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Observation of Two Charged States of a Nickel-Oxygen Vacancy Pair in SrTiO$_3$ by Paramagnetic Resonance

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The paramagnetic resonance of two tetragonal nickel spectra in the cubic phase of SrTiO$_3$ has been investigated below the structural phase transition at 105°K. Both spectra show the same rotation angle measured from the tetragonal directions as the iron-oxygen vacancy complex. This angle is $0.90\pm0.05°$ at 77°K and $1.25\pm0.10°$ at 4.2°K. One of the axial nickel spectra is stable at room temperature and has been reported before by Rubins and Low with $g_{\parallel}=2.029\pm0.01$, $g_{\perp}=2.352\pm0.001$ ($g_{\parallel}<g_{\perp}$). It is now assigned to a substitutional low-spin Ni^{3+} ion situated next to an oxygen-vacancy with the unpaired spin in an e-type, $3z^2$-r^2 orbital directed towards the positively charged vacancy. The second spectrum is generated by light and is thermally unstable at room temperature with $g_{\parallel}=2.375\pm0.001$, $g_{\perp}=2.084\pm0.001$ ($g_{\parallel}>g_{\perp}$), and can be assigned to a low-spin Ni^{3+} ion next to an oxygen vacancy associated with two electrons, the unpaired spin being in an e-type, x^2-y^2 orbital directed *away* from the near neutral vacancy. Observed titanium superhyperfine structure supports these assignments. The importance of this first microscopic evidence of two differently charged states of an oxygen-vacancy defect complex in high-dielectric-constant oxide materials is emphasized. The difficulty of observing by EPR pairs when the defects are singly charged is discussed.

I. INTRODUCTION

IN this paper, part of the work that is summarized was carried out several years ago and its interpretation has remained a puzzle until recently. It is the study and analysis of two tetragonal paramagnetic-resonance spectra with effective spin $S=\frac{1}{2}$ in Ni-doped SrTiO$_3$. One spectrum is thermally stable at room temperature; the other is unstable and observed after light illumination of the crystals. The most likely interpretation is that both spectra are due to the *same* lattice defect-complex, with however different charge configurations. The spectra result from a three-valent Ni ion substituting for a Ti^{4+} ion situated next to an oxygen vacancy (V_{O}). The stable one is observed when the V_{O} donor is empty, the other when two electrons are trapped near the oxygen vacancy. The difference between the spectra arises because in the former case the single paramagnetic e-type electron orbital of low-spin Ni^{3+} with configuration ($t_2{}^6$,e) is directed *towards* the V_{O}, which is positively charged with respect to the lattice. In the latter case the orbit is directed *away* from the near neutral vacancy. The observation of different charged states of a lattice defect by the orientation dependence of an electronic wave function of a next-nearest-neighbor impurity is quite a novel feature in solid-state physics. Furthermore, the present investigation allowed us to gain deeper insight into associated defects, their charged states, and stability in high-dielectric-constant materials of the perovskite family.

In diamagnetic ABO$_3$ oxide "perovskite" crystals, paramagnetic ions have been introduced and observed by electron paramagnetic resonance (EPR) for more than a decade. The radius of the B ion is about half that of the A ion, the latter being comparable to that of oxygen. Therefore size considerations lead to the expectation that the transition-metal ions with radii ranging from 0.5 to 0.7 Å are incorporated at B sites, and those of the rare-earth series with $r\sim1$ Å at A sites. Since the lattice is well packed and an accommodation of interstitials difficult, the above expectation has been verified by EPR and optical methods for a considerable number of species, namely, Mn^{4+}, Cr^{3+}, Fe^{3+}, Ni^{3+}, Co^{3+}, Mn^{2+}, and Ni^{2+} on B sites and Gd^{3+}, Ce^{3+}, Nd^{3+}, and Eu^{2+} on A sites.[1–3] However, under certain conditions of preparation of the materials, exceptions are found. For example, in reduced BaTiO$_3$ Takeda and Watanabe observed the Gd^{3+} ion to be in part substitutional at B sites.[4] The Yb^{3+} ion has probably also been observed on B sites in SrTiO$_3$.[2] For the transition-metal ions, Hannon[5] has shown unambiguously that Fe^{3+} and Ni^{3+} can be located at A sites in KTaO$_3$. The A-site preference appears to be induced by co-doping the K$_2$CO$_3$ flux-grown crystals with Ti^{4+} ions.

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* Supported in part by the National Science Foundation and the U. S. Office of Naval Research, under Contract No. NONR-233(88).

[1] R. S. Rubins, W. Low, K. A. Müller, L. Rimai, and G. A. de Mars in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963), pp. 59, 17, and 51.

[2] W. Low and E. L. Offenbacher, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 17, p. 135.

[3] The assignments of Mn^{2+} to A sites in BaTiO$_3$ by H. Ikushina [J. Phys. Soc. Japan **21**, 1866 (1966)] and in CaZrO$_3$ by B. Henderson [Proc. Phys. Soc. (London) **92**, 1064 (1967)] are not likely to be correct because the isotropic part of the hfs constant of Mn^{55} observed in both cases is equal to 80.7×10^{-4} cm^{-1}, and typical for octahedral coordination.

[4] T. Takeda and A. Watanabe, J. Phys. Soc. Japan **19**, 1742 (1964); **21**, 1132 (1966).

[5] D. M. Hannon, Phys. Rev. **164**, 366 (1967).

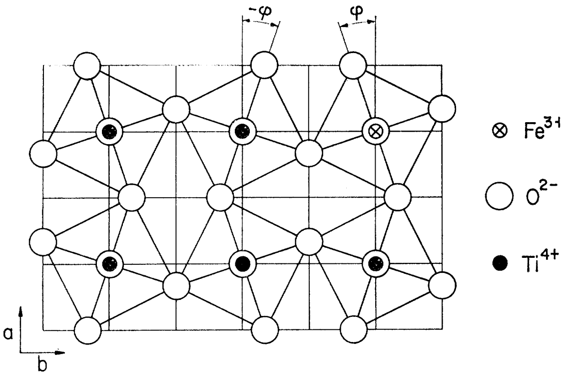

FIG. 1. Rotated oxygen octahedra around tetragonal c axis in $SrTiO_3$ below T_a. The presence of an Fe^{3+} substitutional point defect is indicated.

The question of charge compensation in these double oxides is a very interesting one. In flux-grown crystals this is often accomplished by the incorporation of one or several components of the flux. In $BaTiO_3$ grown by the Remeika method, Arendt made a quantitative chemical analysis.[6] He found in crystals containing known concentrations of Fe^{3+} and Co^{2+} ions, that charge compensation was achieved by the incorporation of F ions at oxygen sites. The amount of F^- for a given concentration of transition-metal ions was about twice as large for Co^{2+} as for Fe^{3+}.[6]

If crystals are grown by the Verneuil technique or by pulling from the melt with a major substitutional impurity present, which differs in charge from the substitute, compensation must be achieved in a way different from the one discussed above. It can occur by intrinsic defects; an example is the addition of Fe_2O_3 to $SrTiO_3$. In this case a substantial part of the ion is incorporated as Fe^{3+} at a Ti^{4+} place, and oxygen vacancies are formed. Evidence for this was first found by the observation of a strong axial EPR Fe^{3+} spectrum in $SrTiO_3$, which was attributed to an Fe^{3+}-O vacancy next-neighbor impurity pair.[7] This assignment was confirmed using Mössbauer spectroscopy by Bhide and co-workers[8] and again by EPR.[9] Recently, the axial Fe spectrum reported by Hannon[5] in $KTaO_3$ was analyzed by Wessel and Goldick,[10] who obtained an axial splitting parameter $|2D|=2.88\ \text{cm}^{-1}$, very near to the one deduced in $SrTiO_3$ of $|2D|=2.701\ \text{cm}^{-1}$.[11]

One purpose of this work is to show that the stable axial Ni^{3+} spectrum observed earlier[1] was indeed due to a Ni^{3+}-V_O defect. This could be accomplished by comparing the angular dependence of the Ni^{3+} spectra with that due to the Fe^{3+}-V_O defect *below* the phase transition in $SrTiO_3$. Recently, understanding of the cubic-to-tetragonal phase transformation in $SrTiO_3$ was elucidated using paramagnetic resonance of S-state ions. From the analysis of the angular dependences of the Fe^{3+} spectra[12,13] as well as those of Gd^{3+} ions, the static properties of the transformation were entirely determined. The transformation consists of alternate rotations of near-rigid TiO_6 octahedra around Ti^{4+} ionic positions along cube-edge directions. The rotation angle φ is the order parameter of this phase transition,[13,14] which is characteristic for the perovskite structure. Unoki and Sakudo[12] obtained the rotation angle φ at 77 and 4.2°K from uncompensated Fe^{3+} spectra (see Fig. 1), which are cubic above the transition temperature $Ta=105°\text{K}$. The rotation angle $\bar{\varphi}$ of the charge-compensated defect Fe^{3+}-V_O is smaller by 40%, due to the missing oxygen ion, i.e.,

$$\varphi(T)=1.4\bar{\varphi}(T)$$

at both temperatures at which they measured (Fig. 2).

If the assignment of Ni axial spectra to a Ni^{3+}-V_O defect is correct, then the same rotation angle $\bar{\varphi}(t)$ should be observed as for the Fe^{3+}-V_O defect; because the ionic radius of Ni^{3+} is very close to the one of Fe^{3+}, the local distortion is also expected to be close.

The experiments from which this angular dependence is deduced will be described in Sec. II. The same data have also been taken for the light-generated axial Ni spectrum, which was observed several years ago.[15] In Sec. III the theory is summarized and some empirical systematics of g values for Ni^{1+} and Ni^{3+} ions are given. In Sec. IV the stable axial spectrum is assigned using steric arguments, the crystal field, measured g shifts, Ti superhyperfine interaction, and the temperature-dependent linewidth broadening. The same is done for the light-generated spectrum in Sec. V. The difficulty of observing the neutral Ni^{3+}-V_O-$(-e)$ center is discussed in Sec. VI, and in Sec. VII; some thoughts on other tetragonal spectra observed by others in $KTaO_3$ and $BaTiO_3$ are expressed.

II. PARAMAGNETIC-RESONANCE SPECTRA

Paramagnetic-resonance spectra of nickel-doped strontium titanate were observed at X- and K-band frequencies for two different crystals, which we denote

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[6] H. Arendt, in *Proceedings of the International Meeting on Ferroelectricity, Prague, 1966* (Czechoslovak Academy of Science, Prague, 1966), p. 231.

[7] E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins, Phys. Rev. **135**, A86 (1964).

[8] V. G. Bhide and M. S. Multani, Phys. Rev. **149**, 289 (1966); V. G. Bhide and H. C. Bhasin, *ibid.* **159**, 586 (1967).

[9] R. Baer, G. Wessel, and R. S. Rubins, J. Appl. Phys. **39**, 23 (1968).

[10] G. Wessel and H. Goldick, J. Appl. Phys. **39**, 4855 (1968).

[11] A strong axial Fe spectrum with $g_\perp \sim 6$ has also been reported by D. J. A. Gainon, J. Appl. Phys. **36**, 2325 (1965). Although the spectrum was not analyzed in terms of a D parameter, it has been assigned to a Fe^{3+}-V_O pair by this author.

[12] H. Unoki and T. Sakudo, J. Phys. Soc. Japan **23**, 546 (1967).

[13] K. A. Müller, W. Berlinger, and F. Waldner, Phys. Rev. Letters **21**, 814 (1968).

[14] H. Thomas and K. A. Müller, Phys. Rev. Letters **21**, 1256 (1968).

[15] R. S. Rubins and K. A. Müller, in *Proceedings of the Twelfth Colloque Ampère, Bordeaux, 1963*, edited by A. Masson (Dunod Cie., Paris, 1964), p. 10.

J and N. Crystal J was the same as that used by Rubins and Low,[1] and contained a nominal 0.15% NiO. Crystal N contained a nominal 0.1% NiO. Both crystals were obtained from the National Lead Co. Apart from lines due to Cr^{3+} [13] and Fe^{3+} [14] impurities, the following Ni spectra were observed in crystal J near room temperature: (a) an isotropic spectrum with $g=2.204\pm0.001$, characteristic of Ni^{2+} in an octahedral site; (b) an isotropic spectrum with $g=2.180\pm0.002$, attributed to Ni^{3+} in an octahedral site; and (c) a spectrum consisting of three axially symmetric lines with mutually perpendicular tetragonal axes, and principal g values

$$g_{\parallel}=2.029\pm0.001, \quad g_{\perp}=2.352\pm0.001.$$

In crystal N, the Ni^{2+} spectrum (a) was observed only at liquid-helium temperatures. The cubic Ni^{3+} spectrum (b) was considerably weaker, although the axial spectrum (c) was of similar intensity to that in crystal J. The intensity ratio of (b) to (c) was approximately 1:2.5 for crystal J and 1:7.5 for crystal N. No significant changes in these values were observed as a function of temperature.

Two experiments were undertaken in order to change the valencies of the Ni ions present in crystal N. In the first experiment, a portion of the crystal was heated for $2\frac{1}{2}$ h at 1000°C in a hydrogen atmosphere, and then for $\frac{1}{2}$ h at 700°C in air. After such treatment, both spectra (b) and (c) were almost indetectable, but a relatively intense axial spectrum, attributed to Fe^{3+} in a Ti^{4+} site with a nearest-neighbor oxygen vacancy, was observed.[7] In the second experiment, the sample was illuminated with a 90-W xenon lamp for 3–4 min, and then dropped without delay into liquid nitrogen. Spectrum (a), previously observed only in crystal J, was present; spectrum (b) was enhanced by a factor of 6; spectrum (c) was diminished in intensity. In addition, a new "light-induced" spectrum, consisting of three axially symmetric lines with mutually perpendicular tetragonal axes, was observed, with principal g values

$$g_{\parallel}=2.375\pm0.001, \quad g_{\perp}=2.084\pm0.001.$$

This spectrum may be seen in Fig. 3, taken at 77 and 180°K; spectra (b) and (c) are observed to be considerably broader than the light-induced spectrum. In fact, in warming the crystal to room temperature, the linewidth of the light-induced spectrum did not change, in contrast to spectra (b) and (c), which broadened considerably. At room temperature, the light-induced spectrum slowly disappeared.

The linewidths of spectra (b) and (c) were measured in the range 195–400°K at X band. Within the experimental error of about 10%, the widths of the two spectra were equal, and increased with temperature as shown in Fig. 4. At room temperature, the widths at K band and X band were equal, indicating that the width is frequency-independent.

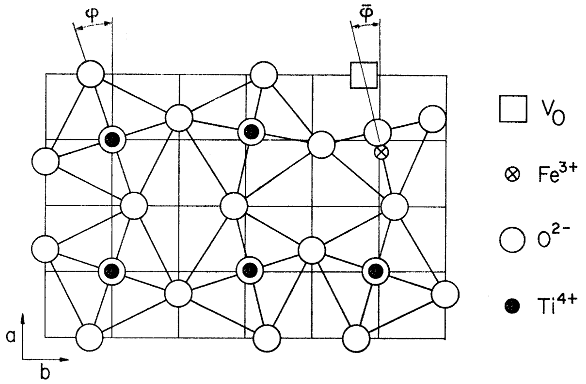

FIG. 2. Schematic representation of rotated oxygen octahedra and oxygen pyramid of an Fe^{3+}-V_O pair.

When $SrTiO_3$ crystals are cooled below the transition temperature at 105°K, the isotropic Ni^{3+} line is observed to split smoothly with temperature into a set of three axially symmetric lines with mutually perpendicular tetragonal axes.[3] These splittings, which represent the effect of the tetragonal distortion on the dynamic Jahn-Teller effect, have recently been investigated both experimentally and theoretically.[16] Because of the local defect association from which the axial spectra result, the change of the g-tensor symmetry to orthorhombic is barely detectable. The most pronounced change of these on cooling through T_a is that the maxima and minima of the resonance fields in part, do not occur along the tetragonal directions of the crystal. Of course, the over-all symmetry of the pattern must still be tetragonal for a particular domain; thus the lines are split. This is due to the alternate rotation of the octahedra along the c axis in each domain, as discussed at some length for the Fe centers in Sec. I (see Figs. 1 and 2).

We have investigated these splittings in detail by rotating the scanning magnetic field in pseudocubic {001} and {110} planes in the presence of domains in the crystal along all three pseudocubic directions. For a rotation in a particular (001) plane, at most four split lines are observed. They are due to **[100]**, **[010]**, and **[001]** domains, where the symbol **[001]** denotes a domain whose c axis is parallel to the pseudocubic [001] direction. For such a domain two lines of equal intensity are seen except for [100] and [010] directions, where they coincide. They result for the alternate rotation $\bar{\varphi}$ of the associate defects around the c axis (see Figs. 1 and 2) and have their defect axes in the plane (001). From each of the **[100]** and **[010]** domains which lie in the magnetic field plane, one line results because, for both the octahedral rotation angles $\bar{\varphi}$ around [100] and [010] and an in-plane defect-association direction, the (001) plane is a mirror plane. Near [110] directions, the lines from the **[100]** and **[010]** domains practi-

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[16] J. C. Slonczewski, K. A. Müller, and W. Berlinger (unpublished).

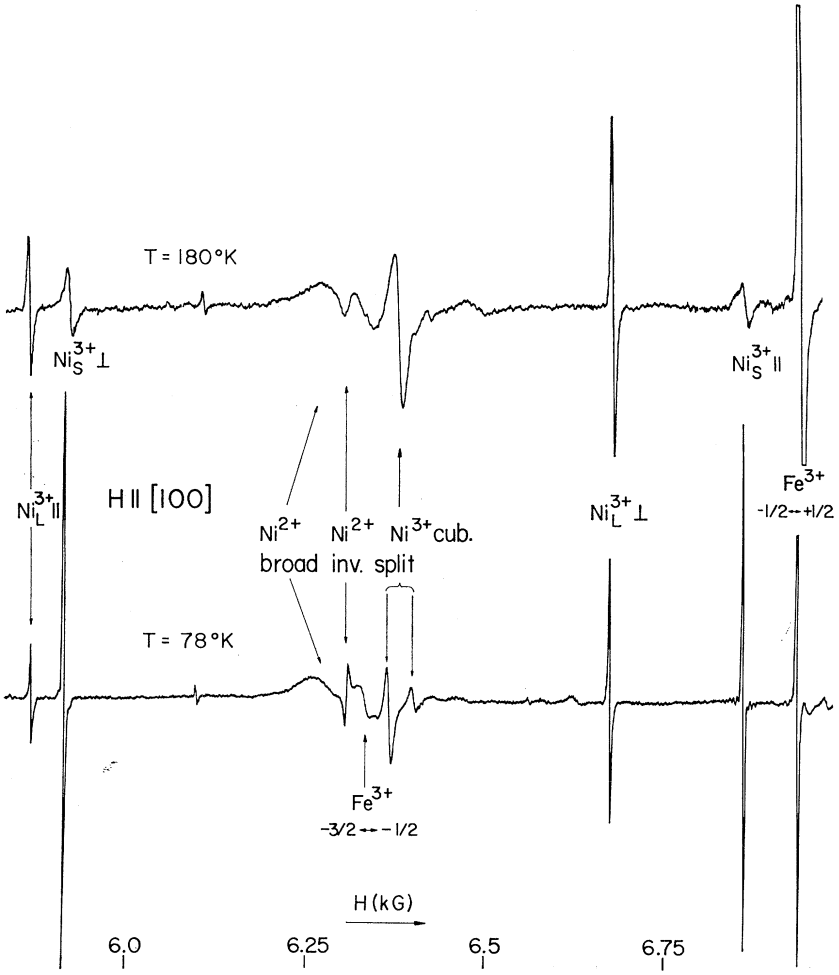

FIG. 3. *K*-band EPR spectrum of a type-J sample of nickel-doped strontium titanate, taken at 77 and 180°K after illumination. The magnetic field is directed along the [001] cubic axis of the crystal.

cally coincide and a symmetric three-line pattern is found. At exactly [110], three lines from axial centers along [100] and [010] directions in the different domains are superimposed (see Fig. 5). At this angle the highest resolution is obtained, and $\bar{\varphi}$ was determined using the oscilloscope and a precision nonius on the Varian magnet. In Table I the results at 77 and 4.2°K are summarized. For the perpendicular resonance magnetic field due to defect associations along [001] directions only one line was resolved. The resonance fields for all the domains are by, at most,

$$\tfrac{1}{2}[\varphi^2(g_\perp^2-g_\parallel^2)/g_\perp]\beta H_\perp$$

close to one another, yielding one broad line.

With the stable axial Ni center, an anisotropic superhyperfine structure (SHS) is detected (see Fig. 6). It results from the interaction with the 7.8% abundant Ti^{47} nuclei with $I=\frac{5}{2}$, and the 5.5% abundant Ti^{49} nuclei with $I=\frac{7}{2}$. The SHS is essentially caused by the interaction of *one* nucleus per impurity. This produces a spectrum consisting of eight lines from the $I=\frac{7}{2}$ nuclei and six lines from the $I=\frac{5}{2}$ nuclei which are superposed on the inner sextet of the octet. Only the outer three lines on each side of the intense one are resolved. The deduced coupling constants for the usual spin Hamiltonian are

$$A_\parallel=4.3\times10^{-4}\text{ cm}^{-1},\quad A_\perp=2.9\times10^{-4}\text{ cm}^{-1}.$$

The parallel direction coincides with the g-tensor axes. The intensity ratio of one of the inner sextet lines to the main line is $(2.2\pm0.3)\%$. For the light-induced center, SHS interaction was detected but could not be completely resolved due to the interaction with more then one kind of Ti nucleus and the anisotropy of the interaction constants. From the incompletely resolved

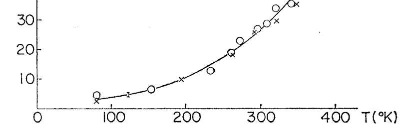

FIG. 4. Graph of linewidth against temperature for the stable axial and isotropic Ni^{3+} spectra in strontium titanate.

TABLE I. Comparison of the rotation angles of Fe and Ni centers in $SrTiO_3$.

Center	Rotation angle 77°K	4.2°K	Ref.
Fe^{3+} uncomp.	1.4 ±1°	2.1 ±0.10°	a
Fe^{3+}-V_O	0.95±0.05°	1.35±0.05°	a, b
Ni^{3+} ax. stable	0.90±0.05°	1.25±0.10°	Present work
Ni^{3+} ax. light gen.	0.90±0.05°	1.25±0.10°	Present work

[a] Reference 12. [b] Reference 13.

structure we deduce an upper limit in the SHS constants, which is half that of the stable spectrum; its estimated intensity ratio is, however, three times that of the latter.

III. *g* VALUES FOR $3d^7$ AND $3d^9$ CONFIGURATIONS

The *g* values of the stable axial spectrum and the light-induced spectrum are very close to those normally observed from d^7 and d^9 ions. In octahedral symmetry, the ground states for d^7 (in the strong-field approximation) and d^9 belong to the irreducible representation ^2E. This state is split by the Jahn-Teller coupling or by lower-symmetry components of the crystal field into the two Kramers doublets. The *g* values of these doublets for the d^9 ion, i.e., one hole in the *d* shell, are well known[17] to be approximately

$$g_{\parallel}(\bar{u})\simeq 2\,,\qquad g_{\perp}(\bar{u})\simeq 2-6\lambda/\Delta\,, \tag{1}$$

$$g_{\parallel}(\bar{v})\simeq 2-8\lambda/\Delta\,,\qquad g_{\perp}(\bar{v})\simeq 2-2\lambda/\Delta\,, \tag{2}$$

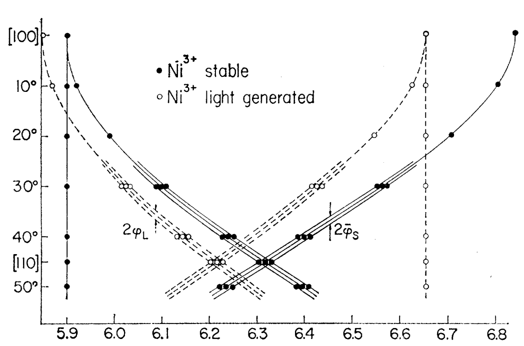

FIG. 5. Resonance fields of the stable and light-induced Ni centers at 77°K, and *K* band for a rotation of the magnetic field in a (001) plane.

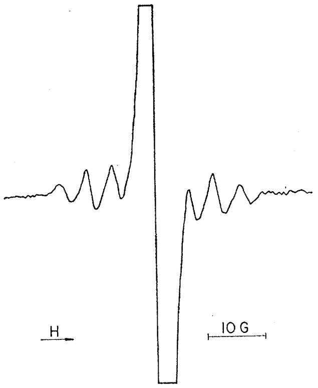

FIG. 6. Resolved Ti superhyperfine interaction of the stable axial spectrum for a parallel orientation.

where λ is the spin-orbit coupling constant and Δ is the crystal-field splitting of the ^2D term. The single-hole orbital parts of the wave functions are denoted by $\bar{u}$ and $\bar{v}$. They are $(1/\sqrt{3})(3z^2-r^2)\,f(r)$ and $(x^2-y^2)\,f(r)$, respectively. The corresponding expressions for d^7, derived by Lacroix, Höchli, and Müller[18] using strong-field hole wave functions of the configuration t^6e $(\equiv\bar{e}^3)$, are

$$g_{\parallel}(U)\simeq 2 \qquad +2\xi^2/\delta^2\,,\qquad g_{\perp}(U)\simeq 2+3\xi/E \quad +2\xi^2/\delta^2\,, \tag{3}$$

$$g_{\parallel}(V)\simeq 2+4\xi/E \quad +2\xi^2/\delta^2\,,\qquad g_{\perp}(V)\simeq 2+\xi/E \quad +2\xi^2/\delta^2\,, \tag{4}$$

where ξ is the spin-orbit coupling constant for a single *d* electron, *E* is given by

$$1/E=1/E_3+1/E_4+0.38(1/E_3-1/E_4)\,, \tag{5}$$

where E_3 and E_4 are, respectively, the lower and higher $^2T_2$ components of the excited t^5e^2 $(\equiv\bar{t}\bar{e}^2)$ configuration, and δ is the energy of the low-lying $^4T_1$ level, whose splitting by spin-orbit coupling and lower-symmetry fields has been ignored. *U* and *V*, which denote the orbital parts of the ^2E hole wave functions for the $\bar{e}^3$ configuration, are triple products of single-hole wave functions $\bar{u}$ and $\bar{v}$. They transform as *u* and *v*, respectively, and are identical with the single-*e*-electron *u* and *v* functions, i.e., $U_\alpha=|\bar{v}_\alpha,\bar{v}_\beta,\bar{u}_\alpha\rangle\equiv u_\alpha$.

Apart from the second-order term $2\xi^2/\delta^2$ in Eqs. (3) and (4), the theoretical *g* values for the doublets in the two systems are seen to be very similar, because ξ is positive and λ is negative. However, in a field of tetragonal symmetry, doublets transforming according to *dissimilar* wave functions lie lower. For example, if a positive V_2^0 component is present, corresponding to an elongated octahedron, the doublet $\bar{v}$ lies lower for d^9, whereas the doublet *U* is lower for d^7. This is easily visualized in looking at *u* and *v* sublevels. For $V_2^0>0$, $E_u<E_v$ with one *e* electron, the *u* sublevel is singly occupied. With three electrons in the *e* shell, *u* is occupied by two electrons with antiparallel spin, and *v* by one electron.

The fact that the ratios λ/Δ and ξ/Δ′ obtained from the measured *g* values are approximately equal (usually

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[17] B. Bleaney, K. D. Bowers, and M. H. L. Pryce, Proc. Roy. Soc. (London) **228**, 166 (1955).

[18] R. Lacroix, U. Höchli, and K. A. Müller, Helv. Phys. Acta **37**, 627 (1964).

TABLE II. Mean g values of Ni ions in octahedral surroundings.

Host lattice	Metal-ligand separation[a] (Å)	Mean g value Ni^{1+}	Ni^{2+}	Ni^{3+}	Refs. and remarks
$SrTiO_3$	1.95	···	2.20	2.18	b
MgO	2.10	2.24	2.21	2.17	c, d
CaO	2.40	2.37	2.33	2.28	c, d
LiF	2.01	2.26	2.22	···	e
$KMgF_3$	1.99	···	2.280	4.163	f, Ni^{3+}: high spin
NaF	2.31	2.33	2.293	···	e, f

[a] R. W. G. Wyckoff, *Crystal Structures* (Wiley-Interscience, Inc., New York, 1960), Vols. I and II.

[b] Reference 1, p. 59.

[c] Reference 19.

[d] J. T. Süss and W. Low, in *Proceedings of ohe International Conference on Electron Diffraclion and Crystal Defects, Melbourne, 1965* (Australian Academy of Science, Melbourne, 1966); and (private communication).

[e] W. Hayes and J. Wilkens, Proc. Roy. Soc. (London) **A281**, 340 (1964).

[f] Reference 21.

lying between 0.04 and 0.09) means that it is not easy to distinguish between octahedrally coordinated d^7 (in a strong field) and d^9 from the paramagnetic-resonance data alone. Although the energy-level schemes of the two systems d^9 and d^7 are quite different, the most definite assignments made to date have been based upon the chemical treatment of the crystal.[19] Usually, tentative assignments have been made from arguments relating to the differences in ionic radius and valency of the two ions.[20] Comparison with resonance data of other 3d transition-metal ions such as Fe^{1+} and Fe^{3+} or Cr^{1+} and Cr^{3+} has proved to be useful.[21]

If the ratio Dq/B were just slightly more than that at the "crossover" of the $^4T_1$ and ^2E levels (approximately 2.2, according to Tanabe and Sugano), then δ would be small, and the term $2\xi^2/\delta^2$ in Eqs. (3) and (4) would cause appreciable deviations from the approximate relations $\Delta g_{\parallel}(V)/\Delta g_{\perp}(V)\simeq 4$, $\Delta g_{\parallel}(U)\simeq 0$, where the symbol Δg represents $g-2$. This is probably the only situation in which it would be possible to assign a strong-field d^7 ion from the resonance data alone. It should be noted that if $\delta\sim\xi$, the single term $2\xi^2/\delta^2$ is not sufficient to describe the effect of the $^4T_1$ because the perturbation breaks down.[22]

The isotropic spectra with $g=2.20$ and 2.18 have been attributed to the replacement of Ti^{4+} by Ni^{2+} and Ni^{3+}, respectively, without local-charge compensation.[1,16] In Table II, we give the g values of spectra attributed to Ni ions in cubic octahedral coordinations. We see that the deviation of the g value from the free-electron value increases in a given lattice as the valency is decreased, and increases for a given ion as the crystal field is decreased (or for a given ligand and lattice type, i.e., NaCl or ABX_3, as the lattice spacing increases). Apart from this, Table II is qualitatively consistent, indicating that the g-value deviation may be used as a means of distinguishing between Ni^{1+} and Ni^{3+} in octahedral coordinations.

IV. ASSIGNMENT OF STABLE SPECTRUM TO Ni^{3+}-V_O DEFECT

A. Steric and Axial Crystal Field Considerations

We assign the stable $S=\frac{1}{2}$ axial spectrum in Ni-doped $SrTiO_3$ to a low-spin Ni^{3+} ion associated with a next-neighbor ionized oxygen-vacancy donor (V_O). There are a number of reasons from which one arrives at this conclusion: The corresponding Fe center Fe^{3+}-V_O has been observed with EPR[7,9] and Mössbauer spectroscopy.[8] Below the cubic-to-tetragonal phase transformation the rotation angle of the parallel axis of the Ni spectrum away from a tetragonal a axis is within the experimental accuracy the same as that of the Fe^{3+}-V_O center at both 77 and 4.2°K, as is seen from Table I. This rotation angle $\bar{\varphi}$ is 1.4 times smaller than the intrinsic rotation φ of the TiO_6 octahedra, due to the missing oxygen ion[12,13] (Fig. 2). Were the spectrum to result from a large Ni^{1+} ion with a radius of approximately 1 Å as compared to the 0.64 Å for Ni^{3+}, then from the different steric behavior we would expect the rotation angle $\bar{\varphi}$ to be reduced. The Ni^{3+}-O^{2-} distance is 1.95 Å, that of Ni^{1+}-O^{2-} 2.24 Å. Assuming the oxygen displacements to be the *same*, a reduction of 15% is obtained. This assumption is only valid if the adjacent TiO_6 octahedra are undistorted. For Ni^{1+} this cannot be the case, and the reduction is expected to be greater.

The observation of axial g values with $g_{\perp}>g_{\parallel}$ shows that the e electron is in a u or $3z^2$-r^2 orbital. This is precisely what one expects from crystal field considerations. The ionized oxygen-donor vacancy represents an effective positive charge in the lattice, thus attracting the negative e-orbital electron charge [see Fig. 5(a)], or, in other words, the axial crystalline potential V_2^0 is positive.

B. g Shifts

The missing oxygen ion of the Ni-V_O center should also reduce the parameter E in Eq. (3) of the Ni^{3+} ion. This expectation is also in agreement with experiment, because the isotropic part of the g value, $\bar{g}=\frac{1}{3}(g_{\parallel}+2g_{\perp})=2.244$, is larger than that of the noncharge-compensated Ni^{3+} ion with an isotropic spectrum at $g=2.180$, characteristic of a dynamic Jahn-Teller effect.[16]

To analyze the observed axial g values we use Eqs. (3) and obtain $2(\xi/\delta)^2=0.029$ from $g_{\parallel}$. Using covalently reduced parameters[5] $\xi=520$ cm^{-1} and $B=660$ cm^{-1}, we obtain $Dq/B=2.8$ from the Tanabe-Sugano[23] diagram for d^7. With this value the extracted E_3 and E_4 energies from the diagram give no agreement with (4) for the observed $g_{\perp}$ value. Thus, as noted in Sec. III, formulas (3) and (4) are incomplete, and near the ^2E-$^4T_1$ crossover the splitting of the $^4T_1$ level must be considered.[22] To

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[19] U. Höchli, K. A. Müller, and P. Wysling, Phys. Letters **15**, 5 (1965); **15**, 123 (1965).

[20] S. Geschwind and J. P. Remeika, J. Appl. Phys. Suppl. 33, 370 (1962).

[21] T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, J. Chem. Phys. **38**, 1977 (1963); **39**, 35 (1963).

[22] R. S. Rubins (unpublished).

[23] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954).

get a rough estimate of the Dq parameter we employ the mean g shift $\bar{g}$, which should be less sensitive to the axial $^4T_1$ level splitting, and obtain $\bar{g}-2=2[\xi/E+(\xi/\delta)^2]=0.244$, $Dq/B=2.5$, and $2(\xi/\delta)^2=0.125$. This proves the importance of the quadratic term in (3) and (4). With the same and only possible procedure for the isotropic line, we get $Dq/B=2.7$ or $Dq=1800$ cm^{-1}, a reasonable value for a sixfold-coordinated Ni^{3+} ion. We see that for the fivefold coordination the Dq parameter is about 8% smaller. However, not too much importance should be attached to this quantity in view of the incompleteness of the theoretical formulas and the possible variation of the ξ and B parameters with coordination which we neglected.

C. Titanium Superhyperfine Interaction

The SHS shown in Fig. 6 clearly results from an interaction with a single Ti^{47} or Ti^{49} nucleus per Ni^{3+} impurity. The measured intensity ratio of one of the sextet lines to the main line is $(2.2\pm0.3)\%$. The computed ratio, assuming the unpaired electron spin is interacting with one *specific* Ti ion, is 2.2%. The SHS can be a consequence from direct or by indirect transfer via oxygen. Although, with the data presently available, we cannot decide which mechanism is dominant, we can show that both support our model for the Ni center in question.

In this model, where the $3z^2$-r^2 orbital is lying along the Ni^{3+}-V_O pair axis, there can be a transfer of spin density to a Ti^{4+} ion via the oxygen opposite to the vacancy or a direct transfer to the Ti^{4+} ion next to the vacancy. The mechanism must now be either the former or the latter. We can exclude the case where both yield accidentally the same SHS constant because the measured intensity ratio would be near 4.4 rather than 2.2%.

We discuss first the direct transfer and compare our data with those observed in rutile, the only other titanium-oxide compound in which SHS with Ti^{47} and Ti^{49} nuclei has been reported. There the interaction has been observed for the d^1 configurations of V^{4+}, Mo^{5+}, and W^{5+}.[24] In Table III these data are compared with the ones obtained here. We see that with the increase of covalency of the d^1 sequence, A increases as expected. The largest superhyperfine interaction is, however, that of the Ni^{3+} ion, which from its charge state and place in the Periodic Table should show the smallest covalency.

TABLE III. Superhyperfine coupling constants of V^{4+}, Mo^{5+}, and W^{5+} in TiO_2 and Ni^{3+}-V_O in $SrTiO_3$.

Defect	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	Refs.
$V^{4+}(3d^1)$	2.1	1.8	a
$Mo^{5+}(4d^1)$	3.4	2.9	b
$W^{5+}(5d^1)$	3.5	2.6	c
$Ni^{3+}(3d^7)$	4.3	2.9	Present work

[a] E. Yamaka and R. G. Barnes, Phys. Rev. **135**, A144 (1964).
[b] Reference 24, Vol. 136, p. 1413.
[c] Reference 24, Vol. 147, p. 264.

In TiO_2 the SHS results undoubtedly from direct transfer. Here the basis functions of the d^1 states are of xy type, and the two nearest Ti ions to the impurity lie at a distance of 3.0 Å along the y axis with *no* intermediate oxygen ion present. In SnO_2, an isotype structure to rutile, Chen *et al.*[25] showed that cation SHS of V^{4+}, Cr^{3+}, and Mn^{4+} observed from Sn^{117} and Sn^{119} nuclei was due to direct transfer. These authors computed the overlap of the $3d$ functions of the transition-metal ions with the next-nearest and second-next-nearest Sn $5s$ functions lying at a distance of 3.19 (Sn_I) and 3.70 Å (Sn_2). They showed that the SHS is directly proportional to the overlap, as the covalency coefficients should be for direct interaction. They also estimated the indirect interaction by computing anion-cation overlaps, and concluded that the indirect mechanism gives an opposite spin density and is an order of magnitude smaller. For us it is also of value that the SHS with the Sn_2 neighbors at 3.70 Å is six times smaller than those at 3.19 Å, although the lobes of the wave functions do not point directly towards the Sn_2.

In $SrTiO_3$ for the Ti ion on the side of the vacancy no intermediate oxygen ion is present. This Ti ion may relax a few tenths of an angstrom towards the vacancy and thus is, by this amount, nearer to the Ni^{3+} than the unit-cell distance 3.9 Å. The $3z^2$-r^2 orbital ($SrTiO_3$) has a charge density about twice as large at a given distance $z=d$ as an xy orbital (TiO_2) along x or y for $x=y=d$ and equal radial distributions. The product of the SHS constant times the spin multiplicity (SHS)$2S$ is for a Me^{3+} ion experimentally and theoretically 0.68 times that for a Me^{4+} ion.[25] Using this number and the data of V^{4+} in TiO_2,[24] we obtain for the constants $A_{\parallel}$ and $A_{\perp}$ for Ni^{3+} due to a Ti^{4+} at 3.0 Å, 2.8 and 2.4×10^{-4} cm^{-1}, respectively. These are roughly $\frac{2}{3}$ those observed experimentally, where the Ti^{4+} ion will not lie nearer than 3.6 Å to the Ni^{3+}. Thus the estimated SHS constants should be still lower, and the overlap mechanism does not appear so likely. However, the $3z^2$-r^2 orbital is probably polarized towards the Ti^{4+} ion in question, enhancing the overlap. Therefore no definitive conclusion can be made except that so far the overlap mechanism does not contradict our model.

Turning our interest towards the indirect mechanism, the only other cation-cation SHS data for σ bonding where this mechanism must be dominant are those of the light-induced center. It will be outlined in Sec. V that for this case only the oxygen-transfer mechanism is possible due to the different orientation of the wave function of the unpaired electron spin. The intensity of the SHS of the light-induced center and the upper limit of its splitting are shown to be compatible with those of the model of the stable spectrum if the indirect transfer is dominant in both.

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[24] T. T. Chang, Phys. Rev. **136**, A1413 (1964); **147**, 264 (1966).

[25] I. Chen, C. Kikuchi, and H. Watanabe, J. Chem. Phys. **42**, 189 (1965).

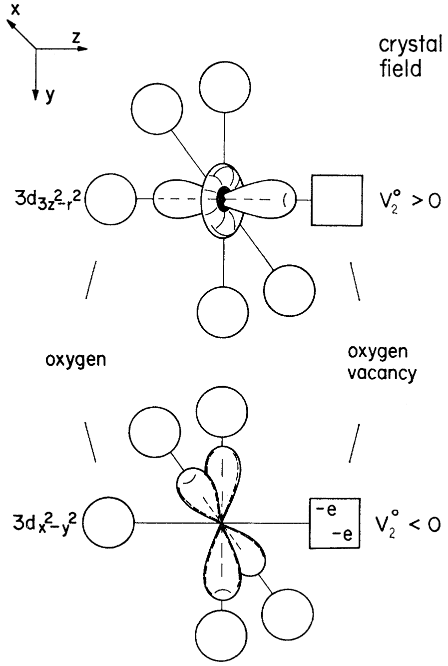

FIG. 7. Schematic representation of the Ni^{3+}-V_O and Ni^{3+}-V_O-($-2e$) center pairs including the sign of the crystal-field V_2^0 component and the unpaired e electron orbitals.

If, instead of an oxygen vacancy, a monovalent anion (F$^-$, Cl$^-$, etc.) had caused the positive V_2^0 component, the corresponding SHS would certainly have been detected due to the narrow lines which are 1.7 G wide.

D. Linewidth Broadening

There is a last reason which supports our assignment, namely, the linewidth broadening as a function of temperature. We see from Fig. 3 that the width of the axial spectrum broadens within the experimental accuracy in the same way as the Ni^{3+} spectrum cubic above Ta, in which u-type orbitals are stabilized.[16] We found such a broadening also for substitutional Ni^{3+} in rutile (TiO$_2$) where, due to the ligand field, the electron u orbital lies lowest. On the other hand, if for Ni^{3+} the v-type orbital is stabilized, then the lines broaden appreciably less. This is observed for the interstitial sixfold-coordinated Ni^{3+} in rutile,[26] the Ni^{3+} centers in KTaO$_3$ at Ta sites,[5] as well as the light-induced axial Ni^{3+} spectrum to be discussed in Sec. V.

V. ASSIGNMENT OF LIGHT-INDUCED SPECTRUM TO A Ni^{3+}-V$_O$-($-2e$) PAIR

A. Steric and Crystal Field Considerations

This spectrum is characterized by $g_{\parallel} > g_{\perp}$ in the cubic phase; therefore it results from either a Ni^{1+} ion in the presence of a positive V_2^0 crystal field component or a Ni^{3+} with negative V_2^0. Clearly, the V_2^0 component must arise from an impurity lying along one of the cubic-edge directions. Earlier the Ni^{1+} possibility was considered to be more likely,[15] because an empty oxygen vacancy yields a positive V_2^0 component. However, there are a number of reasons for rejecting it. The first is the measured rotation angle of this center, which is, within the experimental accuracy, the same as that of the Ni^{3+}-V_O center (Table I). From steric considerations, as already outlined, an angle $\bar{\varphi}$ of less than 0.8° is expected for the large Ni^{1+} ion instead of the observed 0.90±0.05° at 77°K. Second, the isotropic part of the g value $\bar{g} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 2.181$ is, within the experimental accuracy, the same as that for the sixfold-coordinated Ni^{3+} ion.[1,16] If we had a five-fold-coordinated Ni^{1+} ion, its $\bar{g}$ shift should be about 10% larger than 0.25, i.e., 0.27, referring to Table II and assuming a 10% smaller Dq parameter. Thus the ion in question is almost surely Ni^{3+}.

From the $\bar{g}$ value we conclude that the Ni^{3+} shows a splitting parameter ΔE corresponding to six negatively charged nearest neighbors. From the measured rotation angle $\bar{\varphi}$, we deduce that it must be coordinated by five oxygen atoms and not six. Therefore the center is the same as the one yielding the stable axial spectrum, except that here two electrons are situated near the oxygen vacancy. This assignment is in agreement with the stabilization of the v or x^2-y^2 orbital; the average crystal field V_2^0 behaves more like a field of a more negative bond charge than that of O^{2-} because of the absence of the positive core (Kleiner effect). [see Fig. 7(b)]. The location of the two electrons shown is purely schematic. A substantial delocalization, especially on neighboring Sr and Ti cations, will be present, the charge density on the Ti ion being larger than that on the four Sr ions, such that the complex may in a way be described by Ni^{3+}-V_O-Ti^{2+}. The two electrons being delocalized to such an extent that the exchange energy is smaller than the crystal field energy separation between the lowest two levels yielding a configuration with antiparallel spin. A MOLCAO description of the whole complex is needed.

B. g Shifts, SHS, and Linewidth

Equating the axial g shift to expressions (4), one finds that no agreement can be obtained with a *positive* third-order term, whereas the average g shift $\bar{g} - 2 = 0.181$ using the reasonable assumptions of $B = 660$ cm^{-1} and $\xi = 520$ cm^{-1} require $2(\xi/\delta)^2 = 0.080$. This again demonstrates the inadequacy of the $3d^7$ low-spin formulas near the crossover of the ^2E and $^4T_1$ ground-state levels.

Comparing our g values of roughly 2.2 with the ones reported by Hannon, who observed to high-spin Ni^{3+} at A sites in KTaO$_3$ [5] with $g_{\parallel} = 2.216$ and $g_{\perp} = 4.423 \pm 0.05$, we can also exclude this possibility. The small Dq parameter of the A site which makes the $^4T_1$ state of

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[26] H. J. Gerritsen and E. S. Sabisky, Phys. Rev. **125**, 1853 (1962).

Ni^{3+} lowest would also yield a large isotropic g shift for a Ni^{1+} ion at this site, which is not observed.

No fully resolved superhyperfine interaction with Ti^{47} and Ti^{49} nuclei could be observed, indicating the interaction is with more then one Ti ion per complex. The upper limit of the interaction found is a factor of 2 smaller than that of the stable spectrum. Referring to our model of the center in Fig. 7(b), it is seen that the $d_{x^2-y^2}$ orbital points towards four (eventually displaced) oxygen orbitals. Were the SHS constant near the upper limit, this could be a proof for the dominance of the transfer mechanism for the Ni^{3+}-V_O-$(-2e)$ and Ni^{3+}-V_O centers, because for an x^2-y^2 orbital it could be roughly half that for a $3z^2$-r^2 orbital. Were the interaction in the light-induced center appreciably lower than the upper limit, then for the Ni-V_O center the overlap mechanism with the Ti ion on the oxygen-center side would be dominant. ENDOR experiments can probably solve the ambiguity. The computed intensity ratio to the central line for one single resolved SHS line is 8.8%, roughly in agreement with the estimated one from the partially resolved structure.

As a further argument we repeat the remark made at the end of Sec. IV. The width of the EPR line of the center does not appreciably broaden up to 300°K, a behavior observed for Ni^{3+} when the v orbital is stabilized. The difference in the broadening mechanisms for u and v orbitals in high-dielectric-constant materials is at present not understood.

C. Energy, Stability, and Charge

The two possible assignments discussed here for the light-induced center, a Ni^{1+}-V_O-Ti^{4+} or a Ni^{3+}-V_O-$(-2e)$ pair, have the same charge with respect to the lattice. Because of the Coulomb repulsion between electrons, the second possibility appears to yield a lower energy.

The mechanism for creating the light-induced center is at present not understood. It is possible that the illumination excites electrons from some deep levels into the conduction band, which at sufficiently low temperatures freeze out at neutral Ni^{3+}-V_O-$(-e)$ centers, which are possibly better described by Ni^{3+}-V_O-Ti^{3+}. This center is discussed in Sec. VI. A study of the thermal instability of the light-induced center is planned.

VI. MISSING Ni^{3+}-V_O-$(-e)$ CENTER SPECTRUM

The Ni^{3+} represents a singly ionized acceptor in the $SrTiO_3$ lattice if it is substitutional for a Ti^{4+} ion. Association with a singly ionized oxygen-vacancy donor or a V_O-Ti^{3+} pair would represent a neutral defect in the lattice. One may thus ask why this defect is not observed. It is clear that an F-center type or Ti^{3+} electron would couple with the unpaired e electron of the Ni^{3+} ion to form spin $S'=0$ and $S'=1$ states. Even if the coupling were ferromagnetic, and the $S'=1$ state were the lowest, it would be difficult to observe this even-spin state. Due to the considerable axial crystal field present, yielding a large parameter D in the effective spin Hamiltonian, the $|0\rangle$ state would be separated by several wave numbers from the $|+1\rangle$ and $|-1\rangle$ states. Thus lines with effective g values, $g_\perp \sim 0$ and $g_{\parallel} \sim 4$ in $S'=\frac{1}{2}$ notation, can be expected. However, for large D the transition probability of the $\Delta M=2$ transition between the states $|+1\rangle$ and $|-1\rangle$ for $H \| z$ yielding the line near $g \sim 4$ vanishes. The same argument applies for the corresponding Cr^{3+} and Fe^{3+} centers. In both cases, even S' states will result from the coupling. A search for the Fe^{3+}-V_O-$(-e)$ or Fe^{3+}-V_O-Ti^{3+} center with the Mössbauer effect is under way.

In this context it is also interesting to note that so far no axial tetragonal Cr^{3+} spectrum has been observed for chromium-doped $SrTiO_3$. Only an orthorhombic Cr^{3+} spectrum was observed by Meyerling.[27] It is not obvious why Cr^{3+}-V_O pairs are not formed in the same way as observed for Fe and Ni. Therefore it could be that the neutral Cr^{3+}-V_O-$(-e)$ or Cr^{3+}-V_O-Ti^{3+} pairs are the most abundant pair defects present.

Another possibility are the Me^{2+}-V_O-Ti^{4+} complexes, which would be more stable than Me^{3+}-V_O-$(-e)$ or Me^{3+}-V_O-Ti^{3+}. The ionization energy for $Ni^{2+} \rightarrow Ni^{3+}$ is certainly lower than for $Ti^{3+} \rightarrow Ti^{4+}$. Thus, a Ni^{3+}-V_O-Ti^{3+} electronic configuration is more likely to exist. Furthermore, Fe^{2+} spectra have been reported, however, only after heavily reducing $BaTiO_3$ and $SrTiO_3$.[8] They are due to more complex centers, where the coordination around the Fe ion is lower, as concluded from the increase in the Mössbauer f factor.

VII. COMPARISON WITH TETRAGONAL SPECTRA IN $KTaO_3$ AND $BaTiO_3$

A. Low-Spin Ni^{3+} Spectra in $KTaO_3$

In K_2CO_3-T_2O_5 flux-grown $KTaO_3$ crystals, Hannon observed a tetragonal low-spin Ni^{3+} spectrum after Ni doping.[5] The axial g values are $g_{\parallel}=2.234$ and $g_\perp=2.111$, $g_{\parallel}>g_\perp$, indicating that the unpaired spin is located in an x^2-y^2 orbital. The magnitude of $\bar{g}=2.152$ is such that the location of the Ni^{3+} is at a B site. It was the only spectrum observed, and Hannon assumed that it is due to Ni^{3+} with no local-charge compensation present, because for other B substitutional Ni^{3+} ions this spectrum shows the strongest intensity. The observed distortion was then ascribed to the Jahn-Teller effect. However, as Hannon mentions, this is somehow unsettling because the spectrum remains axial up to the highest measuring temperature of 330°K. In contrast, in all the other cases where Ni^{3+} ions in octahedral oxygen environment have been observed, the Jahn-Teller effect is dynamic above 77°K. This is so in MgO, CaO,[19] Al_2O_3,[20] and $SrTiO_3$.[1,15] The latter observation is especially relevant, because the dielectric, optic, and mechanical properties of $SrTiO_3$ and $KTaO_3$ are very similar. Furthermore, it would be the first case where

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[27] D. Meyerling (to be published).

the oxygen octahedron is compressed as a result of the Jahn-Teller effect.[17]

On the whole, it should not be overlooked that the crystals are co-doped with Ti^{4+}. Further, in K_{1-x} Na_x TaO_3 mixed crystals a second Ni^{3+} spectrum with $g_{\parallel}>g_{\perp}$ was observed, which is related to the presence of Na. Although the presence of Ti^{4+} and Na^{1+} impurities may be the reason for the appearance of at least one of the two axial spectra, this cannot be the complete answer because in Fe-doped samples grown in the same way, cubic Fe^{3+} and Fe^{3+}-V_O pair spectra have been observed.[5,10] In $KTaO_3$ the Me^{3+}-V_O is a neutral center consisting of a pair of empty double acceptor (Me^{3+}) and double donor (V_O). Thus for $Me^{3+}=Ni^{3+}$ this should be as stable as found for $Me^{3+}=Fe^{3+}$. The V_O should again stabilize the $3z^2$-r^2 orbital of the e level. This argument is quite strong, taking into account that for the Fe^{3+}-V_O center the observed axial D parameters are to within 6% the same in $SrTiO_3$ and $KTaO_3$.[10] Thus the assignment of Hannon for the first spectrum as resulting from uncompensated Ni^{3+} is still the most probable and for as yet unknown reasons the Jahn-Teller effect stabilizes the x^2-y^2 orbital in $KTaO_3$.

Summarizing, it can be said that the low-spin Ni^{3+} lines detected in $KTaO_3$ and resulting from (x^2-y^2)-type e orbitals are disturbing. They are the only ones which for the moment do not fit with the observations of the other transition-metal ions in $SrTiO_3$ and $KTaO_3$ and the assignments made in the previous sections.

B. "*F* Center" or Ti^{3+} Resonance in $BaTiO_3$

Several years ago Šroubek and Žďánský[28] observed in $BaTiO_3$, reduced for 10 min at 700°C in hydrogen atmosphere, an axial resonance with g values near 1.9. They attributed this spectrum to a single electron trapped at an oxygen vacancy, i.e., an F-center resonance. Further investigations were carried out by Takeda and Watanabe,[29] who found that the center is observed in flux-grown $BaTiO_3$ if the crystals are reduced between 700 and 1000°C. In this region a large conductivity increase in the crystal is also observed. The exact g values are $g_{\parallel}=1.930$ and $g_{\perp}=1.911$. They are close to those found for Ti^{3+}, and subsequently Zítková, Žďánský, and Šroubek[30] interpreted the resonance as due to a Ti^{3+} ion, the unpaired electron spin being sited in a d_{xy} orbital which yields $g_{\parallel}>g_{\perp}$. Such an interpretation would be in agreement with the large Ti hyperfine interaction constant of $A=19$ G found by the Japanese workers.[31] Here A is an order of magnitude larger than the superhyperfine interaction of Mo^{1+} in TiO_2.[25] If their assignment is correct and the electron localization to form a Ti^{3+} is caused by a V_O and not by another defect, it would indicate that for the Ni^{3+}-V_O-$(-2e)$ complex the two electrons are localized to an appreciable extent on the Ti ion along the Ni^{3+}-V_O axis rather than on the four Sr^{2+} neighbor ions. Thus a better description of the Ni^{3+}-V_O-$(-e)$ center would perhaps be Ni^{3+}-V_O-Ti^{2+}, meaning that the two electrons with antiparallel spin are situated to a certain degree in d_{xy} orbitals of the Ti ion.

There is, however, a serious difficulty with the assignment of Zíttková *et al.* because their center has so far been observed only in $BaTiO_3$ and not in strongly reduced $SrTiO_3$ or $KTaO_3$ (where the resonance would be due to a Ta^{4+}). This can have two possible origins. Either the *intrinsic*[32] activation energy of the defect is considerably larger in $BaTiO_3$ than in $SrTiO_3$ and $KTaO_3$, or else the defect is different. The former possibility appears to be less likely because in reduced $KTaO_3$, $SrTiO_3$, and $BaTiO_3$, the activation energy of the first intrinsic stage, which is probably doubly occupied, was estimated to be a few millielectron volts.[33-35] Furthermore, it must be noted that the so-called F-center resonance has so far only been detected in $BaTiO_3$ single crystals grown from KF flux,[6] or in ceramics to which silver ions had been added as an impurity.[36] On the other hand, the investigation in reduced $SrTiO_3$ and $KTaO_3$ have been carried out in single crystals grown by the Verneuil process or from oxide fluxes,[37] and thus are intrinsically "purer."

The examples in $KTaO_3$ and $BaTiO_3$ show how far one is from understanding the defect structure in flux-grown ABO_3 crystals. It would probably be helpful to investigate Czochralski-grown $BaTiO_3$ crystals properly doped which do not exhibit complex centers due to uncontrolled flux co-doping.

VIII. SUMMARY AND CONCLUSIONS

In this study two tetragonal EPR spectra with $S=\frac{1}{2}$, observed in Ni-doped $SrTiO_3$ crystals and grown by the Verneuil process, have been investigated. Both result from the association of a Ni^{3+} impurity with a nearest-neighbor oxygen vacancy V_O. One is a thermally stable center and is observed when the oxygen vacancy is empty. It is a Ni^{3+}-V_O pair center. The other spectrum is light-induced and is created when two electrons are trapped near or at the vacancy, probably to an appreciable extent at the Ti^{4+} near the V_O. This center is thus a Ni^{3+}-V_O-$(-2e)$ or Ni^{3+}-V_O-Ti^{2+} pair. In the

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[28] Šroubek and K. Žďánský, Czech. J. Phys. **B13**, 309 (1963).

[29] T. Takeda and A. Watanabe, J. Phys. Soc. Japan **21**, 267 (1966).

[30] J. Zítková, K. Žďánský, and Z. Šroubek, Czech. J. Phys. **17**, 636 (1967).

[31] T. Takeda and A. Watanabe, J. Phys. Soc. Japan **23**, 469 (1967).

[32] The Ti^{3+}-V_O defect in $SrTiO_3$ or $BaTiO_3$ is here called intrinsic as compared to, say, Ni^{3+}-V_O in the same lattices where the activation energies of electrons in the oxygen vacancy associated to the impurity Ni may be quite different.

[33] S. H. Wemple, Phys. Rev. **137**, A1575 (1965).

[34] H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. **134**, A442 (1964).

[35] C. N. Berglund and W. S. Baer, Phys. Rev. **157**, 358 (1967); C. N. Berglund and H. J. Braun, *ibid.* **164**, 790 (1967).

[36] H. Ikushima and J. Hayakawa, Japan J. Appl. Phys. **4**, 328 (1965).

[37] K. A. Müller (unpublished results).

Ni^{3+}-V_O center the EPR is due to the single unpaired e electron of the low-spin Ni^{3+} (configuration $t_2{}^6$, e^1), the electron occupying a $3z^2$-r^2 orbital along the pair axis. In the Ni^{3+}-V_O-$(-2e)$ center the Ni e electron is in an x^2-y^2 orbital directed away from the near neutral V_O-$(-2e)$. It is the first time in solid-state physics that the charge state of a lattice defect has been monitored by the different electronic *configurations* of an associated defect whose charge remains the same.

The magnitudes and orientations of the g tensors of both centers are in agreement with these assignments as well as steric considerations and the measured tetragonal rotation angles of the tensors below the structural phase transition of $SrTiO_3$ at 105°K. The temperature dependence of the linewidth and the resolved SHS of the Ni-V_O center with *one specific* Ti ion, and the not completely resolved one of the light-induced center, support them further. However, a decision whether the SHS results from overlap or indirect transfer is not possible from the EPR data, and ENDOR experiments are required.

The light-induced Ni center is thermally unstable at 300°K, but is quite stable below 80°K. A certain activation energy for the ionization of the first of the two electrons situated near or at the oxygen vacancy is thus present and remains to be determined. Because the Ni^{3+} acceptor represents an effective negative charge in the $SrTiO_3$ lattice, we are led to the conclusion that the unassociated F' center or the Ti^{3+}-V_O-Ti^{3+}-type center in high-dielectric-constant perovskite materials, if it exists, has a larger activation energy for the ionization of the first electron than the light-induced reported here.

The difficulties in observing by EPR the neutral pair spectra, which are due to the association of a paramagnetic transition-metal ion acceptor Me^{3+} with a paramagnetic V_O-$(-e)$ or V_O-Ti^{3+} center, have been emphasized. Neither is the exact structure of certain centers with tetragonal over-all symmetry in flux-grown $BaTiO_3$ and $KTaO_3$ crystals understood.

Note added in manuscript. Recently we became aware of an investigation by Takeda and Watanabe, who made EPR measurements on $BaTiO_3$ ceramics doped with La^{3+} ions for various Ba/Ti ratios. With Ba/Ti ratios near 1.02, i.e., the same ones they observed earlier,[11] Gd^{3+} ions at Ti^{4+} sites, they found a resonance signal with $g_{\parallel}=1.932$, $g_{\perp}=1.914$ and assigned it to an F center with an La^{3+} neighbor at a Ti^{4+} site. In view of the discussion in Sec. VII B, we reassign the spectrum to a neutral La^{3+}-V_O-Ti^{3+} complex. It thus seems likely, as we postulated in Sec. VIII, that the intrinsic neutral Ti^{3+}-V_O-Ti^{3+} complexes can occur in ATiO$_3$ perovskite-type structures.

Takeda and Watanabe[38] also investigated K^+-doped $BaTiO_3$, finding for sufficiently high K^+ concentrations the spectrum discussed in Sec. VII B. This spectrum they assign to an F center with a Ba^{2+} neighbor at a Ti^{4+} site, but we reassign it now to a Ba^{2+}-V_O-Ti^{3+} complex. We believe that this center is the one first observed by the Prague group[28] in KF flux-grown crystals. It is formed from a neutral Ba^{2+}-V_O-Ti^{4+} center by heating and thus evaporating fluorine,[6] a surplus electron being trapped to give Ba^{2+}-V_O-Ti^{3+}.

In Verneuil-grown $SrTiO_3$, the corresponding Sr^{2+}-V_O-Ti^{3+} center has neither been observed after reduction, optical, uv, x-ray, or neutron irradiation. Thus we conclude that in these crystals the concentration of Sr^{2+} ions on B sites is small. Were it otherwise, one could possibly ascribe the light-induced axial Ni^{3+} center discussed in Sec. V to a Ni^{3+}-V_O-Sr^{2+} configuration instead of to Ni^{3+}-V_O-$(-2e)$ or Ni^{3+}-V_O-Ti^{2+}, as done there. In fact, the electrical charge distribution around the Ni^{3+} would be very similar in both cases. The void left by the oxygen and Ti^{4+} ions can easily accommodate a Sr^{2+} without altering the rotation of the oxygens around the Ni^{3+} appreciably as compared to the stable Ni^{3+}-V_O center. Thus a discrimination between the two centers by measuring the rotation angle below the phase transition may not be easy to perform.

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[38] T. Takeda and A. Watanabe, Japan J. Appl. Phys. 7, 232 (1968).