sion for $J(x_D)$ is an approximation, in that certain details of the three acoustic branches are not included. For high-precision work a theory[4] convenient for computer calculations has been formulated, with particular emphasis on the lowest external modes. In this way, all calculations and computer programs already available for the external-modes approximation[5] may be used.

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Defects in Neutron-Irradiated Strontium Titanate: Ti^{3+} "Off Center" on a Sr^{2+} Site

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Nominally pure $SrTiO_3$ crystals show, after irradiation with fast neutrons, paramagnetic-resonance (EPR) spectra arising from Ti^{3+} ions on Sr^{2+} sites. Because of its smaller radius, the Ti^{3+} sits "off center". In the tetragonal low-temperature phase of $SrTiO_3$ ($T < T_c \approx 105$ K) it moves towards one of the twelve surrounding oxygen ions roughly 0.03 Å in a direction perpendicular to the domain axis. This is proved by the response of the EPR spectra to the application of external electric fields. For $T > T_c$ simultaneously another Ti^{3+} spectrum is seen, which results from a partial averaging of the low-temperature spectrum. The coexistence of both types of spectra is attributed to the critical dynamics of the fluctuations of the order parameter φ near T_c. For $T = (T_c + 4) \pm 0.5$ K a frequency spread of $\Delta\nu = 3.5 \times 10^8$ Hz is obtained corresponding approximately to the width of the *central mode*.

I. INTRODUCTION

In this paper, paramagnetic-resonance (EPR) spectra of a Ti^{3+} center are reported which are observed after fast-neutron irradiation of undoped "pure" $SrTiO_3$. They are identical to those previously observed by van Engelen and Henning[1] in one sample of reduced $SrTiO_3$. These authors, however, did not give a definite interpretation of the spectra. We show here that they result from a Ti^{3+} ion on a Sr^{2+} site. The titanium ion is not found at an ideal lattice position but is moved off center towards one of the 12 surrounding oxygen ions. The assignment of the center was accomplished by investigating the spectra above and below the cubic-to-tetragonal phase transition of $SrTiO_3$ at $T_c \approx 105$ K[2] and by observing the change of the EPR spectra when external electric fields were applied.

It is seen that the orthorhombicity of the centers observed in the tetragonal low-temperature phase is caused by the tilting[2] of the oxygen octahedra. However, in contrast to the response of all other paramagnetic centers in $SrTiO_3$, this orthorhombicity does not follow the order parameter φ but changes to zero at T_c in a rather abrupt manner. This is a consequence of the more indirect coupling between center and lattice and gives the opportunity to compare the number of Ti^{3+} surroundings where a tilting larger than a critical angle φ_c prevails for a certain time with those where $\varphi < \varphi_c$. Because of the fluctuations in the order parameter, both types of Ti^{3+} environments are simultaneously present in the crystal from near T_c up to $T_c + 40$ K. This result is compatible with other information on the structural phase transition of $SrTiO_3$.[2-4]

The center reported is a member of a class of defects in perovskite-type crystals which all show low symmetry although the nominal site symmetry in the high-temperature phase is O_h. A comparison with such centers is given at the end of the paper.

II. EXPERIMENTAL

The nominally pure $SrTiO_3$ crystals used in this study were obtained from the National Lead Co. Some of the specimens were cut in a form yielding a monodomain behavior below T_c.[5] They were irradiated with fast neutrons ($E \geq 0.1$ MeV) to a total flux of $\sim 10^{17}/cm^2$. During irradiation the crystal temperature was (125 ± 5) °C.

The EPR spectra were taken at 9 and at 20 GHz. The resonances treated here could be enhanced by a factor of about 2 by shining the light of a high-pressure mercury lamp, filtered with a 4-mm Schott KG 1 filter to reduce the ir content, onto the crystals. (By this procedure the signal intensity of the substitutional Fe^{3+} impurities, also present in the crystals, was reduced.)

III. EXPERIMENTAL RESULTS

A. $T<T_c$

In a three-domain (3*D*) crystal the spectra [see Fig. 1(a) for an example] consist of 12 lines for a general orientation of the static magnetic field [Fig. 2(b). Four of these resonances are strongly enhanced in a monodomain (1*D*) crystal. If the magnetic field is rotated in a plane perpendicular to the domain axis, they appear as those marked heavily in Fig. 2(b). The angular dependence of the center in the 1*D* crystal can be best understood by assuming an effective spin $S' = \frac{1}{2}$. In a 3*D* specimen one thus deals with 12 equivalent centers showing orthorhombic symmetry with $g_z = 1.9945(5)$, $g_x = 1.9228(5)$, $g_y = 1.8530(5)$. As concluded from the angular dependence in a 1*D* crystal, the *z* axis of a representative member among these 12 centers nearly coincides with a pseudocubic [100] axis lying perpendicular to the domain axis. It is tilted from this direction by 2.5° ± 0.1° towards the domain axis [001]. This tilting angle is independent of temperature if $T < T_c$ (Fig. 3). The *y* axis includes this same angle with the domain axis [001] while *x* lies along [010]. In one domain there are three more magnetically inequivalent centers originating from the one described by fourfold rotation around the domain axis and/or reflexion at the [001] mirror plane of the crystal structure. Twelve lines are observed in a 3*D* crystal because of the equivalence of the three possible domains.

The hyperfine (hf) splitting was best resolved for line *b* in Figs. 1 and 2. Here $A_x^{47} = 13.50(5) \times 10^{-4}$ cm^{-1} for Ti^{47} ($I = \frac{5}{2}$; 7.75% natural abundance) and $A_x^{49} = 13.4(5) \times 10^{-4}$ cm^{-1} for Ti^{49} ($\frac{7}{2}$; 5.51%). The other parameters are $A_y^{47} = 16.4(4) \times 10^{-4}$ cm^{-1}; $A_z^{47} = 2.7(1) \times 10^{-4}$ cm^{-1}. The parameters given in Ref. 1 have to be multiplied by $g/2.0023$ to be consistent with those listed here.

The intensity of the $Ti^{46,48,50}$ ($I = 0$) line relative to the hf-split resonances allows the conclusion that there is hf coupling with only one Ti nucleus in each

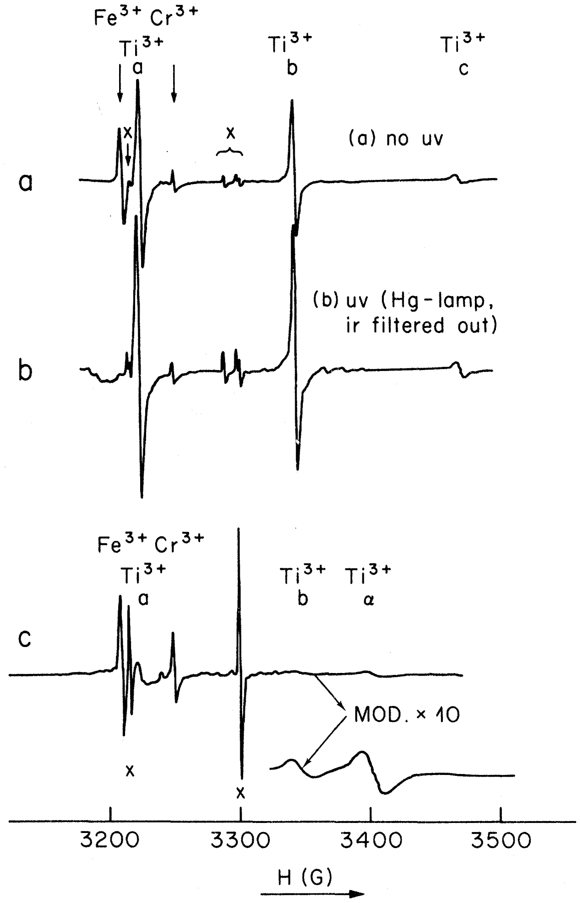

FIG. 1. ESR spectra of a monodomain $SrTiO_3$ crystal, irradiated with fast neutrons, for $H \parallel [100]$ (perpendicular to domain axis), $\nu = 9.1$ GHz. (a) 77 K, no uv irradiation. The origin of the lines is indicated by the following symbols: Fe^{3+}: $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition of substitutional Fe^{3+}; Ti^{3+}: Ti^{3+} on a Sr^{2+} site; Cr^{3+}: resonance of substitutional Cr^{3+}; *x*: different neutron-induced centers. (b) Same spectrum at 77 K after uv irradiation. (c) Same spectrum at 111 K after uv irradiation. Lines *b* and *α* are shown separately, taken with higher modulation amplitude.

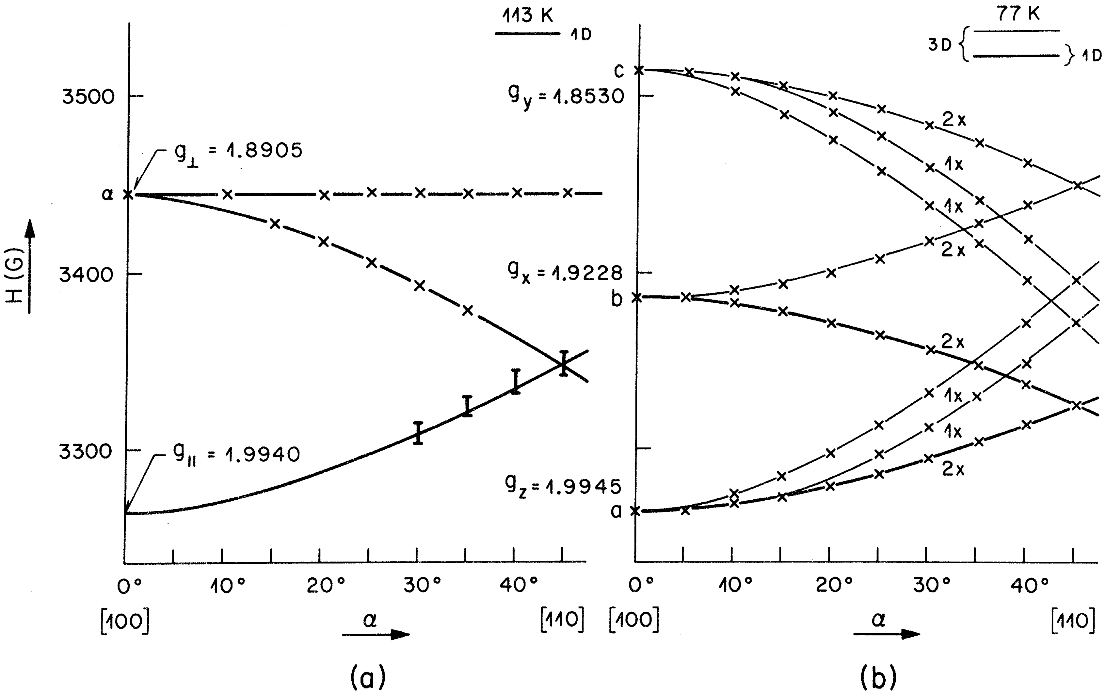

FIG. 2. Angular dependences of the resonances of Ti^{3+} on a Sr^{2+} site for a rotation of H in a (001) plane. (a) Axial part of spectrum observed at 113 K with a monodomain crystal. (b) Orthorhombic spectrum taken at 77 K. The strong lines mark resonances which are strongly enhanced in a monodomain crystal.

center.

If an electric field is applied to a $3D$ crystal along a pseudocubic [100]-type axis parallel to the static magnetic field, the intensity ratio of lines b and a in Fig. 1(a), I_b/I_a, decreases with increasing field at 77 K in the manner shown in Fig. 4. The ratio I_c/I_a falls down in a similar way, but the decrease is significantly steeper.

B. $T>T_c$

On raising the temperature to T_c and above the lines become broad and a new line, α in Figs. 1(c) and 2(a), appears between b and c for $\vec{H}\parallel[100]$, which belongs to a center having axial symmetry around the, now ideally, cubic [100]-type directions of the crystal [see Fig. 2(a)]. The g values of these centers are $g_\parallel = 1.9940(30)$ and $g_\perp = 1.8905(10)$. Whereas the line at $g_z = 1.9945$ was not observed in the low-temperature spectra and for H along the domain axis, the corresponding value $g_\parallel = 1.9940$ is now also seen for this orientation of the static field.

While these new axial spectra appear, the intensity of the orthorhombic ones decreases. The intensity ratio of lines b and α, I_b/I_α, is shown in Fig. 5. The coexistence of both types of centers near T_a can be seen by inspecting Fig. 6. It is seen that line α, though rather broad, is present below T_c already. Near T_c, line b is seen to split into two components, one of which, β, shows a decreasing g value. At present, the origin of this line is not understood. In the range $T_c < T < T_c + 2$ K the structure between lines b and α cannot be resolved definitely into separate components.

IV. INTERPRETATION

A. Model of Center

As already pointed out by van Engelen and Henning,[1] the resonances are due to $Ti^{3+}(3d^1)$; the lines are too sharp to belong to the non-Kramers configuration Ti^{2+} (d^2). The possibility of a Ti^{+} ion is

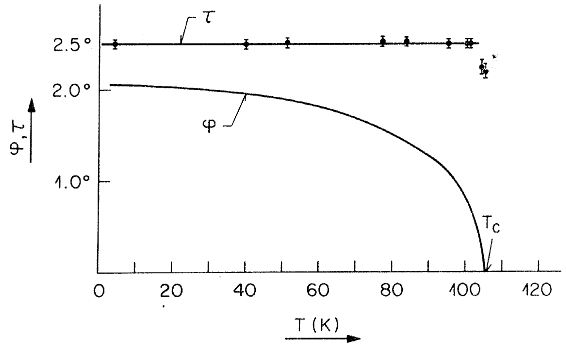

FIG. 3. Temperature dependence of the tilting angle τ as compared to that of the mean value of the order parameter φ.

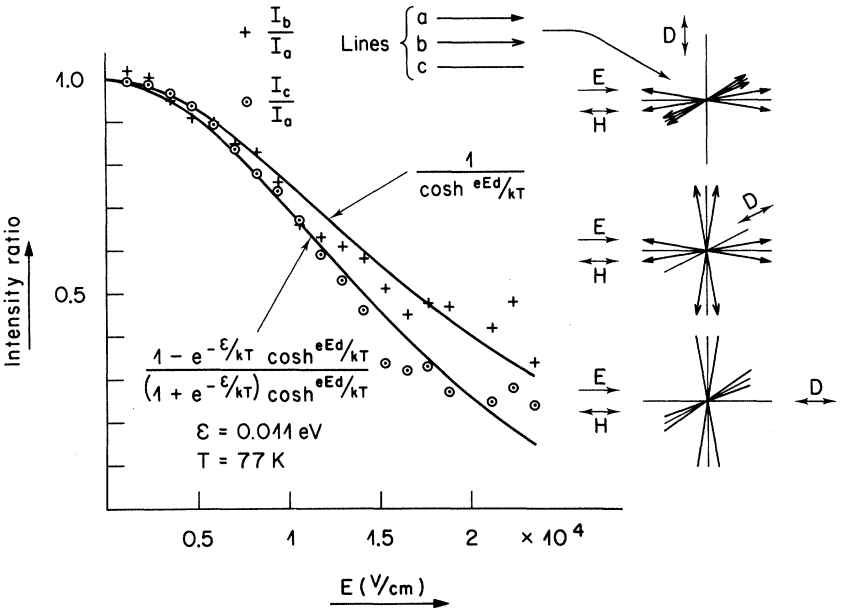

FIG. 4. Dependence of the intensity ratio of lines *a* and *b*, I_b/I_a (Fig. 1) and *a* and *c*, I_c/I_a, on a static electric field *E* applied along a [100] axis of a 3*D* crystal at 77 K. The ratios were normalized to unity for $E = 0$. The full lines are least-squares fits of the given expressions (see text) to the data. The relative orientations of *E*, *H*, and the domain axes *D* are shown on the right-hand side.

ruled out because in the configuration d^3, g values near 2 can be explained only if the noncubic crystal field is small. But then a zero-field splitting should have been observed. From the angular dependence (Fig. 2) one must clearly conclude that the ion is subject to a crystalline environment of orthorhombic or lower symmetry, which lifts all orbital degeneracy of the $3d^1$ orbitals. For a d^1 ion, a g value of ~ 2, as found for g_z (1.9945), occurs only if the unpaired electron occupies a $3z^2 - r^2$ orbital and if the external magnetic field H points along the axis of this orbital. In the other two principal directions, the g values will be shifted from 2, to first order by[6]

$$\Delta g_x = -6\lambda/E_{yz}, \quad \Delta g_y = -6\lambda/E_{xz}, \tag{1}$$

where λ is the spin-orbit coupling constant of Ti^{3+} and E_{yz} and E_{xz} are the energy differences between the ground state and the yz and xz orbitals, respectively. Since the g_z value appears in the spec-

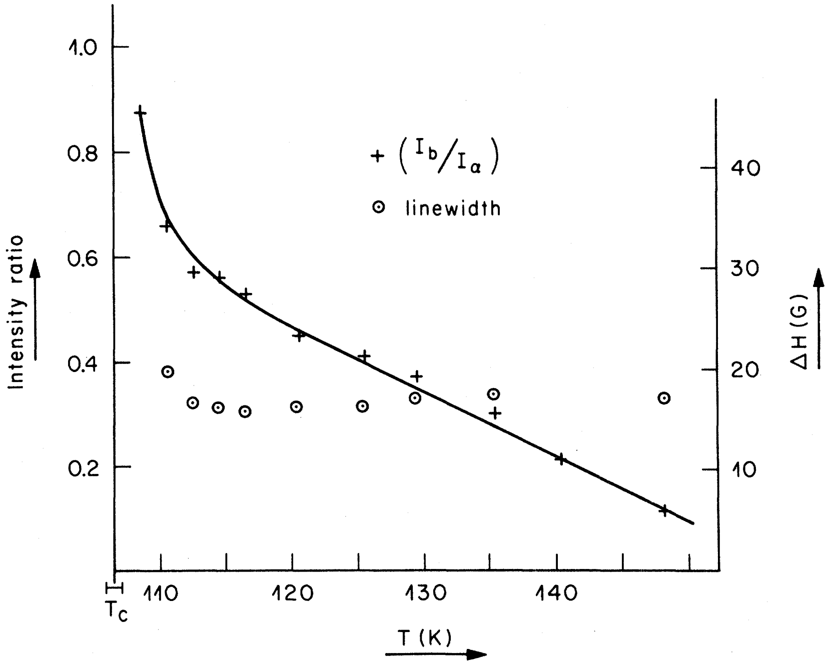

FIG. 5. Temperature dependence of the intensity ratio of lines *b* and *a*, I_b/I_a, above T_c. The intensities were calculated by multiplying the square of the linewidths with the signal heights. The dots show the temperature dependence of the width of line *a* (right-hand scale).

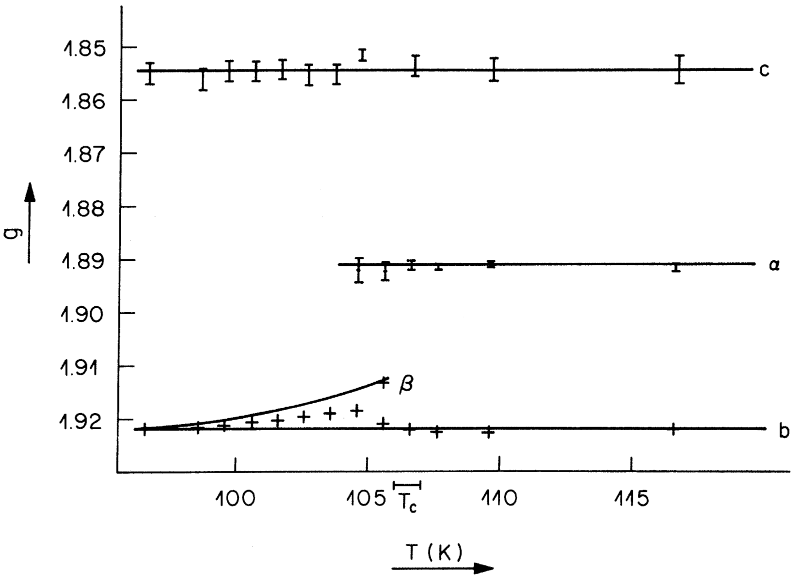

FIG. 6. Temperature dependence of the observed line positions for $H \parallel [100]$ near T_c. The bars indicate the uncertainty of the line positions.

tra taken with a monodomain crystal for a rotation around the domain axis, as shown in Fig. 2, we conclude that the z axis of the centers nearly coincides with pseudocubic axes perpendicular to the domain axis. For the rotation shown, the line originating at g_z is seen to continue to $g_x = 1.9928$. This value thus describes the position of the resonance if H is perpendicular to both the domain axis and the $3z^2 - r^2$ axis. The third principal value, g_y, which is only weakly observed in a 1*D* crystal for the rotation shown, therefore corresponds to H parallel to a domain axis and perpendicular to the orbital occupied by an electron $3z^2 - r^2$.

In order to establish a microscopic picture of the center, the observation is important that the orthorhombic spectra start to vanish near T_c where new axial spectra appear instead. Therefore the low-symmetry configuration of the centers is caused by the distortions present in the tetragonal phase of a SrTiO$_3$ host lattice and not by the association of a defect with the Ti^{3+} ion. Neither does the axial symmetry persist above T_c due to such an association, since the domain directions, forbidden for the z axes of the centers below T_c, now become allowed in a very small temperature range near T_c. It is not conceivable that the mobility of a defect, possibly associated with Ti^{3+}, should have such a pronounced temperature dependence.

Thus the Ti^{3+} ion sits at an unperturbed site in the crystal, surrounded by the lattice ions in such a way that the $3z^2 - r^2$ orbital is lowest. These conditions are fulfilled by a Ti^{3+} ion replacing a Sr^{2+} lattice ion. At such a site, the axial or orthorhombic fields can be caused if the Ti^{3+} ion sits slightly off center towards one of the surrounding O^{2-} ions (Fig. 7).

We now show that this model is sustained by all additional observations, especially by the features of the center in the low-symmetry phase of SrTiO$_3$ and by the effect of external electric fields on the resonances. To this purpose we consider the distortion of the surroundings of a Sr^{2+} ion in the tetragonal phase of the crystal (see Fig. 7). Ti^{3+} has an ionic radius of 0.76 Å, smaller than that of the replaced Sr^{2+}, 1.10 Å. Since the Ti^{3+} is less repelled by its O^{2-} neighbors than a Sr^{2+} ion it is likely that the Ti^{3+} sits off center. It is most plausible to assume that it adheres to one of the O^{2-} ions next to it (ions *a* or *b* in Fig. 7). At such a position the crystalline environment has only a mirror plane as a symmetry element, which is compatible with the orthorhombicity exhibited by the low-temperature spectra. For electrostatic reasons, the Ti^{3+} orbitals should roughly be oriented as shown in Fig. 7. The negative charge in the lobes of the $3z^2 - r^2$ orbital is attracted by the Sr^{2+} neighbor and repelled by the O^{2-} charge. Furthermore the zy orbital shown dashed in Fig. 7, whose admixture into the ground state by spin-orbit coupling is responsible for Δg_x, is energetically higher than the zx orbital. Taking Eq. (1) into account, this can explain the observed sequence of the g values. In Fig. 7, the z axis is tilted by the angle τ away from the [100] axis. There are analogous Sr^{2+} sites in a 1*D* SrTiO$_3$ crystal in its low-temperature configuration for which it is tilted upwards, and other ones where the ion sits off center along the [010] direction, making a total of four magnetically inequivalent centers for each domain, as indicated by the insets in Fig. 4. Apparentlv. it is energetically unfavorable for Ti^{3+} to move off center along the [001] domain axis.

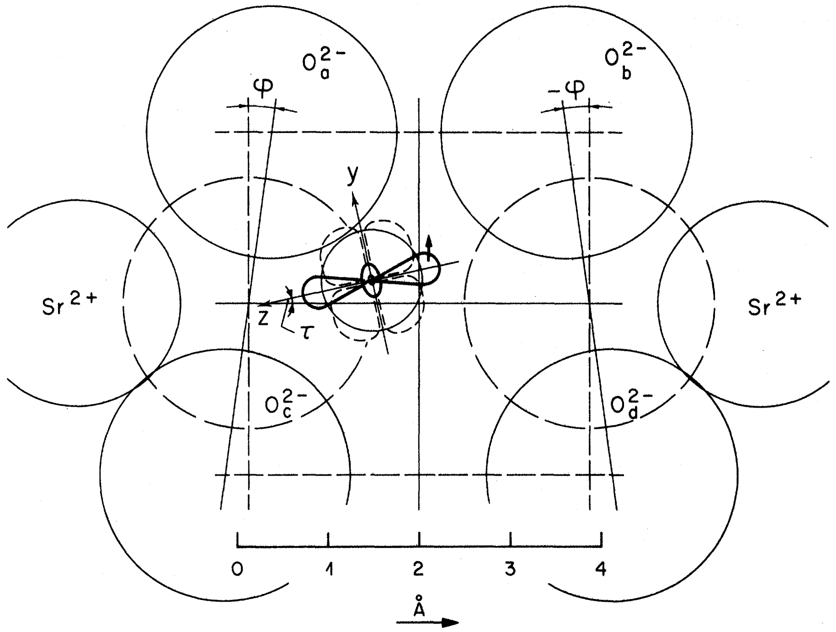

FIG. 7. Model of the paramagnetic center originating from a Ti^{3+} ion substituting for a Sr^{2+} ion in a SrTiO$_3$ lattice. The angle φ indicates a momentary value of the order parameter; τ is the tilting angle of the center. The ground-state wave function is sketched in full lines, the dashed orbital is the yz state responsible for the g shift for H perpendicular to the plane of the figure.

B. Electric Field Effects

The change of the ESR spectra under applied static electric field (Fig. 4) proves unequivocally that the Ti^{3+} sits off center. To understand these effects, let us first assume that the electric field E is applied perpendicular to a domain axis in a 1D crystal parallel to H, both pointing along [100]; see the two uppermost inserts in Fig. 4 (for experimental reasons the electric field effects could be measured in 3D crystals only). The energy of Ti^{3+} ions sitting off center along E (one-half of the full arrows in Fig. 4) will be lowered by $-eEd$ with respect to the on-site position [here E is the local value of the static electric field which can be approximately calculated from the external field by multiplying with the Lorentz factor $\frac{1}{3}(\epsilon+2)\approx 530$ for SrTiO$_3$ at 77 K[7]; e is an effective charge of the Ti^{3+} ion and d the off-center distance from the on-site position]. Ions moved into the opposite direction have their energy increased by eEd while those moved perpendicular to E (light arrows in Fig. 4) are unaffected. (It is always assumed that the crystalline potential is changed only weakly by the applied electric field.) If only the domain directions corresponding to the two upper insets in Fig. 4 were present, the intensity ratio of lines a and b, I_b/I_a (see Fig. 1 or 2), should behave as $I_b/I_a \propto 1/\cosh(eEd/kT)$ with temperature T. In a 3D crystal, however, also the third type of domains (lowest inset in Fig. 4) is found. For these, the motion of the Ti^{3+} ions into the domain direction is hindered by a potential ϵ, as discussed above. If E is strong enough for eEd to become comparable with this energy ϵ, an appreciable fraction of Ti^{3+} ions will be pulled into the direction of E. In this position, a g value comparable to that of line a will be measured for the given orientation of H with respect to the crystal axes. The intensity I_a will thus be increased by $e^{-\epsilon/kT}\cosh(eEd/kT)$. Adding this to the denominator in the expression above, one arrives at

$$\frac{I_b}{I_a}\propto\frac{1}{(1+e^{-\epsilon/kT})\cosh(eEd/kT)}\ .$$

If this is normalized to unity for $E=0$,

$$\left(\frac{I_b}{I_a}\right)_{\text{norm}}=\frac{1}{\cosh(eEd/kT)}\ .$$

This expression has been fitted by a least-squares procedure to the experimental data in Fig. 4, yielding $ed=0.1e$ Å. If e is taken to be three elementary changes, this leads to an off-center distance of roughly 0.03 Å.

In calculating the intensity ratio I_c/I_a, one has to consider that a fraction $e^{-\epsilon/kT}\cosh(eEd/kT)$ is withdrawn by E from the intensity of line c and added to line a:

$$\frac{I_c}{I_a}\propto\frac{1-e^{-\epsilon/kT}\cosh(eEd/kT)}{(1+e^{-\epsilon/kT})\cosh(eEd/kT)}\ .$$

Again normalizing this to unity at $E=0$,

$$\left(\frac{I_c}{I_a}\right)_{\text{norm}}=\frac{1-e^{-\epsilon/kT}\cosh(eEd/kT)}{(1-e^{-\epsilon/kT})\cosh(eEd/kT)}\ .$$

A least-squares fit of this relation to the relevant data in Fig. 4 gives $\epsilon=11\pm3$ meV, which is 1.7

times higher than $k\times(77\,\mathrm{K})$. This can explain why the Ti^{3+} ion is not observed going off center along the domain axis spontaneously at 77 K.

C. Orthorhombicity of Centers

We now discuss the relation of the orthorhombicity of the centers, independent of temperature in the range 4.2–103 K (Fig. 3) to the distortion of the environment of a Sr^{2+} site in the tetragonal phase of $\mathrm{SrTiO_3}$ described by the order parameter φ. These two phenomena are clearly related to each other, as can be seen by the fact that the orthorhombic centers start to vanish near T_c. The tilting angle τ, however, can depend on φ in an indirect way only, as revealed by their quite different sizes and temperature dependences (Fig. 3). We assume that the only effect of a nonzero φ is singling out certain O^{2-} ions of those surrounding the Ti^{3+} ion by shifting them closer to the ideal lattice site than the remaining ones. As discussed above, the Ti^{3+} ion will adhere to one of these O^{2-} ions closest to it. The interaction, however, is mutual, and it is likely that the Ti^{3+} also pulls its O^{2-} partner towards the empty Sr^{2+} site, decoupling the O^{2-} ion in this way to some extent from the surrounding lattice. The geometry of the resulting Ti^{3+}-O^{2-} complex will then determine the tilting angle (see Fig. 7). (We must exclude the possibility that the Ti^{3+} $3z^2-r^2$ orbital is engaged in a σ-type molecular orbital with O^{2-}; the resulting antibonding orbital would then not be the lowest state and the unpaired electron would not be found in an orbital of $3z^2-r^2$ symmetry.) The stability of the tilting angle τ also points to the fact that the Ti^{3+} ion is bound by one definite energy as long as it adheres to one O^{2-} ion. This will happen if the local-order parameter φ is larger than a certain critical value φ_c.

If φ is smaller than this critical angle, the four O^{2-} ions in a certain [100]-type direction become equivalent and the Ti^{3+} ion will start to hop between them. This will lead to an averaged axial spectrum around such a [100] direction if the hopping frequency $1/\tau_h$ is high compared to the difference of the resonance frequencies $\Delta\nu$, which the Ti^{3+} shows if it is locked to one of the O^{2-} ions to which it passes during the hopping motion. The position of the average line, of course, is given by the average of the g values in the locked position.

Take, for example, the configuration shown in Fig. 7. If H is perpendicular to the plane of Fig. 7, the Ti^{3+} ion will give rise to line b in Fig. 1. The same will happen if it adheres to O_c^{2-} after this has become equivalent to O_a^{2-}. If the Ti^{3+} is locked to either one of the O^{2-} ions shown dashed in Fig. 7, the situation is similar to that giving rise to line c in Fig. 1 (H perpendicular to z and parallel to a domain axis). It is thus expected to find the new line near the average position of lines b and c. For this average one calculates $\frac{1}{2}(1.9228+1.8530)=1.8879$; the line is observed at $g=1.8905(10)$. With this interpretation we can calculate the frequency difference $\Delta\nu=(1.9928-1.8530)\mu_B H=3.3\times10^8$ Hz at a typical X-band magnetic field of 3.4 kG.

As stated above, among these axial centers there are also those belonging to the Ti^{3+} going off center along a (former) domain axis [horizontal line in Fig. 2(a)]. A cubic spectrum, resulting from a hopping of the Ti^{3+} among the several [100]-type directions, equivalent at least above T_c, is not observed even at higher temperatures. Apparently, the barriers between the four O^{2-} ions grouping around one [100]-type direction are much lower than those between the several [100] axes. Excessive line broadening due to an increased spin-lattice relaxation time might prevent the observation of an isotropic (cubic) spectrum at higher temperatures.

A hopping frequency high compared to the frequency difference of the lines to be averaged is a prerequisite to observe ideally motionally narrowed lines. If this condition is not fulfilled, the lines will still become narrower upon raising the temperature, for this increases the hopping frequency. In our case, however, the width of line α did not change appreciably during heating above T_c (see Fig. 5).

This must not necessarily be traced to the fact that line α is ideally motionally averaged; broadening due to other reasons, such as inhomogeneous linewidths, lifetime broadening, etc., might overlay the motional narrowing. Since the observed width of line α, however, is still small compared to the distance of the averaged lines b and c, we can conclude that the hopping time for line α is short compared to $1/\Delta\nu$.[8]

This is not the case for line b. Apparently, kT is not sufficiently large near T_c to let the locked orthorhombic centers participate in the averaging. This is demonstrated by the fact that near T_c these spectra are still observed, not shifted from their former positions, simultaneously with the axial averaged spectra. From this argument one can also derive that there are essentially only two potential states available for the Ti^{3+}: one deep level, if it is locked at a displaced O^{2-} ion, and a high-energy state, equally found at all four eligible O^{2-} ions if φ is smaller than the critical angle φ_c.

If there were a continuum of states between these two, one should also expect a continuum of hopping times with the τ_h corresponding to the averaged line α as a lower bound. Thus, not completely averaged lines should also be observed; the superposition of which would cover the entire range between the positions of the lines to be averaged.

This, apparently, is not the case. This argument, pointing to the existence of a rather sharply defined energy in the "locked" state, is consistent with the observation that the tilting angle does not vary in the entire regime $T < T_c$.

D. Fluctuations near T_c

What then is the reason for the coexistence between the orthorhombic and the axial averaged spectra? Apparently, simltaneously there are regions in the crystal where φ is higher and regions where it is lower than φ_c. A natural explanation is the existence of fluctuations in the order parameter, especially large and nearly static, close to T_c. Do our results yield any information on the fluctuation spectrum? From the above discussion it is apparent that $\varphi > \varphi_c$ will give an orthorhombic spectrum only if this angle prevails longer than the reciprocal frequency difference $1/\Delta\nu$ between lines b and c; otherwise these lines would be averaged. (As we have seen, the hopping time τ_h being shorter than $1/\Delta\nu$ is not the critical time.) The fraction of orthorhombic spectra then gives a quantity proportional to the number of Ti^{3+} ions on a Sr^{2+} site for which at least one of the surrounding O^{2-} ions is tilted by more than φ_c for a time longer than $1/\Delta\nu$. All other Ti^{3+} ions yield averaged spectra. Figure 5 shows that this is qualitatively consistent with experiment. Near T_c, where the deviations from $\langle\varphi\rangle = 0$ (for $T > T_c$) are large, a high number of orthorhombic centers is observed. This quantity decreases relative to the axial spectra upon raising the temperature, both because the fluctuations become smaller and last a shorter time.

From Fig. 5 it is seen that still at $T_c + 40$ K there is a sizable portion of Ti^{3+} surroundings whose fluctuations last longer than $1/\Delta\nu = 3\times10^{-9}$ sec. Such a far extending fluctuation range has also been observed in other experiments, such as the investigation of paramagnetic linewidths,[2] central-mode neutron scattering,[3] and intrinsic optical absorption of SrTiO$_3$.[4]

While a quantitative explanation of the curve in Fig. 5 is still lacking, we ascribe the marked change of slope near $T_c + 4$ K to the fact that at this temperature the fluctuations described by the central mode[3,9] start to last shorter than $1/\Delta\nu$ and thus no longer contribute to I_b. As has recently been shown, the width of the central peak Γ_c is about 70 MHz at $T_c + 1$ K.[10] Since it varies with temperature[11] as

$$\Gamma_c = \Gamma_c^0\,[(T - T_c)/T_c]^\gamma ,$$

where $\gamma = 1.28$,[12] one calculates $\Gamma_c \approx 4.2\times10^8$ Hz for $T = T_c + 4$ K. This is about the size of $\Delta\nu$. The linewidth broadening of the Fe^{3+}-V_O center[10] and I_b/I_a (Fig. 5) is seen to vary up to 150 K. This shows that a sizable quasistatic order-parameter variation prevails up to this temperature.

V. HYPERFINE INTERACTION

The ground state of the Ti^{3+} ion can only approximately be described by a $3d$ $(3z^2 - r^2)$ orbital. In the low symmetry of the ion site, the wave function will contain admixtures compatible with $3z^2 - r^2$, in self-evident notation:

$$\psi = N\left[(3z^2 - r^2) + \alpha(x^2 - y^2) + \beta(zy) + \gamma(4p_z) + \delta(4p_y) + \epsilon(4s)\right] .$$

As shown in Ref. 1, only $x^2 - y^2$ contributes to the hf interaction in first order of the admixture coefficient α. Using the above wave function, the formalism of Abragam and Pryce[13] leads to the following description of the principal values of the hf coupling tensor:

$$\begin{aligned}
A_z &= A + \mathcal{P}\left[\tfrac{4}{7} - \tfrac{1}{14}(\Delta g_x + \Delta g_y)\right],\\
A_x &= A + \mathcal{P}\left(-\tfrac{2}{7} + \Delta g_x - \tfrac{1}{14}\,\Delta g_y - \tfrac{4}{7}\sqrt{3}\,\alpha\right),\\
A_y &= A + \mathcal{P}\left(-\tfrac{2}{7} + \Delta g_y + \tfrac{1}{14}\,\Delta g_x + \tfrac{4}{7}\sqrt{3}\,\alpha\right),\\
\Delta g_i &= g_i - 2.0023.
\end{aligned} \tag{2}$$

A describes the contact hf interaction; $\mathcal{P} = g g_n \beta_n \beta\,\langle r^{-3}\rangle$. These expressions are identical to those derived in Ref. 1 except for the + sign in front of the last term of A_y (the − sign at this place in Ref. 1 is evidently a printing error) and the terms multiplied by $\frac{1}{14}$. These arise from a more complete evaluation of the formulas in Ref. 13. As in Ref. 1, we assume all $A_i > 0$. Comparison of Eq. (2) with the experimental parameters then leads to

$$\begin{aligned}
A &= (9.8 \pm 0.4)\times10^{-4}\ \mathrm{cm}^{-1},\\
\mathcal{P} &= -(12.4 \pm 0.5)\times10^{-4}\ \mathrm{cm}^{-1},\\
\alpha &= -0.45 \pm 0.25.
\end{aligned}$$

The value of A corresponds to a hyperfine field of − 61.2 kOe per electron. This value is much smaller than the core polarization field reported for Ti^{3+} in a tetragonally distorted sixfold oxygen environment, − 90 kOe.[14] A field of that size is also expected from an extrapolation of the hf fields derived from data for the isoelectronic Cr^{5+} [15] and V^{4+} ions.[16] An analogous statement holds for the magnitude of $\mathcal{P}$; it corresponds to $\langle r^{-3}\rangle = 1.2$ a.u. For an isolated Ti^{3+} ion, one calculates 2.55 a.u.[17] Both facts can be attributed to a strong delocalization of the unpaired electron, which is to be expected in a tightly bound (TiO)$^+$ "molecule." An admixture of $4s$ character to the ground-state wave function could also play a role.

VI. COMPARISON WITH OTHER NONCENTROSYMMETRIC CENTERS IN PEROVSKITE-TYPE CRYSTALS

The center discussed here belongs to a class of defects consisting of ions sitting on sites nominally having O_h symmetry in perovskite ABO_3-type lattices, but which still show lower-than-cubic symmetry. We list them here for comparison with the present results. Since we are interested only in centers whose low symmetry arises from local disturbances, we omit those whose symmetry is lowered by the polarization field in ferroelectric crystals, as in $BaTiO_3$.

The centers to a certain extent similar to that treated in the present paper are Mn^{4+} [18] and Cr^{5+} [15] on Ti^{4+} sites in $SrTiO_3$. In both cases an axiality of the spectra was found in the cubic phase. Since the radii of these ions are smaller than that of the replaced Ti^{4+}, it is likely that they go off center and thus reduce the symmetry of their surroundings. This has been proved for Cr^{5+}: Its tetragonal axis is rotated by φ on going below T_c.[15] This can only be explained if Cr^{5+} in the surrounding oxygen cube is shifted towards one of the corners not lying on the cube rotation axis.

Other noncentrosymmetric centers arise in perovskite-type crystals doped with transition-metal ions having a lower valency than the replaced B ions. Charge compensation is achieved by forming neighboring oxygen vacancies. This results in strong tetragonal fields at the site of the transition-metal ion. Examples are Fe^{3+}-V_O, Co^{2+}-V_O, and Ni^{3+}-V_O in $SrTiO_3$, Fe^{3+}-V_O in $BaTiO_3$, and Co^{2+}-V_O and Mn^{2+}-V_O in $KTaO_3$.[19] There is a similar center in $BaTiO_3$, showing axial symmetry around a [100] direction with $g_\parallel = 1.939$, $g_\perp = 1.911$, and Ti hyperfine-structure (hfs) interaction of $A_\parallel = 19.6 \times 10^{-4}\ \mathrm{cm}^{-1}$. $A_\perp$ could not be measured. This center was assigned earlier to an F center (one electron at an oxygen vacancy). The spectrum, especially the hfs interaction and g shifts, shows that the xy state of a Ti^{3+} is occupied. Because of several counterdoping experiments it was thus reassigned to the straight complexes Ti^{3+}-V_O-La^{3+} and Ti^{3+}-V_O-Ba^{2+}.[20]

Except for the center reported in this paper there is only one originating from a transition-metal ion on an A site having lower-than-cubic symmetry. Hannon[21] identified a high-spin Ni^{3+} ion ($3d^7$, $S=\frac{3}{2}$) on this site in $KTaO_3$ with symmetry ($g_\parallel = 2.216$, $g_\perp = 4.423$). No reason for the axial-site symmetry was given. Since Hannon also observed spectra resulting from Fe^{3+} ions on K^+ sites seeing cubic symmetry, a size effect resulting in axial Ni^{3+} appears highly unlikely. A straightforward explanation would be a Ni^{3+} ion next to a K^+ vacancy. This is compatible with the observation of axial Fe^{3+} ions on A sites. A Ni^{3+} clamped on an interstitial site is improbable, both because a charge excess of +3 is unlikely under normal chemical conditions and because of ionic size considerations.

VII. SUMMARY AND CONCLUSIONS

We have analyzed spectra originating from Ti^{3+} on a Sr^{2+} site in $SrTiO_3$. The Ti ion, which is knocked from its original position by fast-neutron irradiation, sits off center in a direction towards one of the surrounding oxygen ions. This was proved by the effect of an external electric field on the ESR spectra of the center. To our knowledge this is the first time that the eccentricity of an ion has been investigated using ESR. The orthorhombicity of the center depends on the order parameter φ in a rather indirect way, but it yields evidence for the fluctuations of the order parameter near and above T_c. It was possible to estimate the frequency spread at $T < T_c + 4$ K to be of the order of $\Delta\nu = 3.5 \times 10^8$ Hz corresponding to the width of the central mode.

Because of the high dielectric constant of $SrTiO_3$ at low temperatures, nearly complete orientation of the Ti^{3+} ions should be obtained on applying rather low external electric fields, possibly to be used for paraelectric cooling. The zero-field splitting of the Ti^{3+} system should be rather small. First, the high dielectric constant of $SrTiO_3$ screens the Ti^{3+} dipoles against each other. Second, the Ti^{3+} ions are stabilized against tunneling by the corresponding small zero-field splitting due to their high mass and by the interaction with the lattice. Observations can again be made with ESR.

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Plasmons and Characteristic Energy Loss in Periodic Solids

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Existing formulations for systems with complete translational invariance relate the dielectric function to the scattering probability in characteristic-energy-loss experiments. We have extended this relationship to the case of periodic systems. Energy-loss vs momentum-transfer measurements are of value because they provide a probe of the system for momentum transfer not accessible to optical measurements. Periodicity is shown to cause the formation of plasmon bands, and the possibility of long-lived higher-band plasmons is discussed. It is concluded that materials with a strong crystalline potential are the best candidates for such higher-band plasmons. The effect of the crystalline potential on the dispersion and damping of the lowest plasmon band, whose existence is well established experimentally, can also be obtained from the formulas that have been derived (which include the effects of local field).

I. INTRODUCTION

At the time when characteristic-energy-loss experiments on thin films were first being performed,[1] the theoretical apparatus for their interpretation was just being developed. Results applicable to the free-electron gas and its collective excitations, the plasmons, were modified in order to explain (in a qualitative fashion) the experiments which were being performed on real solids.[2] These modifications proved highly successful, so much so, that workers in the area were not forced to make more detailed studies. However, had such detailed studies been necessary, they would have been severely handicapped by two major difficulties. First, in most of the early experiments one could not be sure that the thin film was a single crystal, rather than polycrystalline or amorphous. Second, the calculation of properties of periodic solids hinged upon accurate band-structure calculations, which were still in an early stage of development.

Since that time, both experiment and theory have developed considerably. Experiments on thicker films have yielded cartographs of energy loss versus scattering angle which clearly show peaks associated with diffraction by the periodic lattice.[3] In addition, theoretical energy-band calculations have been able to explain numerous properties of periodic solids. However, to our knowledge, no theoretical work has been directed towards explaining the details of the characteristic-energy-loss experiments, including the effects of periodicity on the local field.

We believe it is now appropriate to make such detailed theoretical studies of the energy-loss experiments. Neutron-scattering experiments have revealed much about the vibrations of ions in periodic solids; the analogous electron-scattering experiments should reveal much about the electron energy levels and wave functions in periodic solids. Such studies should provide more detailed information than, e.g., optical studies. We mention that the first detailed calculation of the wave-vector–