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Electron paramagnetic resonance of three manganese centers in reduced $SrTiO_3$†

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Three paramagnetic centers associated with manganese substituting for Ti^{4+} have been observed at 300 K by EPR in reduced crystals of $SrTiO_3$. The first is a Mn^{2+} ion having cubic symmetry, with isotropic g and A values given by $g = 2.0036 \pm 0.0005$ and $A = (82.6 \pm 0.1) \times 10^{-4}$ cm^{-1}. The second center is characterized by an axially symmetric EPR spectrum with effective g values of $g_{\parallel}^{e} \cong 2.00$ and $g_{\perp}^{e} \cong 5.9$ at X band. The spectrum is attributed to $\Delta M = \pm 1$ transitions between the $S_z = \pm 1/2$ levels of a Mn^{2+} ion located in a strong tetragonal crystalline field. The tetragonal field presumably arises from a nearest-neighbor oxygen vacancy, hence we designate it as Mn^{2+}-V_O, in analogy with the previously investigated Fe^{3+}-V_O center. An exact computer diagonalization of the $S = 5/2$ matrix, together with data on a second fine-structure transition, yielded a zero-field splitting parameter $|2D''| = 1.088 \pm 0.0010$ cm^{-1}, and g values of $g_{\perp} = 2.0030 \pm 0.0005$ and $g_{\perp} = 2.0082 \pm 0.0060$. The hyperfine-structure splitting parameters were determined to be $A = (76 \pm 1) \times 10^{-4}$ cm^{-1} and $B = (65 \pm 1) \times 10^{-4}$ cm^{-1}. The normally forbidden $\Delta m = \pm 1$ transitions were also observed for this center, and their separations are consistent with an $S = 5/2$ formalism. The third paramagnetic center also gives rise to a highly-anisotropic spectrum with effective g values of $g_{\parallel}^{e} = 7.945 \pm 0.001$ and $g_{\perp}^{e} < 0.4$, and a hyperfine constant $A = (37.3 \pm 0.1) \times 10^{-4}$ cm^{-1}. The center is assigned to a Mn^{3+} ion associated with a nearest-neighbor oxygen vacancy, hence we designate it as Mn^{3+}-V_O. The one fine-structure transition observed is assigned to occur between the $M = \pm 2$ levels of $Mn^{3+}(3d^4, S = 2)$. By careful measurements at X- and K-band frequencies, the cubic zero-field splitting between these levels was determined to be $a = 0.054 \pm 0.001$ cm^{-1}.

I. INTRODUCTION

A variety of transition-metal ions can be incorporated in the diamagnetic ABO_3 perovskite structures. Since the ionic radius of the A site is about twice that of the B site, ions from the iron-group series normally substitute at the B sites, while ions from the rare-earth series substitute at A sites. Previous investigations have shown that both divalent and trivalent states of substitutional iron-group ions can be charge compensated by a nearest-neighbor oxygen vacancy. These centers include the ion-vacancy pairs $Fe^{3+} - V_O$ in $SrTiO_3$,[1,2] $KTaO_3$,[3] and $BaTiO_3$,[4] $Co^{2+} - V_O$ in $SrTiO_3$,[5] and $KTaO_3$,[6] and $Ni^{3+} - V_O$ in $SrTiO_3$.[7] Recently, the $Fe^{3+} - V_O$ pair center in $SrTiO_3$ was used as a probe to study critical phenomena near the cubic-tetragonal structural phase transition at 105 K.[8-10] One of the interesting features of this center which makes it a sensitive probe for these studies is the large axial crystalline-field splitting.[1,2]

This paper presents some results on the EPR spectra associated with three manganese centers in reduced crystals of manganese-doped $SrTiO_3$.[11] An earlier EPR investigation[12] on *as-grown* (oxidized) crystals of manganese-doped $SrTiO_3$ reported an isotropic sextet of lines characterized by the parameters $g = 1.994$ and $A = 69.4 \times 10^{-4}$ cm^{-1}. This spectrum has been attributed to $Mn^{4+}(3d^3, S = \frac{3}{2})$ substitutional for Ti^{4+}. In this investigation, we provide evidence that the process of heating such a crystal in a reducing atmosphere for several hours converts the Mn^{4+} into lower charge states, namely, Mn^{3+} and Mn^{2+}. This conversion, observed directly by EPR, is based on the disappearance of the Mn^{4+} *cubic* spectrum after reduction with a corresponding appearance of several new spectra associated with manganese. The reduction process produces oxygen vacancies which can act as charge compensators for the trivalent and divalent impurity ions. Two types of Mn^{2+} centers are observed, one having approximately cubic symmetry and the other axial symmetry about one of the cube edges. The *cubic* Mn^{2+} center, which is observed abouve 105 K (the temperature of the cubic-tetragonal phase transition) is assigned to $Mn^{2+}(3d^5, S = \frac{5}{2})$ substitutional for Ti^{4+} with no local charge compensator. The second Mn^{2+} center is characterized by a highly anisotropic fine structure transition with *effective g* values of $g_\parallel^e = 2$ and $g_\perp^e = 5.9$ at 3 cm wavelength. Analysis of these data suggests that the center is due to Mn^{2+} in a field of tetragonal symmetry. The large zero-field splitting is believed to be associated with a nearest-neighbor oxygen vacancy which acts as a local charge compensator. Hence, the center is called the Mn^{2+}-V_O pair center, which is isoelectronic with the Fe^{3+}-V_O center.[1,2] Finally, we have observed a second, highly anisotropic EPR spectrum whose effective g values are given by $g_\parallel^e \cong 8$ and $g_\perp^e < 0.4$. This spectrum is believed to be associated with a transition between the $M = \pm 2$ levels of $Mn^{3+}(3d^4, S = 2)$ situated in a crystalline field of lower than cubic symmetry. Further experimental data suggest that the Mn^{3+} ions observed with EPR are also charge compensated by a nearest-neighbor oxygen vacancy, which in turn produces a large crystal-field splitting. This Mn^{3+}-V_O center is thus isoelectronic with the most recently found Fe^{4+}-V_O center in $SrTiO_3$,[13] with the same fine-structure anisotropy.

II. EXPERIMENTAL PROCEDURE

EPR data were taken with two spectrometers operating at wavelengths of 1.65 and 3 cm. The K-band spectrometer utilized superheterodyne detection at 30 MHz, while the X-band spectrometer (Varian E-9) utilized the 100-kHz detection scheme.[14] Magnetic field strengths were measured with a proton resonance magnetometer. Microwave frequencies were determined using a neutron-irradiated LiF sample as a reference g marker. Most of the data were taken at room temperature, although the intensity of the Mn^{3+} center was greatly enhanced at 4.2 K. Below 105 K, the temperature of the cubic-to-tetragonal phase transition, the EPR spectrum in the region of $g = 2$ was much more complex than the spectrum above this temperature. This is to be expected, owing to the lower symmetry of the crystal below 105 K and the formation of domains.[2]

Single crystals of $SrTiO_3$ were cut from boules grown by the National Lead Co., using the Verneuil flame-fusion technique. These boules were nominally doped with 0.48 at.% manganese. Experimental data were taken with the dc magnetic field rotated in the (001) plane and the (011) plane of the crystal. Crystal orientations were established using the cubic Fe^{3+} spectral lines as references. The crystals were reduced by heating to 1000 °C in an atmosphere of 5% hydrogen and 95% nitrogen for about 3 h. These were then slowly cooled to room temperature in the same atmosphere. It is interesting to note that the Mn^{2+}-V_O center was not observed in those crystals where reduction was incomplete as evidenced by the presence of some residual Mn^{4+} spectral intensity.[12] Therefore, care was necessary in selecting crystals which were well reduced for the study of the Mn^{2+}-V_O center. Such crystals show an intense Mn^{2+} cubic spectrum, no Mn^{4+} spectrum, and an Mn^{2+}-V_O spectrum whose intensity is typically 50 times weaker than the Mn^{2+} cubic spectrum. Typical room-temperature EPR spectra of the reduced crystals are shown in Fig. 1. These data were recorded at X band with the Zeeman field along the [100] and [110] directions. Optical absorption measurements on *as-grown* and reduced samples tallied with the EPR measurements.[15] The *as-grown* crystals showed a strong absorption at 2.2 eV resulting from a transition of Mn^{4+}. In the reduced crystals, this transition was less intense, and a new absorption band at 2.5 eV was observed, presumably due to a transition of Mn^{3+}.

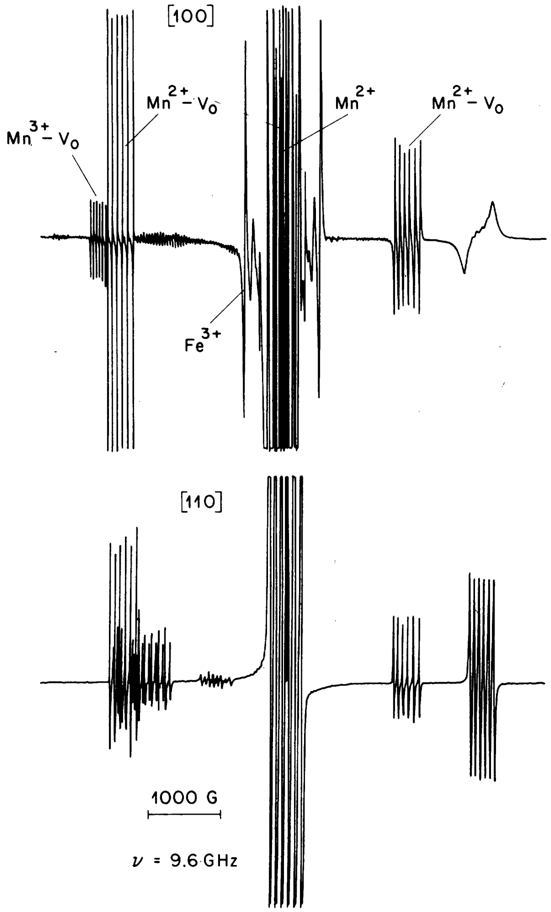

FIG. 1. EPR absorption spectra of reduced $SrTiO_3$ containing 0.48-at.% manganese. These data were taken at 300 K, X-band frequency, field-scan range 0–6000 G, with H oriented along [100] (top) and [110] (bottom). The spectra centered at $g = 2$ arise from Mn^{2+} (cubic), Fe^{3+} (cubic), and Mn^{2+}-V_O. The origin of the highest field sextet is unknown.

III. CUBIC Mn^{2+} CENTER

The most intense EPR spectrum observed in the reduced crystals at room temperature is an almost isotropic sextet of lines centered at $g = 2$. The spectrum taken with the Zeeman field along a crystal [100] direction is shown in Fig. 2. The spectrum can be interpreted with the conventional Hamiltonian

$$\mathcal{H} = g\mu_B \vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S}, \qquad (1)$$

with $g = 2.0036 \pm 0.0005$ and $A = (82.6 \pm 0.1) \times 10^{-4}$ cm^{-1}. We assign this spectrum to $Mn^{2+}(3d^5, S=\frac{5}{2})$ substitutional for Ti^{4+} with no local charge compensator. This assignment is based on the facts that (i) the spectrum is nearly isotropic and (ii) the magnitude of the g and A values are close to what one would expect for this paramagnetic ion. In fact, the spin-Hamiltonian parameters are similar to those reported for Mn^{2+} in the cubic phases of $PbTiO_3$ and $BaTiO_3$.[16] Although substitution in the Sr^{2+} site cannot strictly be ruled out, it is highly improbable owing to the great difference in ionic radii between Mn^{2+} and Sr^{2+}. In addition, since the Sr^{2+} is dodecahedrally coordinated, one would expect a value of $A \geq 90 \times 10^{-4}$ cm^{-1} for such a site.[17] For this reason, the cubic Mn^{2+} spectrum in $CaZrO_3$ with $A = (80.6 \pm 0.1) \times 10^{-4}$ cm^{-1}, $g = 2.0022$, reported by Henderson, is due to the Mn^{2+} in octahedral coordination at a Zr site, and not to a dodecahedral Ca^{2+} site as he assumed.[18] In this crystal the Mn^{4+} resonance has also been observed after annealing in oxygen at 1200℃. Thus, a partial conversion of Mn^{2+} into the Mn^{4+} state took place which is the inverse of our reduction experiments.

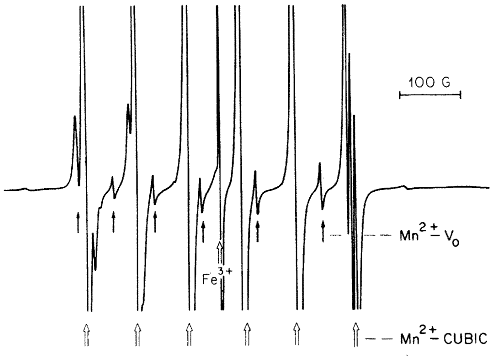

FIG. 2. EPR absorption spectrum of reduced $SrTiO_3$ containing 0.48 at.% manganese. This spectrum was recorded at 300 K, X-band frequency, with H along a crystal [100] direction. The sextet of lines is assigned to Mn^{2+} substituted for Ti^{4+}, with no local charge compensation. The structure in each component is unresolved and varies with orientation. The weak line at $g = 2$ is due to the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition of Fe^{3+} (cubic). The weakest lines are due to the Mn^{2+}-V_O center.

An unresolved anisotropic splitting is observed for the hyperfine lines where the splittings are most pronounced for the $m = \pm\frac{5}{2}$ and $\pm\frac{3}{2}$ components as shown in Fig. 2. The maximum observed splitting of these components is around 10 G. Similar splittings have been observed for Mn^{4+} in cubic sites of $SrTiO_3$ and are believed to arise from a distribution of small axial fields produced by distant charge compensators.[12] When the specimen is cooled to temperatures near 100 K, the spectral lines are broadened to the extent that they are no longer observable. Upon further cooling to 4.2 K, a much more complex anisotropic spectrum appears, centered at $g = 2$. This spectrum consists of several groups of sextets having approximately the same hyperfine splitting as the Mn^{2+} cubic center. Warming the sample again causes this spectrum to disappear, while the Mn^{2+} cubic spectrum is again observed above 100 K. The low-temperature spectra are not well resolved and are not analyzed in this study.

IV. Mn^{2+}-V_O CENTER

The second center observed in reduced crystals of manganese-doped $SrTiO_3$ at 300 K gives rise to a highly anisotropic fine-structure transition with *effective* g values of $g^e_{\parallel} \cong 2.00$ and $g^e_{\perp} \cong 5.9$ at X band. The parallel orientation corresponds to one of the crystal ⟨100⟩ directions. The angular variation of the center of gravity of this spectrum taken at K band with the Zeeman field rotated in the crystal (001) plane is shown in Fig. 3. Two components of the anisotropic spectra correspond to those defects whose axes of distortion are in the plane of rotation of the Zeeman field, these axes being along the [010] and [001] directions. The isotropic spectrum, whose effective g value is 5.9 at X band, corresponds to the defects whose axes of distortion, [100], are always perpendicular to H for a rotation in the (001) plane. This transition is typical of resonances between the $|\pm\frac{1}{2}\rangle$ doublet of a spin-$\frac{5}{2}$ ion in a strong axial field.[1-4] In a field of tetragonal symmetry, the spin Hamiltonian of a d^5 ion can be written as

$$\mathcal{H} = \tfrac{1}{3}DO_2^0 + \tfrac{1}{120}a(O_4^0 + 5O_4^4) + \tfrac{1}{180}FO_4^0 + g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B(H_x S_x + H_y S_y) + A_z S_z I_z + B(S_x I_x + S_y I_y), \qquad (2)$$

where the various terms have their normal spectroscopic meaning. When D is large compared to the Zeeman and hyperfine interaction terms, the transition between the $|\pm\frac{1}{2}\rangle$ Kramers levels can be treated by perturbation theory. If we neglect the hyperfine term in Eq. (2), the experimental g values of this transition may be shown to have the following angular dependence[1,2]:

$$g^e = [g_\parallel^2 + (9g_\perp^2 - g_\parallel^2)\sin^2\theta]^{1/2} \times [1 - 2(g\mu_B H/2D'')^2 F(\theta)], \tag{3}$$

where

$$2D'' = 2D - \tfrac{5}{2}a - \tfrac{5}{3}F \tag{4}$$

and

$$F(\theta) = (\sin^2\theta)\frac{(9g_\perp^2 + 2g_\parallel^2)\sin^2\theta - 2g_\parallel^2}{(9g_\perp^2 - g_\parallel^2)\sin^2\theta + g_\parallel^2} . \tag{5}$$

At $\theta = 0$, Eq (3) reduces to $g^e = g_\parallel$, while at $\theta = \frac{1}{2}\pi$, Eq. (3) gives

$$g_\perp^e \doteq 3g_\perp[1 - 2(g\mu_B H/2D'')^2] . \tag{6}$$

Measurements of g^e at $\theta = 0$ and $\theta = \frac{1}{2}\pi$ at two different frequencies can therefore provide values for $g_\parallel$, $g_\perp$, and $2D''$, assuming $2D'' \gg g\mu_B H$. Using such a procedure, where $g_\parallel^e \cong 2.0$, $g_\perp^e \cong 5.5$ at K band and $g_\perp^e \cong 5.9$ at X band, we find that $|2D''| = 1.14 \pm 0.05$ cm^{-1}. Since the zero-field splitting energy is of the order of $g\mu_B H$ at the frequencies used in this investigation, it is necessary to proceed with a direct computer diagonalization of the $S = \frac{5}{2}$ matrix. This procedure, together with the observation of a second fine-structure transition at $\theta = \frac{1}{2}\pi$, provided a more reliable set of spin-Hamiltonian parameters. This second transition is identified as arising between the $|\pm\frac{3}{2}\rangle$ states (in the high-field designation), and occurs at around 5000 G at X band (see Fig. 1). Such a transition is forbidden in the parallel orientation but is allowed in the perpendicular orientation where the states are heavily mixed. This is consistent with the fact that we were only able to observe the transition at orientations close to $\frac{1}{2}\pi$. As can be seen in Fig. 1, one component of this spectrum is isotropic for a rotation in the (001) plane. A third spectrum was observed at $\theta = 0$ corresponding to the $|-\frac{1}{2}\rangle \rightarrow |-\frac{3}{2}\rangle$ transition; however, this spectrum was not reliable, owing to the broad linewidths.

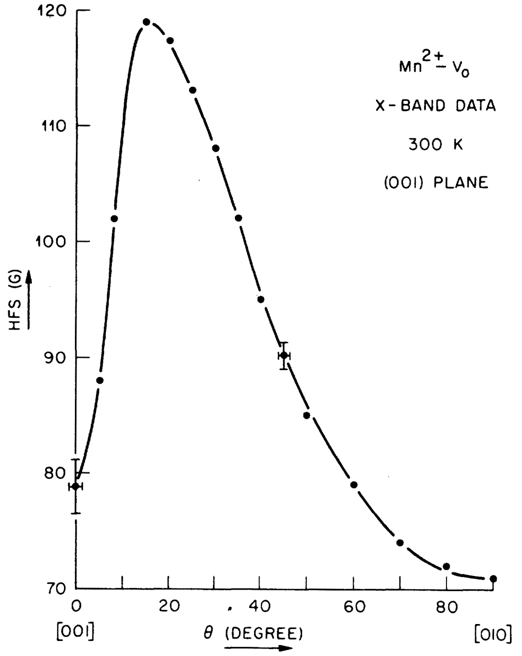

FIG. 4. Angular variation of the measured $-\frac{1}{2} \rightarrow \frac{1}{2}$ hyperfine transition of the Mn^{2+}-V_0 center in reduced $SrTiO_3$ containing 0.48-at.% manganese. The data were taken at 300 K, X band, and with H rotated in a crystal (001) plane.

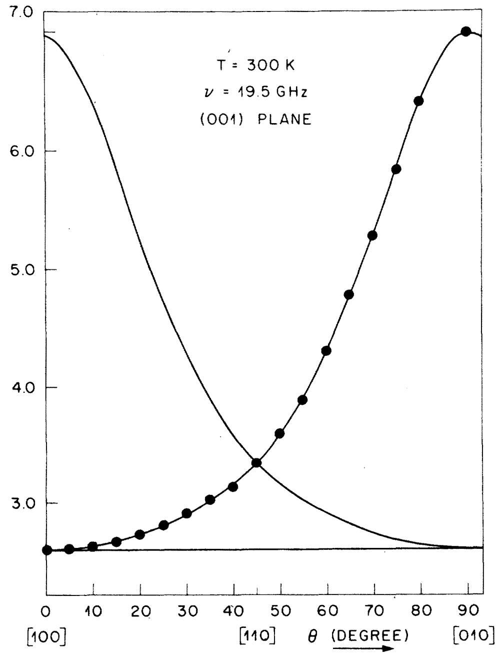

FIG. 3. Angular variation of the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition of the Mn^{2+}-V_0 center in reduced $SrTiO_3$, with H rotated in a crystal (001) plane. The isotropic component at low field ($g^e \approx 5.9$) corresponds to those centers whose axes of distortion are always perpendicular to H.

Energy levels were computed from the best-fit spin-Hamiltonian parameters given by $|2D''| = 1.088 \pm 0.001$ cm^{-1}, $g_\parallel = 2.0050 \pm 0.0040$, and $g_\perp = 2.0082 \pm 0.0060$. These energy levels for $\theta = 0$, $\theta = \frac{1}{4}\pi$, and $\theta = \frac{1}{2}\pi$ are shown in Fig. 4. An attempt was made to determine the sign of D by measuring the intensities of the transitions near 4 K. The results were inconclusive, owing to the large variation of the dielectric constant of $SrTiO_3$ with temperature in this region. However, no loss in intensity was observed for the $|-\frac{1}{2}\rangle \rightarrow |\frac{1}{2}\rangle$ transition upon cooling to 2 K, suggesting that D is positive. Since the quartic terms in a and F which appear in the spin Hamiltonian are usually small compared

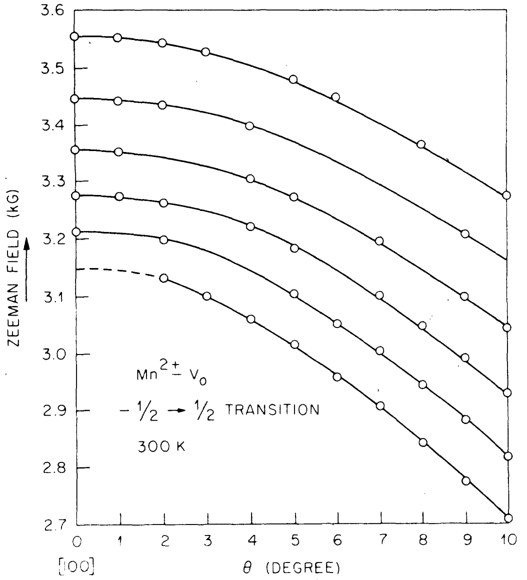

FIG. 5. Angular variation of the hyperfine structure of the Mn^{2+}-V_O center $|-\frac{1}{2}\rangle \rightarrow |\frac{1}{2}\rangle$ transition near $\theta = 0°$. The data were taken at 300 K, at $\nu = 9.471$ GHz, with the Zeeman field rotated in a crystal (001) plane. Note the asymmetry in the splittings between successive hyperfine components at $\theta = 0$.

to D, the axial crystal-field term D is estimated to be 0.54 cm^{-1}. This is about an order of magnitude larger than the splittings observed for Mn^{2+} in the tetragonal phases of PbTiO_3 and BaTiO_3,[16] and suggests that there is no local charge compensation for these systems. On the other hand, very large axial fields have been reported for the Fe^{3+} ion in SrTiO_3 which arises from a nearest-neighbor oxygen vacancy.[1,2] This center is designated as Fe^{3+}-V_O, where the oxygen vacancy lies along one of the three equivalent cube edges $\langle 100\rangle$. In analogy to this center, we assign the present axial manganese spectrum to the Mn^{2+}-V_O center. This assignment also corroborates well with the Mn^{3+}-V_O center to be discussed in the next section. Because the Mn^{2+} is at a site of Ti^{4+} and an O^{2-} is lacking, the Mn^{2+}-V_O center is neutrally charged with respect to the lattice.

An unusual variation of the measured hyperfine splitting with orientation is observed for this spectrum, as plotted in Fig. 4. The measured splitting is largest when the field is at an angle of $(15 \pm 2)°$ with the axis of distortion, while the smallest splitting is observed with the Zeeman field perpendicular to the axis of the distortion. In addition, the separation between the successive hyperfine components increases with increasing field for the $\theta = 0°$ spectrum at $g = 2$ (see Fig. 5). This effect is not observed for orientations at 10° or greater (see Fig. 6). Data in the vicinity of $\theta = 0°$ were difficult to obtain, owing to the near superposition of the *cubic* Mn^{2+} transitions. We were able to explain the asymmetry in the splittings at $\theta = 0°$ by performing an exact solution to the Hamiltonian at $\theta = 0°$:

$$\mathcal{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)] + \mu_B[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)] + [A I_z S_z + B(I_x S_x + I_y S_y)] . \tag{7}$$

A computer program including a diagonalization subroutine utilizing Jacobi's method of successive rotations was written in FORTRAN IV, and a solution for $\theta = 0°$ was obtained for each set of input parameters D, $g_\parallel$, A, and B. D and $g_\parallel$ were kept constant, and the parameters A and B were fitted to the observed data at $\theta = 0°$. At K band, only four of the six hyperfine transitions were observed. Field positions of the observed transitions could be determined to an accuracy of ±0.1 G. A fifth transition was measured to an accuracy of ±1 G. The best-fit parameters to the data at X and K bands were found to be

$$D = 0.544 \pm 0.001\ \mathrm{cm}^{-1} ,$$

$$g_\parallel = 2.0030 \pm 0.0005\ \mathrm{cm}^{-1} ,$$

$$A = (76 \pm 1) \times 10^{-4}\ \mathrm{cm}^{-1} ,$$

$$B = (65 \pm 1) \times 10^{-4}\ \mathrm{cm}^{-1} .$$

Note that the value of B agrees well with the experimental hyperfine splitting at $\theta = 90°$. Table I compares the observed asymmetric splittings with the five calculated values. The larger discrepancies are believed to be due to crystal misalignments of 0.5°. The Zeeman-field positions at X band were predicted to an accuracy of one part in six thousand with this choice of parameters.

We did not attempt to fit the hyperfine-structure

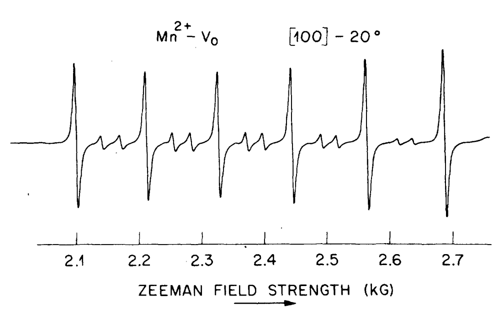

FIG. 6. EPR absorption spectrum of the $|\frac{1}{2}\rangle \rightarrow |-\frac{1}{2}\rangle$ transition of the Mn^{2+}-V_O center in reduced SrTiO_3 containing 0.48 at.% manganese. This spectrum was recorded at 300 K, X band, and with the Zeeman field 20° away from [100]. The weak doublets which are observed between each hyperfine component correspond to the *normally forbidden* $\Delta m = \pm 1$ transitions.

TABLE I. Calculated versus observed values of the Zeeman-field separations between successive hyperfine components of the Mn^{2+}-V_O center at $\theta = 0°$. Asterisks indicate that splittings could not be determined, since some transitions were obscured by the *cubic* Mn^{2+} spectrum.

Field separations	X-band splittings (G) Observed	Calculated	K-band splittings (G) Observed	Calculated
ΔH_1	*	52.3	60.3	59.8
ΔH_2	62.7	65.1	67.8	69.2
ΔH_3	77.8	78.4	*	78.7
ΔH_4	92.9	92.4	*	88.1
ΔH_5	106.7	107.6	98.1	97.6

data at other orientations, since Byfleet and coworkers have already described and interpreted similar asymmetries and angular dependences for Mn^{2+} in a strong crystalline field.[19,20] They explain their results using an approximate solution to the Hamiltonian, whereby the Zeeman-energy term in the fine-structure Hamiltonian is expanded up to seventh order in powers of the magnetic field. The sum of the fine structure and hyperfine matrices in the new eigenvector basis are then diagonalized to obtain all the proper hyperfine energy levels. However, at $\theta = 0°$ the fine-structure matrix is diagonal in the original basis elements and degenerate perturbation theory is no longer necessary.

The normally forbidden $\Delta m = \pm 1$ hyperfine transitions were also observed as a set of doublets between each normal hyperfine component (see Fig. 6). The intensities of these transitions reach a maximum value at about $\theta = 20°$, unlike the usual intensity behavior of such transitions in systems with much smaller crystal-field splittings.[21] However, the separation between the doublets at $\theta = 20°$ (where the transitions are well resolved) is consistent with the $S = \frac{5}{2}$ formalism.

Recently, Hannon[22] reported an axial [100] EPR spectrum of Mn^{2+} in $KTaO_3$ with $D = 0.147$ cm^{-1}, $A = 86.5 \times 10^4$ cm^{-1}, and $B = (84 \pm 1.5) \times 10^{-4}$ cm^{-1}. He ascribed the spectrum to Mn^{2+} with an adjacent oxygen vacancy. In view of the much larger D value of the Mn^{2+}-V_O center in $SrTiO_3$, such an assignment seems quite improbable, because the isoelectronic Fe^{3+}-V_O center in $KTaO_3$ and $SrTiO_3$ shows essentially the same D splitting of 1.4 cm^{-1}.[2,3] A [100] axial Mn^{2+} center in an ABO_3 perovskite-type structure can also occur for substitutional Mn^{2+} ions on an A site with an A vacancy next to it, or if the Mn^{2+} is sitting off center along a [100] direction. For $KTaO_3$ this would be the K site. This assumption is also favored by the smaller difference between the axial hyperfine values A and B of only 2.5%, as compared to the Mn^{2+}-V_O center of 13%. Furthermore, the average absolute values $A = \frac{1}{3}(A + 2B)$ for the $KTaO_3$ axial Mn^{2+} center is 21% larger than that of the Mn^{2+}-V_O center. According to Simanek and Müller,[17] the measured $\bar{A}$, from Fig. 1 of their work, corresponds to a covalency for the Hannon center of only $c/n = 9\%$ (i.e., a large ionicity), whereas $c/n = 16.5\%$ for Mn^{2+}-V_O. Now the oxygen coordination number of the Mn^{2+}-V_O center is $n = 5$ and one would expect for an Mn^{2+} at a dodecahedral K^+ cation site in $KTaO_3$, $(c/n)_K \sim 7\%$. The deduced $c/n = 9\%$ (for $A = 86.5 \times 10^{-4}$ and $B = 89 \times 10^{-4}$ cm^{-1}) thus indicates that the effective coordination number n is about 9, lower than 12, but certainly not $n = 5$. For an A site, $n = 9$ is not surprising, in view of the considerably smaller ionic radius of Mn^{2+} of 0.80 Å, as compared to 1.33 Å of K^+ which allows for local oxygen distortion and effective reduction of coordination number.

V. Mn^{3+}-V_O

A second, highly anisotropic sextet spectrum is observed in reduced $SrTiO_3$: Mn from 2 to 300 K, with an *effective g* value of $g_\parallel^e \cong 8$. No perpendicular EPR line is observed at the low-field side $g_\perp^e \sim 8$, in contrast to the axial $S = \frac{5}{2}$ spectrum shown in Fig. 3, at $g_\perp^e \sim 5.9$. The angular variation of this spectrum with the Zeeman field rotated in the crystal (001) plane is shown in Fig. 7. Within experimental error, the variation is identical when H is rotated in the crystal (010) plane. Thus the principal $g_\parallel$ value is measured along a fourfold axis of the crystal with general direction $\langle 100 \rangle$. For such a direction, the Hamiltonian (2) must apply for symmetry reasons. A $g_\parallel^e \sim 8$ can only be observed within an $S = 2$ manifold. Assuming a large enough D value, $D \gg h\nu$, (2) leads to a splitting into M_S states: $|0\rangle$, $|\pm 1\rangle$, and $|\pm 2\rangle$, the last two being further split by the cubic crystal-field parameter a. The $|\pm 2\rangle$ non-Kramers states are lowest for $D < 0$. Using this formalism, the Zeeman energy including the hyperfine interaction with nuclear-spin quantum number m is

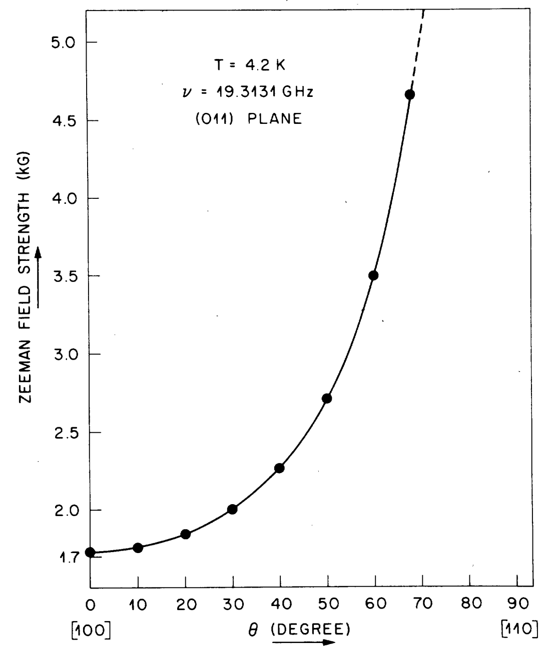

FIG. 7. Angular variation of the center of gravity of the Mn^{3+}-V_0 center in reduced $SrTiO_3$ containing 0.48 at. % manganese. The data were taken at 4.2 K, *K*-band frequency, and *H* rotated in a crystal (011) plane.

$$(E_{\pm 2,m})^2 = 4(g_{\parallel}\mu_B H\cos\theta + Am^2) + a^2 \,. \tag{8}$$

Putting $4g_{\parallel} = g_{\parallel}^e$, the Zeeman-field strength is predicted to vary with orientation according to the expression

$$H = \frac{1}{g_{\parallel}^e \mu_B \cos\theta}\left[(h\nu)^2 + a^2\right]^{1/2} - \frac{Am}{g_{\parallel}^e \mu_B \cos\theta} \,, \tag{9}$$

where θ is the angle between *H* and the tetragonal axis of a crystalline ⟨100⟩ direction. The parameters $g_{\parallel}^e$ and *a* were determined by careful measurements at two microwave frequencies (*X* and *K* band) with $\theta = 0$. The results at 300 K are $g_{\parallel}^e = 7.945 \pm 0.001$ and $a = 0.0540 \pm 0.0001$ cm^{-1}. Using these parameters and Eq. (9), the angular dependence of the *center of gravity* of the hyperfine sextet was fitted to within ±2 G for orientations up to $\theta = 68°$. The spectrum could not be followed for larger angles, owing to excessive line broadening and the limitation of the magnetic field intensity at *K* band. However, measurements at *X* band for angles up to 85° showed that $g_{\perp}^e < 0.4$.

The measured hyperfine splitting as obtained from Eq. (9) varies with orientation according to the expression

$$A' = A/\cos\theta \,, \tag{10}$$

where $A = (37.3 \pm 0.1) \times 10^{-1}$ cm^{-1} at 300 K and $A = (36.8 \pm 0.1) \times 10^{-4}$ cm^{-1} at 4.2 K. The measured hyperfine splittings agree with this expression to within ±1 G for angles up to 68°. The angular variation of *A* with *H* rotated in the crystal (011) plane is shown in Fig. 8. Here again, the angular dependence is the same when *H* is rotated in the crystal (001) plane.

The paramagnetic species giving rise to this spectrum is assigned to $Mn^{3+}(3d^4, S = 2)$ for three reasons: (i) the value of $g_{\parallel}^e \cong 8$ is what one would expect for a spin-2 configuration, (ii) the hyperfine splitting is similar to that reported by Gerritsen and Sabisky[23] for Mn^{3+} in TiO_2, and (iii) the parameter *a* is comparable to that reported for other $3d^4$ systems in a strong crystalline field.[23,24] It is a third of that observed for the isoelectronic Fe^{4+}-V_O, $3d^4$ system in a strong, pure tetragonal field.[13] The higher charge of Fe^{4+} yields a larger spin-orbit coupling constant and thus a larger parameter *a*.

The considerable tetragonal distortion for the Mn^{3+} ion in $SrTiO_3$ cannot be explained by a Jahn-Teller effect, since the spectra at 300 and 4.2 K are essentially equivalent. On the other hand, it is very likely that the large tetragonal distortion along one of the crystal [100] axes is caused by a nearest-neighbor oxygen vacancy which stabilizes the Mn^{3+} configuration, thus the designation Mn^{3+}-V_O. For the isoelectronic Fe^{4+}-V_O center, the the rotation of the center axis by $\pm\varphi$ away from the ⟨100⟩ axis below the cubic tetragonal phase transition has been observed.[13] The amount of $\overline{\varphi}$ is the same as that reported for the Fe^{3+}-V_O cen-

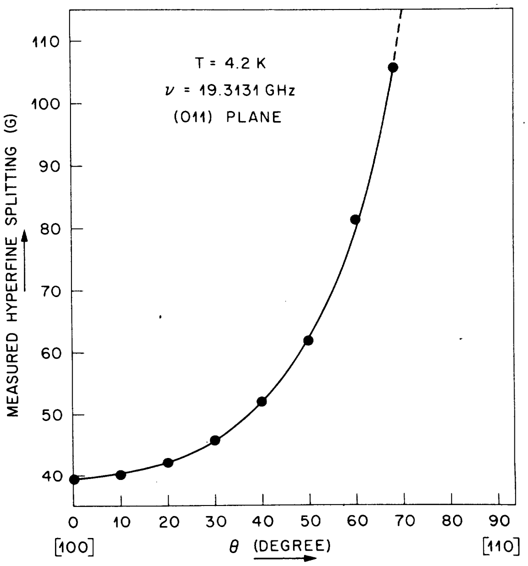

FIG. 8. Angular variation of the measured hyperfine splitting for the Mn^{3+}-V_0 center in reduced $SrTiO_3$ containing 0.48 at. % manganese. The data were taken at 4.2 K, *K* band, with *H* rotated in a crystal (011) plane.

ter and confirms the assignments.

In a purely octahedral field, the $3d^4$ configuration would have a degenerate ground state which is only split by second-order effects of the spin-orbit and spin-spin interactions.[25] In a field of tetragonal symmetry, the ground ^5E states are split into $^5A_1 + {}^5B_1$. If the ground state is $^5B_1$, $x^2 - y^2$, the $M = \pm 2$ levels are lowest, with $g_\parallel < 2$ in an ionic case. This is in agreement with our observation that $g_\parallel = \frac{1}{4} g_\parallel^e = 1.9863 \pm 0.0010$. Further evidence that the $M = \pm 2$ levels lie lowest is the apparent increase in signal intensity upon cooling to 2 K.

In the isoelectronic Fe^{4+}-V_O center $g_\parallel = 2.007$ was observed, larger than the free g value $g_f = 2.0023$. The progression of g values towards positive g shifts, $\Delta g = g - g_f$, for the higher valency states was compared.[13] It was shown that $g_\parallel$ from Mn^{3+}-V_O to the one for Fe^{4+}-V_O was nearly the same as the progression of the isotropic g values of the cubic $3d^3$, $S = \frac{3}{2}$ states from Cr^{3+} to Mn^{4+} and Fe^{5+}. The latter again has $g = 2.011$ larger than g_f. This occurs from the admixture of O^{2-} ligand hole states to the $3d$ wave function and is more important for the higher valence states because the charge-transfer energies are smaller. Thus such an admixture may already be present to a smaller extent for the $x^2 - y^2$ Mn^{3+}-V_O ground state.

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