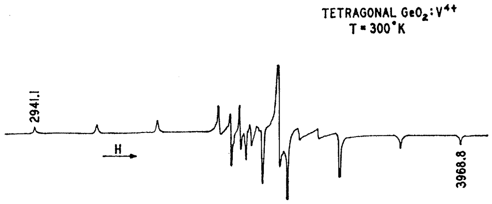

FIG. 2. First derivative recorder tracing of the EPR spectrum of V^{4+} in polycrystalline tetragonal GeO_2. The magnetic field scale is indicated by the values shown for the $H_z(\pm7/2)$ derivative peaks at the extreme ends of the spectrum.

The tetragonal GeO_2 spectrum was decomposed by trial and error, using the two criteria involving line positions and derivative characteristics as described above. Three sets of line positions $H_x(m)$, $H_y(m)$, and $H_z(m)$ were thus obtained which gave the best fit between the experimental and calculated spectra (*vide infra*).

The spin Hamiltonian for V^{4+} in a rhombic crystalline field, when rearranged to yield the line positions $H_z(m)$, was taken as[14]

$$H_z(m)=H_z^0-A_zm-\frac{A_x^2+A_y^2}{4H_z^0}[I(I+1)-m^2], \quad (4)$$

where $H_z^0=h\nu_0/\beta g_z$ and where the other terms have their usual significance. The positions $H_x(m)$ and $H_y(m)$ may also be determined using Eq. (4) upon cyclic permutation of subscripts in this expression.

Our analysis of the data yields the following results:

$g_z=1.963_2\pm0.0003$ $|A_z|=(134.36\pm0.02)\times10^{-4}$ cm^{-1}
$g_x=1.921_3\pm0.0006$ $|A_x|=(\ 36.69\pm0.01)\times10^{-4}$ cm^{-1}
$g_y=1.921_3\pm0.0001$ $|A_y|=(\ 37.54\pm0.01)\times10^{-4}$ cm^{-1}.

For a $3d^1$ ion, the signs of A_x, A_y, and A_z cannot be found from the spectrum due to the absence of fine structure. Thus, only the absolute values of the hyperfine splitting constants are given above.

A comparison of the experimentally determined line positions with those calculated using Eq. (4), etc., and the above values is given in Table I. The close agreement is gratifying considering the complexity of the spectrum and the assumptions used in its decomposition.

C. Hexagonal GeO_2

No EPR spectra were observed at 300 or at 77°K[18] for V-doped polycrystalline hexagonal GeO_2. Hexagonal

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[16] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1960), Vol. II, Chap. IV.

[17] F. K. Kneubühl, J. Chem. Phys. 33, 1074 (1960).

[18] I am indebted to Dr. R. H. Borcherts for the search at 77°K.

TABLE I. Comparison of experimental and calculated absorption-line positions (in gauss) of V^{4+} in polycrystalline tetragonal GeO_2. Operating frequency = 9498.0 Mc/sec, $T = 300°K$.

$H_z(m)$		$H_x(m)$		$H_y(m)$	
Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
2941.1	2942.6	3384.1	3383.0	3382.7	3379.6
3087.3	3087.7	3412.5	3414.0	3410.3	3411.6
3233.9	3233.4	3447.6	3448.3	3445.6	3446.9
3379.8	3379.5	3488.1	3485.9	3486.0	3485.5
3525.9	3526.1	3525.8	3526.9	3527.4	3527.4
3674.2	3673.2	3572.1	3571.1	3573.8	3572.5
3821.0	3820.7	3619.3	3618.5	3622.6	3620.9
3968.8	3968.8	3664.5	3669.3	3668.6	3672.6

GeO_2 crystallizes in the α quartz structure.[3] Thus, assuming that vanadium appears as V^{4+} substituting for Ge^{4+}, the vanadium is tetrahedrally coordinated to four oxygen atoms. This is an interesting contrast with the situation for both tetragonal and amorphous GeO_2 where the vanadium appears in sixfold coordination and for which vanadium EPR spectra are readily observable at room temperature.

IV. DISCUSSION AND CONCLUSIONS

The linear VO^{++} unit appears when a V^{4+} ion forms a strong, double covalent bond with an oxygen ion.[9,19] In chemical combination, the first coordination sphere around the central cation is completed, giving the typical coordination number of six. The V^{4+} ion is presumably situated in the plane of the four nonaxial oxygens, although this seems unlikely because of the asymmetric nature of the axial bonding.

It may seem surprising to find octahedrally coordinated VO^{++} complexes in the tetrahedrally coordinated GeO_2 glass. However, since the glass structure does not have an extended three-dimensional periodicity, the associated requirements for cation coordination are not necessarily so strictly operative as for crystals. Therefore, the presence in the glass of atypical structural units cannot be ruled out *a priori* and, apparently, octahedral coordinated VO^{++} complexes are readily accommodated in the amorphous GeO_2 structure (at least in the small concentrations used in this work).

An optical absorption spectrum was obtained for the amorphous GeO_2 sample using a Beckmann DK-2A spectrophotometer.[20] An absorption peak observed at 13 300 cm^{-1} is taken to be the height of the first excited state, $^2E(I)$, above the ground state, $^2B_2$, in the molecular orbital model[9] of VO^{++}. For this transition, we may write[21,22]

$$g_{\perp} = g_e[1 - \alpha^2(\lambda_0/\Delta)], \qquad (5)$$

where Δ is the energy difference between the $^2B_2$ and $^2E(I)$ levels, g_e is the spin-only g value = 2.0023, λ_0 is the spin-orbit coupling constant for the free ion, and α^2 is a coefficient describing the covalent character of the magnetic ion's bonding. The coefficient α^2 may assume values between 0.5 and 1, the limits for pure covalent and pure ionic bonding, respectively. Since λ_0 is not known for VO^{++}, we may use the λ_0 value[23] for V^{4+} (250 cm^{-1}), since this ion is formally involved in the vanadyl ion structure. Solution of Eq. (5) using the observed values of $g_{\perp}$, Δ, and $\lambda_0 = 250$ cm^{-1} yields $\alpha^2 = 0.69$. This value for the reduction coefficient is similar to those found for other transition-metal ions in various crystals.[13] Thus, the apparent, i.e., effective, spin-orbit coupling constant of VO^{++} (or of V^{4+}) in amorphous GeO_2 is $\lambda = \alpha^2\lambda_0 = 173$ cm^{-1}. The reduction of λ_0 by about 31% indicates[21,22] that the single $3d$ electron from VO^{++} spends about 69% of its time on the magnetic ion and, on the average, about 5% of its time on each of the six oxygen ligands. (Of course, we would expect the electron to spend more time near the vanadyl oxygen than near any of the remaining five oxygen ions.)

For tetragonal GeO_2, we have assumed that vanadium enters the structure as V^{4+} substituting for Ge^{4+} ions. With the low vanadium concentrations used, the occurrence of highly distorted VO^{++} complexes in the crystal would seem to be improbable due to the prevailing symmetry of the crystalline host.

Comparison of Figs. 1 and 2 shows that the polycrystalline tetragonal GeO_2 spectrum is better resolved than is the amorphous spectrum. Both samples, however, are composed of randomly oriented magnetic complexes. The difference in spectral resolution probably results from the presence in the glass of VO^{++} complexes having various degrees (and/or kinds) of distortion.[24] The amorphous GeO_2 spectrum would therefore represent the envelope of individual lines for a random spatial distribution of variously deformed complexes. In the tetragonal GeO_2, however, the octahedral V^{4+} complexes presumably have a more uniform structure thereby leading to a sharper spectrum.

Studies of Mn^{2+} in various host crystals have shown[25,26] that the hyperfine splitting decreases with increasing covalency of the cation bonding. Using this criterion, comparison of the V^{4+} spectra in TiO_2 and in tetragonal GeO_2 indicates that the vanadium bonding is slightly more covalent in the GeO_2. This is consistent with the g values of $V_{.}^{+}$ in the two samples. Also, if we take $g_{\parallel} = g_z$ and $g_{\perp} = \frac{1}{2}(g_x + g_y)$, then $\Delta g = g_{\parallel} - g_{\perp}$ has the same value (0.042) in both cases.

Although the V^{4+} spectrum in TiO_2 is not observable at room temperature,[14,15] the ion's resonance in the isomorphous GeO_2 is readily observable at 300°K. The orbital level schemes in both cases are expected to be the same since both involve a $3d^1$ configuration in octa-

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[19] M. B. Palma-Vittorelli, M. U. Palma, D. Palumbo, and F. Sgarlata, Nuovo Cimento 3, 718 (1956).

[20] F. T. King (unpublished).

[21] J. Owen, Proc. Roy. Soc. (London) **A227**, 183 (1955).

[22] J. Owen, Discussions Faraday Soc. **19**, 127 (1955).

[23] T. M. Dunn, Trans. Faraday Soc. **57**, 1441 (1961).

[24] N. R. Yafaev and Yu. V. Yablokov, Fiz. Tverd. Tela **4**, 1529 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1123 (1962)].

[25] J. S. van Wieringen, Discussions Faraday Soc. **19**, 118 (1955).

[26] On Matumura, J. Phys. Soc. Japan **14**, 108 (1959).

hedral coordination. It is possible that differences in the effective spin-orbit coupling constant for V^{4+} in the two samples (as influenced by the degree of covalent bonding present) may affect the respective spin-lattice relaxation times. However, we would expect differences in electrical conductivity to affect somewhat the results for the two samples.

It would be difficult for octahedrally coordinated VO^{++} complexes to fit into the tetrahedrally coordinated Ge sites in hexagonal GeO_2. However, even if present, we would expect to observe the vanadyl resonance at room temperature. The absence of an observable spectrum at both 300 and 77°K therefore implies the absence of VO^{++} in the hexagonal GeO_2 and suggests that vanadium is present substitutionally as V^{4+} in tetrahedral coordination at Ge sites.

Observable EPR spectra for tetrahedrally coordinated $3d^1$ systems have been found only at reduced temperatures. Carrington *et al.*[27] could observe the spectrum of the manganate ion $(MnO_4)^{2-}$ in Mn-doped K_2CrO_4 only at 20°K or below. The resonance of tetrahedrally coordinated Cr^{5+} in several compounds[28] was observable only "well below 80°K," while V^{4+} in heptane solutions of VCl_4 gave no spectra between 90 and 300°K.[29] Recently, Johannesen and Candela[30] have observed resonance in undiluted VCl_4 at 4°K (but not at 77°K). A spectrum was also obtained for dilute solutions of VCl_4 in $TiCl_4$ at 4°K but this disappeared at approximately 6°K. (However, these workers believe that the disappearance of the vanadium spectrum at 6°K is due probably to cavity detuning rather than to line broadening.)

The above information suggests that very effective relaxation processes are operative in tetrahedrally coordinated $3d^1$ systems. For such systems, departures from cubic symmetry apparently give a first-excited orbital level which lies rather close to the ground state (i.e., $<kT$ at 77°K). The resulting short relaxation times would give absorption lines sufficiently broad to make the resonances observable only at low temperatures.

The amorphous and polycrystalline tetragonal GeO_2 spectra included several apparently extraneous derivative peaks. A spectrum of undoped tetragonal GeO_2 indicated the absence of any paramagnetic impurity which would give an absorption line at 300°K. A spectrum for "undoped" amorphous GeO_2, however, showed a single line 10 G wide with $g_{\parallel}=2.001$ and $g_{\perp}=1.995$ which overlapped the VO^{++} spectrum. The source of this impurity line is unknown, but the line was excluded from the VO^{++} analysis for the amorphous specimen. The remaining extra derivative peaks in our spectra (i.e., those not attributable to impurities), are possibly of the extraneous type first discussed by Neiman and Kivelson[31] and observed also by others.[32] According to Neiman and Kivelson, these additional peaks arise because of certain peculiar properties of the analytic function describing the distribution of magnetic axes in polycrystalline or amorphous solid samples. The extra peaks, if of this origin, probably supply no additional physical information beyond that deducible from the rest of the spectrum. Another possible explanation of the extra peaks is that they are artifacts of the spectra, arising from the fortuitous overlapping of adjacent spectrum features.

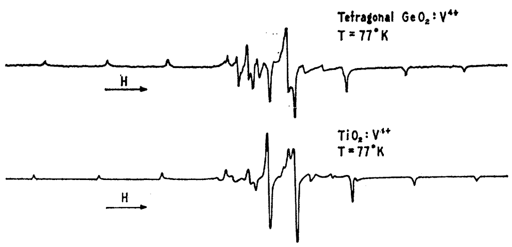

Fig. 3. First derivative recorder tracings of the EPR spectra of polycrystalline tetragonal $GeO_2:V^{4+}$ and polycrystalline $TiO_2:V^{4+}$. Both spectra were obtained at 77°K with $\nu=9043$ Mc/sec.

After completing the analysis of the vanadium-doped tetragonal GeO_2 powder spectrum, a spectrum was run for polycrystalline[33] $TiO_2:V^{4+}$ at 77°K; the GeO_2 sample was run immediately thereafter at the same temperature and operating frequency. The similarity of these two spectra (shown in Fig. 3) appears to substantiate the analysis presented in Sec. IIIB for the GeO_2 spectrum.

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[28] L. L. Van Reijen, P. Cossee, and H. J. van Haren, J. Chem. Phys. **38**, 572 (1963).

[29] J. C. W. Chien and C. R. Boss, J. Am. Chem. Soc. **83**, 3767 (1961).

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