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Electron-Paramagnetic-Resonance Spectrum of Mo^{5+} in $SrTiO_3$—An Example of the Dynamic Jahn-Teller Effect

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The EPR spectrum of Mo^{5+} in $SrTiO_3$ at $T = 1.65$ °K is reported. The spectrum is stable in suitably prepared samples or light-induced (3900–4300-Å light) in photochromic samples, and can only be observed at liquid-helium temperatures. The g tensor is $g_{\parallel} = 1.72$, $g_{\perp} \sim 0$. The hyperfine (hf) constant is $A_{\parallel} = 39 \times 10^{-4}$ cm^{-1}. $A_{\perp}$ was not measured but the hf splitting is not very anisotropic. The linewidth varied from 3 to 8 G for $\vec{H} \parallel \langle 100 \rangle$ direction but broadened to 60 G at $\theta = 60°$. The spectrum cannot be explained by crystal-field theory alone but does fit the dynamic Jahn-Teller effect as calculated by Macfarlane, Wong, and Sturge for the d^1 ions Ti^{3+} and V^{4+} in Al_2O_3. We find a Jahn-Teller energy $E_{JT} = 480$ cm^{-1} for $SrTiO_3 : Mo^{5+}$. To obtain a reasonable first excited state (~ 10 cm^{-1}), a small tetragonal distortion (~ 20 cm^{-1}) must be assumed, as expected for $SrTiO_3$ below the 105 °K phase transition.

I. INTRODUCTION

Our initial interest in the EPR spectrum of Mo^{5+} in $SrTiO_3$ stemmed from its role in the photochromic (PC) process in double-doped Fe : Mo and Ni : Mo in $SrTiO_3$.[1,2] In this process the PC or colored state is achieved via a photoinduced charge transfer between the Fe or Ni ion and the Mo ion, which changes from Mo^{6+} to Mo^{5+}. The above model was determined through a combination of optical and EPR studies under a variety of light irradiations and heat treatments. However, the expected Mo^{5+} EPR resonance was not observed. Mo^{5+} has been observed in other hosts,[3,4] in particular in TiO_2.[5,6] In fact, we observed the expected light-induced Mo^{5+} EPR spectrum in PC TiO_2.[1] In all the aforementioned cases the Mo^{5+} ion was in a site of less-than-cubic symmetry, and the measured g tensors were not too far from the free-spin value of 2. In the case of $TiO_2 : Mo^{5+}$, the interpretation of the g tensor is still uncertain.[6] Since the Ti^{4+} site in $SrTiO_3$ is cubic, except for a small tetragonal distortion[7,8] below the phase transition, and the T_{2g} ground state of a d^1 electronic configuration is not split by a cubic field, the properties of the g tensor are uncertain. The electronic degeneracy should be lifted, however, through the combined action of spin-orbit splitting and the dynamic Jahn-Teller (JT) effect[9] and an EPR spectrum is expected.

We have recently observed an EPR spectrum in $SrTiO_3$: Mo at low temperature which we ascribe to Mo^{5+} in a Ti^{4+} site. The g tensor, which is very anisotropic, can be accounted for by using the theory of the dynamic JT effect for T_2 ions. Two other d^1 ions, Ti^{3+} and V^{4+}, have been studied recently in Al_2O_3,[10–12] and the ground-state g tensor and the first two excited states have been explained in terms of a dynamic JT effect.[11] Mo^{5+} in $SrTiO_3$ can be fitted into the same scheme and provides another interesting example of the dynamic JT effect. It differs from Ti^{3+} and V^{4+} in that the Mo ion is a $4d$ rather than a $3d$ ion and sits in a site with a very small tetragonal distortion rather than the trigonal distortion of Al_2O_3. The distinction is very important for the first-order JT effect.[11] The dynamic JT effect of an E level, Ni^{3+} in $SrTiO_3$, has recently been studied as a function of strain below the phase transition.[13]

In Sec. II we deal with the experimental observations of the Mo^{5+} EPR spectrum. In Sec. III the experimental results are analyzed using the dynamic JT perturbation calculations of Macfarlane *et al.*[11] A discussion follows in Sec. IV and finally the summary, Section V.

II. EXPERIMENTAL RESULTS

The Mo^{5+} EPR spectrum was observed in three different samples, which we shall label A, B, and C. Sample A, which showed the strongest signal, and which was not light dependent, was doped with 0.02% Fe, 0.10% Ni, and 0.40% Mo. All concentrations refer to weight percent of metal oxide added during growth. The crystals were grown for us by the National Lead Co. Spectroscopic analysis of similarly grown crystals shows that the actual concentration can be as low as 20% of the nominal, especially for Ni and Mo, whose oxides are more volatile than the Fe oxide. Sample B was doped with 0.01% Mo and sufficient Al to compensate the Mo so that the $SrTiO_3$ did not become semiconducting. In this sample the resonance was observed only after irradiation with 3900–4300-Å light. Finally, the Mo^{5+} EPR signal was observed in a third sample, C, doped with 0.02% Fe and 0.12% Mo. This last sample is typical of the concentrations used for the PC studies in $SrTiO_3$: Fe,

TABLE I. Observation of Mo^{5+} in $SrTiO_3$. $g_{\parallel}=1.72$, $g_{\perp}\sim 0$, $A_{\parallel}=39\times 10^{-4}$ cm^{-1}, and $T=1.65$ °K.

Sample	Nominal dopant concentration	Conditions for observation	Estimated number of Mo^{5+} spins/cm^3	Linewidth (G) $\vec{H}\parallel\langle 100\rangle$ direction
A	0.02% Fe, 0.10% Ni, 0.40% Mo	Always present	6×10^{18}	8.0
B	0.01% Mo	Only after uv irradiation	4×10^{17}	3–4
C	0.02% Fe, 0.12% Mo	Only after uv irradiation	4×10^{17}	6

Mo.

The experimental results are summarized in Table I. The spectrum could only be observed at very low temperatures. We used $T=1.65$ °K. Even at $T=4.2$ °K, the spin-lattice relaxation is sufficiently rapid to broaden the lines so that the spectrum is unobservable. The lines are sharpest for $\theta=0°$, i.e., $\vec{H}\parallel\langle 100\rangle$ direction. The appearance of the spectrum for this direction of the magnetic field is shown in Fig. 1. Detailed angular data were taken only on sample A. The results are plotted in Fig. 2. Data could not be obtained beyond $\theta=60°$ because the signal deteriorates rapidly off axis and varies rapidly with magnetic field beyond $\theta=60°$. The spectra were taken with a superheterodyne spectrometer and could be observed over a wide range of incident power (10^{-10}–10^{-6} W approximately). The spectrum of sample B (Fig. 1) shows, in addition to Mo^{5+}, some trace impurities of Fe^{3+} and an unknown light-sensitive defect center which will not be discussed in this paper. In this trace, the Fe^{3+} line is highly saturated but the Mo^{5+} signal is not. The Mo^{5+} signal is asymmetrical because of a slight bridge unbalance.

Let us consider sample A in more detail. This sample was chosen because the high Mo concentration resulted in large areas of the crystal having a blue coloration, whereas other regions were clear. The optical absorption in the "blue region" shows a single absorption band with $\lambda_{\text{peak}}=6500$ Å which has previously been identified as Mo^{5+}.[2] We interpret these results as follows. There is more Mo in the crystal boule than can be fully compensated in the form Mo^{6+} by the Fe^{3+} and Ni^{2+} also present. Therefore, some of the Mo will reduce to Mo^{5+}. However, the dopant concentration is not uniform and a concentration variation of 10–20% could account for the formation of clear and "blue" regions. For example, starting with the nominal concentrations and assuming all the Fe but only 25% of the Ni and Mo remain in the boule, we obtain the following results: 0.8×10^{19}-cm^{-3} Fe^{3+}, 1.0×10^{19}-cm^{-3} Ni^{2+}, and 2.0×10^{19}-cm^{-3} Mo. 50% of the Mo could be compensated by Ni^{2+} in the form Mo^{6+}, while the remaining 50% could be compensated by the Fe^{3+} in the form Mo^{5+}. The observation that parts of the crystal are clear and parts are colored would indicate that even less of the nominal Mo is incorporated in the crystal. Actually, we estimate a concentration of 6×10^{18}-cm^{-3} Mo^{5+} centers—based on a measurement of the optical absorption of the sample used in these experiments, together with the previously calculated oscillator strength for the Mo^{5+} transition.[2] It is interesting that in sample B, where the concentration is a factor of 10 lower, the linewidth at $\theta=0°$ is also less.

The identification of the spectrum as Mo^{5+} in a Ti^{4+} site is made on the following bases.

(a) The six-line hyperfine (hf) spectrum is what is expected for Mo^{5+}. For the three examples of Mo^{5+} cited in the references,[3–6] the average hf constant $\frac{1}{3}(A_{\parallel}+2A_{\perp})$, is approximately 47, 51, and 41×10^{-4} cm^{-1} for $K(InCl_6)\cdot 2H_2O:(MoCl_6)$, K_2SnCl_6: Mo, and TiO_2: Mo, respectively. For $SrTiO_3$: Mo we find approximately $A_{\parallel}=39\times 10^{-4}$ cm^{-1} and $A(\theta=60°)=44\times 10^{-4}$ cm^{-1}, after the experimental splitting is corrected for the low g value. Therefore, the average for $SrTiO_3$ is quite close to that found for TiO_2. The ratio of the amplitude of the hf lines to the main line is 5%, which is cor-

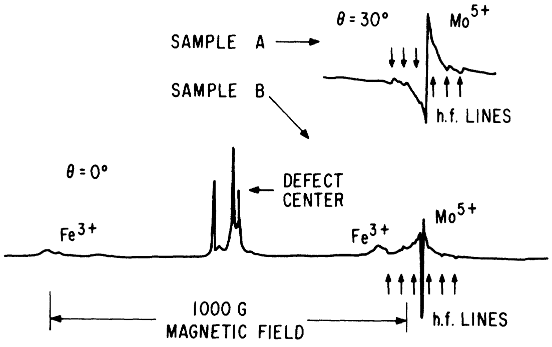

FIG. 1. EPR spectrum of Mo^{5+} in $SrTiO_3$ at $T=1.65$ °K. θ is the angle the magnetic field makes with the [100] direction while rotating in the (001) plane. The spectrum in sample A is stable. The Mo^{5+} spectrum in sample B appears after irradiation with 3900- to 4300-Å light.

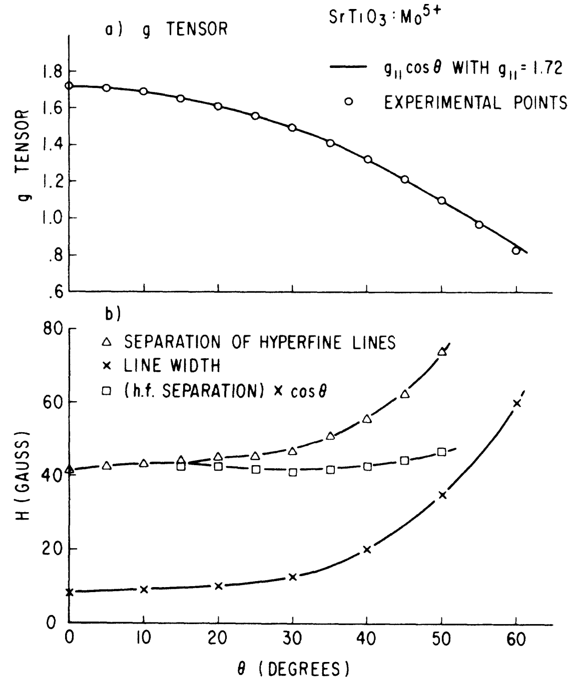

FIG. 2. Angular variation of (a) g tensor, (b) hf separation and linewidth. $\theta=0°$ corresponds to $\vec{H}\parallel[100]$ direction. Magnetic field is rotated in the (001) plane. $T=1.65\,°K$. Data taken on sample A.

rect for Mo^{5+}, since the hf splittings for Mo^{97} and Mo^{95} are not resolved.

(b) The presence of Mo^{5+} in $SrTiO_3$, for identical experimental conditions for which the present EPR spectrum is observed, has already been inferred from the study of the PC effect.

(c) Mo^{5+} should be a good fit to the Ti^{4+} site and indeed it is found to substitute for Ti^{4+} in TiO_2.[5,6]

(d) The g tensor can be explained in terms of a dynamic JT effect of a d^1 ion in a cubic environment with a very small tetragonal distortion. The only other possible site for the Mo ion is the Sr^{2+} site, which has a lower symmetry. In fact, the EPR spectrum of Ti^{3+}, another d^1 ion, has been reported in $SrTiO_3$.[14] The g tensor which is completely different from the one reported here is explained by assuming that the Ti^{3+} substitutes a Sr^{2+} site. If the Ti^{3+} were on a Ti^{4+} site, its g tensor should be similar to the one reported here.

The behavior of the spectrum of sample A off axis is shown in Fig. 2, where the magnetic field is rotated in the {001} plane. It is seen that the experimental points follow the curve $g_{\parallel}\cos\theta$ quite well. We infer that $g_{\parallel}=1.72$ and $g_{\perp}<0.1$. In Fig. 2(b) we show the behavior of the hyperfine separation and the linewidth. If the hyperfine splitting is multiplied by $g_{\parallel}\cos\theta$ to convert to energy, it remains fairly constant at $A=39\times10^{-4}\ cm^{-1}$ although the value at $\theta=60°$ is 10% higher than this. Our data are not sufficiently accurate to determine the anisotropy in the hyperfine tensor.

The increase in linewidth off axis cannot be explained in the same way. Even if the measured linewidth in gauss is multiplied by $g_{\parallel}\cos\theta$, a large increase with angle remains. This was also found by Kask *et al.*[10] for Ti^{3+} in Al_2O_3.

III. DYNAMIC JAHN-TELLER EFFECT

The g tensor for Mo^{5+} cannot be explained by crystal-field theory alone, even including a covalency orbital-reduction factor. The crystal-field solution for a d^1 state in a cubic field with spin-orbit coupling plus a trigonal or tetragonal distortion has been obtained by Bleaney.[15] The energy-level scheme is shown in Fig. 3. The solution is the same for trigonal or tetragonal distortion except that the sign of δ_1 is reversed. However, either distortion (trigonal or tetragonal) may have either sign and this is usually determined experimentally. No assumption is made about the relative size of the axial-field splitting and the spin-orbit splitting, as long as both are small compared with the cubic-field splitting Δ. For this reason we have not labeled the final states using crystal-symmetry labels. Rather, the three states derived from the T_{2g} term are labeled A, B, and C following Bleaney's notation. The g tensor differs greatly depending on the sign of δ_1. For one choice of sign, the level B is lowest. For this case, when the axial-field parameter v is large compared with the spin-orbit splitting ζ, both $g_{\parallel}$ and $g_{\perp}$ are close to 2, the spin-only value. As v/ζ is reduced $g_{\parallel}$ and $g_{\perp}$ follow an elliptical curve on a $g_{\parallel}$-versus-$g_{\perp}$ plot, passing through $g_{\parallel}=g_{\perp}=0$ when $v=0$ (cubic symmetry). This model was used by Bleaney to

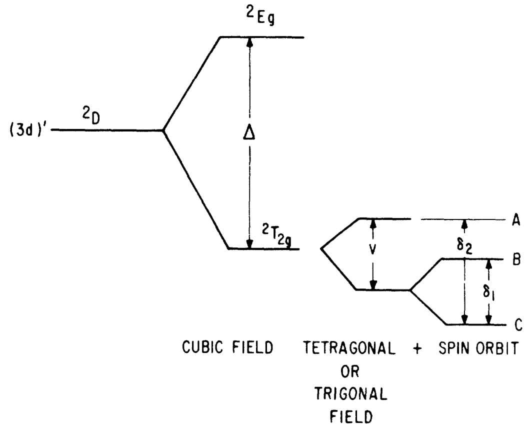

FIG. 3. Energy-level splitting of a d^1 ion in a cubic field (splitting Δ), and a small tetragonal or trigonal distortion (splitting v) and spin-orbit coupling. No assumption is made about the relative size of the axial distortion and the spin-orbit splitting.

fit the g tensor of Ti^{3+} in cesium titanium alum, which has the values $g_{\parallel} = 1.25$ and $g_{\perp} = 1.14$. No value of v/ζ from 0 to ∞ fits the data for Mo^{5+}. However, when v/ζ has the opposite sign, state C is lowest and $g_{\parallel} = g_{\perp} = 0$ for all values of v/ζ. In an orbital-reduction factor k is included, the g tensor becomes

$$g_{\parallel} = 2(1-k) , \quad g_{\perp} = 0 . \tag{1}$$

It is not reasonable to take k less than about 0.8 due to covalency alone.[11] Therefore we have $g_{\parallel} = 0.4$ and $g_{\perp} = 0$. If the interaction with the cubic-field-split E_g states is taken into account,[11] the crystal-field-only g tensor becomes $g_{\parallel} = 0.54$ and $g_{\perp} = 0$.

This is the starting point of Macfarlane *et al.*,[11] who consider the dynamic JT effect of the d^1 ions Ti^{3+} and V^{4+} in Al_2O_3. We will show that a reasonable fit for Mo^{5+} can be obtained using their formulation even though the ions observed in Al_2O_3 sit in a cubic crystal field with a trigonal distortion of approximately $v = 700\ \text{cm}^{-1}$, whereas Mo^{5+} sits in a cubic field with only a very small tetragonal perturbation below the lattice phase transition at 105 °K.

Macfarlane *et al.*[11] used perturbation theory to calculate the g tensor of a d^1 ion in the presence of spin-orbit coupling and a small trigonal field, through the mechanism of the dynamic JT effect. This calculation successfully fits the experimentally determined g tensor and the position of the two excited states δ_1 and δ_2 (see Fig. 3) for Ti^{3+} in Al_2O_3. They also predicted the g tensor for V^{4+} which was quite close to the subsequently measured value.[12] The magnitudes of the relevant parameters assumed by Macfarlane *et al.* which apply to $Al_2O_3 : Ti^{3+}$ are $v = 700\ \text{cm}^{-1}$ for the trigonal field splitting and $\zeta = 120\ \text{cm}^{-1}$ for the spin-orbit coupling. This assumes that ζ is reduced 20% from the free-ion value. $\hbar\omega = 200\ \text{cm}^{-1}$, where ω is an effective frequency of the E_g mode of the octahedral complex surrounding the Ti^{3+} ion.[16] Finally, $k = 0.80$ is the orbital-reduction factor. Using these values, their best fit to the data is obtained if $E_{JT} = 200\ \text{cm}^{-1}$ and $\gamma = \exp(-3E_{JT}/2\hbar\omega) = 0.21$.

According to Macfarlane *et al.*,[11] the g tensor and the position of the two excited levels can be written

$$\begin{aligned} &g_{\perp} = 0 \ \text{(by symmetry)} , \\ &g_{\parallel} = 2 - (2k/\hbar\omega)(a^2+b^2)^{1/2} , \end{aligned} \tag{2}$$

$$\delta_1 = \gamma(\tfrac{1}{2}v + \tfrac{3}{4}\zeta) + (f_a/\hbar\omega)(-\tfrac{3}{8}\zeta^2 + \tfrac{1}{2}\zeta v - \tfrac{1}{6}v^2) - \tfrac{1}{2}A , \tag{3a}$$

$$\delta_2 = \delta_1 + A , \tag{3b}$$

where

$$A^2 = \gamma^2(v^2 - \zeta v + \tfrac{9}{4}\zeta^2) + (f_a/\hbar\omega)^2(\tfrac{1}{9}v^4 + \tfrac{2}{9}v^3\zeta + \tfrac{1}{6}\zeta^3 v^3 + \tfrac{1}{2}\zeta^3 v + \tfrac{9}{16}\zeta^4) - (\gamma f_a/\hbar\omega)(\tfrac{2}{3}v^3 + \tfrac{1}{3}v^2\zeta + \tfrac{1}{2}\zeta^2 v + \tfrac{9}{4}\zeta^3)$$

and

$$\begin{aligned} &a = -\tfrac{2}{9}\zeta f_b - \tfrac{7}{9}\zeta f_a - \tfrac{2}{3}v f_a - \gamma\hbar\omega , \\ &b = \tfrac{1}{9}\sqrt{2}\,\zeta(f_b - f_a) , \end{aligned}$$

where γ, f_a, and f_b are all functions of $x = 3E_{JT}/2\hbar\omega$ introduced by Ham[9] and defined by him. They are essentially overlap integrals of the vibronic wave functions and effectively reduce the matrix elements of the spin-orbit-and axial-field-splitting operators. If only the first-order JT effect is considered, only γ appears in the theory and multiplies off-diagonal matrix elements such as the angular momentum and trigonal-field-splitting operators. A tetragonal-field splitting is diagonal in the T_{2g} representation and does not get multiplied by γ. If the second-order perturbation due to the first excited vibronic level ($E = \hbar\omega$) is considered, f_a and f_b appear in the perturbation matrix. In the limit of large x (static JT effect), γ and f_a approach zero as $e^{-x/2}$ or faster, whereas $f_b \sim 1/x$ is the only term which survives. Macfarlane *et al.* found for Ti^{3+}, $\gamma = 0.21$, $f_a = 0.11$, $f_b = 0.41$, $g_{\parallel} = 1.14$, $g_{\perp} = 0$, $\delta_1 = 43\ \text{cm}^{-1}$, and $\delta_2 = 107\ \text{cm}^{-1}$.

Such a detailed calculation is probably not justified in the present case, since we do not know the position of the excited levels δ_1 and δ_2. However, we could try to adapt the calculation of Macfarlane *et al.* to the case of Mo^{5+} in $SrTiO_3$ to see if it can reasonably account for our results. First we shall neglect the small tetragonal distortion in $SrTiO_3$ below the phase transition. Equations (2) and (3) should apply with $v = 0$ (no trigonal field). The free-ion spin-orbit coupling of Mo^{5+} is approximately $1000\ \text{cm}^{-1}$, considerably greater than Ti^{3+}. We assume, following Ref. 11, a 20% reduction from the free-ion value in the solid, i.e., $\zeta = 800\ \text{cm}^{-1}$. In spite of the larger spin-orbit coupling, the orbital contribution to the g tensor is more strongly quenched ($g_{\parallel}$ closer to 2, the spin-only value) than either Ti^{3+} or V^{4+} in Al_2O_3. Hence, the g tensor can only be fitted by assuming a larger value of x. This simplifies things since under these conditions $2 - g_{\parallel}$ depends primarily on f_b rather than γ or f_a, so that

$$2 - g_{\parallel} \sim \frac{2k}{\hbar\omega}\,\frac{\sqrt{6}}{9}\,\zeta f_b . \tag{4}$$

To determine f_b and hence x we need to know $\hbar\omega$, the frequency of the E_g phonon mode that couples to the T_{2g} electronic term. Macfarlane *et al.* find for both the TiO_6 and VO_6 complex in Al_2O_3, $\hbar\omega = 200\ \text{cm}^{-1}$. The MoO_6 complex should be quite similar in $SrTiO_3$. The average metal-ion–oxygen distance differs by only a few percent, and if a 200-cm^{-1} E_g mode exists in Al_2O_3, it is reasonable to assume a similar mode, perhaps shifted slightly,

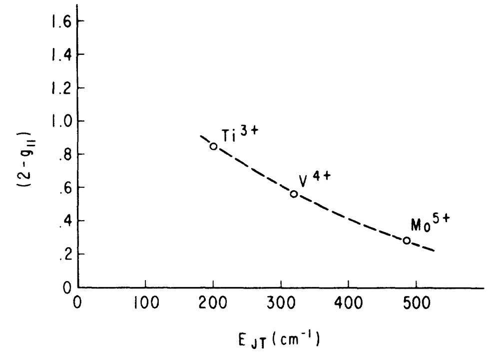

FIG. 4. Schematic diagram of the variation of $2-g_{\parallel}$ and E_{JT} (Jahn-Teller energy) for Ti^{3+} and V^{4+} in Al_2O_3 (Ref. 11) and Mo^{5+} in $SrTiO_3$. $2-g_{\parallel}$ is experimental and E_{JT} is calculated.

in $SrTiO_3$. Therefore we assume that $k=0.8$ (assumed orbital reduction due to covalency), $\hbar\omega = 200$ cm^{-1} (same as Al_2O_3), $\zeta = 800$ cm^{-1} (reduced from free-ion value of 1000 cm^{-1}), and $2-g_{\parallel} = 0.28$ (experimental value). Therefore $f_b = 0.16$, $x = 7.25 = 3E_{JT}/\hbar\omega$, and $E_{JT} = 480$ cm^{-1}. In addition, $\gamma = 0.026$ and $f_a = 0.01$, although their values do not affect the value of $2-g_{\parallel}$. A plot of $2-g_{\parallel}$ versus E_{JT} for Ti^{3+}, V^{4+}, and Mo^{5+} is shown in Fig. 4. The value of E_{JT} will not be greatly affected by the uncertainty of $\hbar\omega$. If $\hbar\omega$ were considerably smaller, then $x \gg 1$, and $f_b \sim 1/x = \hbar\omega/3E_{JT}$. In this case $E_{JT} = 415$ cm^{-1} independent of the assumed value of $\hbar\omega$.

We can estimate the energy of the first excited state. Using Eq. (3) with $v=0$, $\zeta = 800$ cm^{-1}, $\gamma = 0.026$, $f_a = 0.01$, and $\hbar\omega = 200$, we find $\delta_1 = 1.4$ cm^{-1} and $\delta_2 = 5.8$ cm^{-1}. These values are too low. The EPR of the gound state would not be observable with such low-lying excited states. The values of δ_1 found for Ti^{3+} and V^{4+} in Al_2O_3 are 28 and 37 cm^{-1}, respectively. There is some indication of a low-lying level in Mo^{5+}. The EPR is only observable at low temperature and the resonance saturates at a much higher power level (approximately 10^3 times higher) than the Fe^{3+} resonance. Both facts are indicative of a fast relaxation which could be due to a low-lying excited state, via the Orbach mechanism.[17]

However, the Ti^{4+} site is not exactly cubic below the phase transition, but has a small tetragonal distortion. The crystal-field splitting due to this distortion will be much smaller than the spin-orbit-coupling constant, $\zeta = 800$ cm^{-1}, or the trigonal-field parameter used in the Al_2O_3 calculation, $v = 700$ cm^{-1}. But first-order matrix elements of a tetragonal distortion are diagonal in the perturbation Hamiltonian used and so will not be reduced by γ (no Ham effect). Slonczewski *et al.*[13] in their discussion of the strain-dependent JT effect in $SrTiO_3:Ni^{3+}$ estimate the size of this tetragonal splitting. They obtain a lowering of the JT minima by 23 cm^{-1} at $T = 0$ °K due to the strain associated with the tetragonal distortion. Slonczewski *et al.* introduce a strain term into the JT perturbation Hamiltonian, but also point out that Ham[18] has shown that this is equivalent to a strain-dependent crystalline field,

$$H = V_2\epsilon \ ,$$

where

$$V_2 = 3\times 10^4 \text{ cm}^{-1} \text{ for } SrTiO_3 \ ,$$

$$\epsilon = 8\times 10^{-4} = \text{strain at } 1.6\ ^\circ\text{K} \ .$$

This produces a shift in energy $E \approx 24$ cm^{-1}. Therefore, we will take $v_{tet} = 24$ cm^{-1}. On the other hand, the matrix elements of the spin-orbit operator are still off diagonal in first order and their contribution to the energy will be of the form $\gamma\zeta = 0.026 \times 800 = 20.8$ cm^{-1}. Thus, the reduced spin-orbit matrix elements and the (unreduced) tetragonal-field contribution are the same order of magnitude.

Let us estimate δ_1 using Eq. (3) by substituting $\gamma v \equiv v_{tet}$ in the first-order contribution, and setting $v=0$ in the second-order terms $[\sim f_a/\hbar\omega$ or $(f_a/\hbar\omega)^2]$. This procedure may be justified since the second-order contribution comes from diagonal terms where the spin-orbit interaction is much larger than v_{tet}. We have

$$\delta_1 = \tfrac{1}{2}v_{tet} + \tfrac{3}{4}\gamma\zeta - \tfrac{3}{8}(f_a/\hbar\omega)\zeta^2 - \tfrac{1}{2}A \ , \qquad (5)$$

where

$$A^2 = [v_{tet}^2 - v_{tet}(\gamma\zeta) + \tfrac{9}{4}(\gamma\zeta)^2] + (f_a/\hbar\omega)^2 \tfrac{9}{16}\zeta^4 - (\gamma f_a/\hbar\omega)\tfrac{9}{4}\zeta^3 \ ,$$

$v_{tet} = 24$ cm^{-1}, $\zeta = 800$ cm^{-1}, $\gamma\zeta = 20.8$ cm^{-1}, $f_a = 0.01$, $\gamma = 0.026$, and $\hbar\omega = 200$ cm^{-1}. Putting those numbers into Eq. (5), we find $\delta_1 = 10.6$ cm^{-1}. This value of

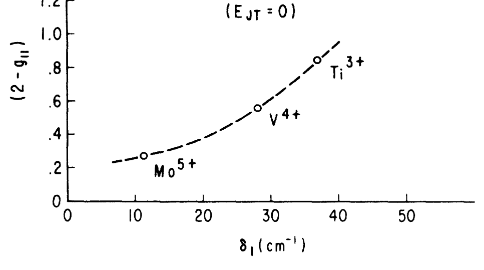

FIG. 5. Schematic diagram of the variation of $2-g_{\parallel}$ and δ_1, the first excited state for Ti^{3+} and V^{4+} in Al_2O_3 (Ref. 11) and Mo^{5+} in $SrTiO_3$. The data for Ti^{3+} and V^{4+} are experimental. δ_1 for Mo^{5+} is calculated.

TABLE II. Comparison of $SrTiO_3:Mo^{5+}$ with other d^1 ions exhibiting dynamic Jahn-Teller effects.

Ion	Host	Site symmetry	Estimated[a] spin-orbit splitting of ion in solid (cm^{-1})	g tensor[b] $g_\parallel$	$g_\perp$	Linewidth (G)	Position of first and second excited states (cm^{-1})	E_{JT} (cm^{-1})	$x = \frac{3E_{JT}}{2\hbar\omega}$
Ti^{3+}	Al_2O_3	cubic + trigonal ($v \sim 700$ cm^{-1})	120	1.11	0	40	37.8, 107.5	200	3.0
V^{4+}	Al_2O_3	cubic + trigonal ($v \sim 700$ cm^{-1})	200	1.43	0	not observed	28, 52.8	320	4.8
Mo^{5+}	$SrTiO_3$	cubic + small tetragonal ($v_{tet} \sim 24$ cm^{-1})	800	1.72	0	5	10.6, 21.6[c]	480	7.3[d]

[a] 80% of free-ion value.

[b] According to Reference 11, the crystal-field-only g tensor (no JT effect) would be $g_\parallel = 0.56$, $g_\perp = 0$.

[c] Values for Mo^{5+} are only an estimate, not experimentally measured.

[d] This assumes $\hbar\omega = 200$ cm^{-1} in $SrTiO_3$ just as in Al_2O_3.

δ_1 is subject to some uncertainty both in the value of v_{tet} and in the procedure used to calculate it. We have not really demonstrated that v_{tet} makes no contribution to the second-order correction to the energy. Figure 5 shows the variation of $2 - g_\parallel$ and δ_1 for the three ions Ti^{3+}, V^{4+}, and Mo^{5+}. The estimate of δ_1 is probably a lower limit, since a smaller value would significantly increase the spin-lattice relaxation rate through the Orbach mechanism.

A summary of the results for Mo^{5+} compared with Ti^{3+} and V^{4+} is shown in Table II.

IV. DISCUSSION

We have tried to fit the g tensor for Mo^{5+} in $SrTiO_3$ to the theory developed by Macfarlane *et al.* to explain Ti^{3+} and V^{4+} in Al_2O_3. Unfortunately there is really only one experimental datum, namely, $g_\parallel = 1.72$, and many parameters in the theory, so that this does not constitute a good test of the theory. However, the experimental g tensor is very different from the crystal-field-only value and our choices of parameters are reasonable and consistent with those of Macfarlane *et al.* Therefore, we think that the explanation in terms of the dynamic JT effect is correct but more experimental work is needed. It would be especially useful to measure the position of the two excited levels δ_1 and δ_2.

It would also be of interest to measure other d^1 ions in $SrTiO_3$ to obtain a better check on the theory of Macfarlane *et al.* Ti^{3+} has been observed in $SrTiO_3$[14] but not on a Ti^{4+} site. With suitable heat treatment, it may be possible to obtain Ti^{3+} on the Ti^{4+} site. If further experimental work is done, then the theory of the dynamic JT effect with small tetragonal distortions would have to be examined more carefully. By studing the g tensor as a function of temperature, the strain-dependent tetragonal distortion would vary just as in the case of $SrTiO_3:Ni^{3+}$.[13] In this case, however, the g tensor would not change, but only the excited levels δ_1 and δ_2. A more detailed study of the hyperfine structure could yield additional information.

A word should be said about the validity of perturbation theory in the present case. Ham[18] has criticized the use of perturbation theory by Macfarlane *et al.* in the case of Ti^{3+} in Al_2O_3 on the grounds that, in order for the perturbation theory to be valid, one should have δ, $v \ll 3E_{JT}$. However, in their case $v = 700$ $cm^{-1} > 3E_{JT} = 600$ cm^{-1}. Nevertheless, Ham further states in the same article that preliminary results of more exact calculations[19] indicate that only modest adjustments need be made to the parameters determined by Macfarlane *et al.* The same criticism and presumably the same reprieve apply to Mo^{5+} in $SrTiO_3$. In this case $\lambda = 800$ cm^{-1}, which is not very much smaller than $3E_{JT} = 1440$ cm^{-1}.

V. SUMMARY

We have demonstrated that the EPR spectrum reported here is due to Mo^{5+} on the Ti^{4+} site. The spectrum is observable only at low temperature, indicating a low-lying excited state. The g tensor cannot be explained by crystal-field theory alone, but fits well into the dynamic JT scheme developed by Macfarlane *et al.* to account for the EPR spectra of Ti^{3+} and V^{4+} in Al_2O_3. A close check of the theory is not possible, because the theory contains too many adjustable parameters for the amount of experimental data available. Further experimental and theoretical work on d^1 ions in $SrTiO_3$ would be useful for further development of the theory of the dynamic JT effect in degenerate T_{2g} states.

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Further Measurements of Absolute Signs of Second-Harmonic-Generation Coefficients of Piezoelectric Crystals

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The signs of the second-harmonic-generation (SHG) coefficients have been determined for SiC ($d_{31}+$, $d_{33}-$), $AgGaS_2$ ($d_{36}+$), $ZnGeP_2$ ($d_{36}+$), $PbTiO_3$ ($d_{31}-$, $d_{33}+$), $Ba_{0.5}Sr_{0.5}Nb_2O_6$ ($d_{31}-$, $d_{33}-$), and $PbNb_4O_{11}$ ($d_{32}-$, $d_{33}-$). Where comparisons between theory and experiment can be made, the agreement is good except for $PbTiO_3$. In addition, the phases of the SHG coefficients for CdTe, CdSe, and ZnTe have been redetermined in a spectral region where the crystals are transparent and the phases were found to agree with expectations—all d's positive except d_{31} for CdSe.

I. INTRODUCTION

This paper describes some recent determinations of the absolute signs of the second-harmonic-generation (SHG) coefficients d_{ij} of a number of piezoelectric crystals not previously measured. In addition, some crystals studied earlier[1] in spectral regions in which the nonlinear coefficients were found to be complex (presumably due to absorption effects) have been remeasured at longer wavelengths where these effects are expected to be absent. Of particular interest are the results on SiC, $PbTiO_3$, and $AgGaS_2$, all of which are relevant to important tests of the theories of d_{ij}.

The more successful of the earlier theories which considered the absolute signs and magnitudes of the SHG coefficients treated the tetrahedrally coordinated compounds (e.g., III-V compounds) and predicted positive bond nonlinearities with the positive direction defined from the metal to the nonmetal atom.[2–4] Subsequently, a dependence of the nonlinearity on the relative covalent radii of the two atoms making up the bond was presented by Levine[5] to explain the negative d_{33}'s observed for ZnO, $LiGaO_2$, and BeO, the $+d_{11}$ for SiO_2,[1] and the observed signs for both d's of potassium dihydrogen phosphate (KDP).[6] This theory also predicts a negative d_{33} for SiC.[5]

More recently it has been reported that d_{14} for CuCl is negative,[7] and hence in conflict with Refs. 2–5. It is well known that the $3d$ electrons in Cu are close in energy to the $4s$ electrons and may therefore influence the magnitude and sign of the nonlinearity of Cu-containing compounds.[8–10] A somewhat similar situation exists between the $5s$ and $4d$ electrons in Ag; hence the interest in $AgGaS_2$.[8–10] Most recently Levine has shown[10] how to include contributions to the nonlinear susceptibility from the d electrons of Cu- and Ag-containing compounds. In particular, d_{14} for CuCl is predicted to be minus (as observed), and d_{36} for $AgGaS_2$ is expected to be positive.

Ferroelectric crystals $BaTiO_3$ and $PbTiO_3$ are isomorphous at room temperature; however, $PbTiO_3$ is characterized by an unusually large displacement of the Pb^{2+} ions from their paraelectric prototype positions.[11,12] The contribution of the Pb^{2+} ions to the nonlinearity of $PbTiO_3$ may there-