analogy between the two cases is treated by Trifonov.[9] For the Mössbauer case, Visscher[10] has specifically calculated the absorption cross section for a monochromatic γ-ray beam incident on an absorber with a simple Debye spectrum of phonons. Strong absorption maxima are very clearly shown at energies corresponding to high-phonon probability densities near the cutoff frequency and at integral multiples of this frequency.

We feel that the almost universal agreement found here between observed and theoretical phonon energies must be taken as very strong experimental evidence that individual normal lattice phonons of many modes near the Brillouin zone boundary may be excited with high probability, and that a large part of the broadening of at least the R_2 and N bands in the alkali halides is due to lattice interactions involving normal lattice phonons of appreciable wave vector. In support of these conclusions, we feel it is reasonable that excitation of

⁹ E. A. Trifonov, Dokl. Akad. Nauk. SSSR 147, 826 (1962) [English transl.: Soviet Phys.—Doklady 7, 1105 (1963)].
¹⁰ W. M. Visscher, Ann. Phys. (N. Y.) 9, 194 (1960).

phonons near the zone boundary is observed, as these are the phonons with highest density of states and also of wavelength comparable to the dimensions of the defects involved. Thus, they should be most efficiently coupled to transition processes in these defects. Also, the defects which give rise to (so far) observable fine structure are all relatively complex three-dimensional structures. It seems reasonable that if normal lattice phonons are to be excited at all in these complexes, that the transition processes should be coupled to a variety of different lattice modes.

In conclusion, we would like to acknowledge our appreciation for the efforts of a number of people who have contributed significantly to this work. We would especially like to extend our thanks to D. B. Fitchen and R. H. Silsbee for detailed discussions of their results prior to publication, to R. S. Claassen, D. K. Brice, and D. C. Wallace, in particular, and many other associates at Sandia Laboratory for many fruitful discussions, and to D. D. TerHaar for performing the major part of the experimental work.

Strong Axial Electron Paramagnetic Resonance Spectrum of Fe³⁺ in SrTiO₃ Due to Nearest-Neighbor Charge Compensation

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An axial electron paramagnetic resonance (EPR) spectrum in iron-doped (cubic) strontium titanate has been observed at 3.3 and 1.85 cm wavelength with effective g values $g_\perp^e = 5.993 \pm 0.001$ and $g_\perp^e = 5.961 \pm 0.001$, respectively, and $g_{||}^e = g_{||} = 2.0054 \pm 0.0007$. The same spectrum was found after charge displacement due to heat treatment in the dark or by reduction in crystals which contained, in addition to iron, other transition metal ions. The spectrum is attributed to $\Delta M = 1$ transitions of the $S_z = \pm \frac{1}{2}$ level of Fe³⁺($3d^5$) in a strongly tetragonal electric crystalline field produced by local charge compensation at a nearest-neighbor oxygen site. The theory is developed for ions of half-integral spin in an axial field much greater than the Zeeman splitting. By applying the theory to the special case of $S = \frac{5}{2}$ and using the measured effective $g_\perp^e$ values and resonance magnetic fields $g_\perp = 2.0101 \pm 0.0008$ and a zero-field splitting parameter $|2D|$ of 2.85 ± 0.15 cm⁻¹ is obtained. This is the largest splitting which has so far been observed for Fe³⁺ in any inorganic crystal and could be useful for submillimeter maser applications.

I. INTRODUCTION

IT has been shown by Watkins,[1] for Mn²⁺ in NaCl, that impurity ions substituting for ions of different valency attract charge compensating defects in the lattice at temperatures at which the ions become mobile.

The majority of reported EPR studies of transition metal ions in the three oxide crystals SrTiO₃,[2] BaTiO₃,[3] and rutile (TiO₂),[4] have indicated that there is no definite evidence for local charge compensation when divalent or trivalent transition metal ions replace the tetravalent titanium ion. It seemed possible that this might be due to the high dielectric constant of these crystals, which is 100 or more at room temperature. At about 1000°K, when the ions in these oxide crystals become mobile, the dielectric constant is still an order

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¹ G. D. Watkins, Phys. Rev. 113, 79 and 91 (1959).
² K. A. Müller Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962 (Academic Press Inc., New York, 1963), p. 17.
³ A. W. Hornig, R. C. Rempel, and H. E. Weaver, Phys. Chem. Solids 10, 1 (1959).
⁴ H. J. Gerritsen, Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962 (Academic Press Inc., New York, 1963), p. 3.

of magnitude higher than in normal inorganic dielectrics (e.g., NaCl, MgO, etc.), and the Coulomb interaction between defects is accordingly much lower.

The first indications of possible local charge compensation have come from recent EPR studies on Cr^{3+} in TiO_2,[4] and on nickel in $SrTiO_3$.[5] Further study on the $SrTiO_3$: Ni system[6] has shown that the axial spectrum observed in Ref. 5 is due to Ni^{3+} in a field of tetragonal symmetry. As a cubic Ni^{3+} spectrum is also present in these crystals, it appeared likely that the tetragonal field is produced by local charge compensation, although, due to the high polarizability of Ti^{4+} sites, the possibility that the Ni^{3+} ion sits in a corner of the octahedron could not be excluded.

In this paper we report a strongly axial EPR spectrum found in iron-doped strontium titanate. The same axial spectrum was obtained by heating nickel and chromium-doped $SrTiO_3$ crystals (which contained Fe^{3+} in cubic sites) in the dark to 80°C, and also by a reduction experiment described in this paper. In the former case, the axial Fe^{3+} spectrum disappeared on exposure to light. By considering the general theory of the effective g values of ions with half-integral spin in an axial field much stronger than the Zeeman splitting, we are able to show conclusively that the spectrum is due to $Fe^{3+}(3d^5)$ in a strong tetragonal field. The only possible explanation for such a strong field is that local charge compensation takes place at a nearest oxygen site in the octahedron.

II. THEORY

The g Values of Ions of Half-Integral Spin $(S \geqslant \frac{3}{2})$ in a Strong Positive Axial Field

It is convenient to consider the crystal axis as axis of quantization. If the magnetic field H lies in the xz plane, making an angle θ with the z axis, the spin Hamiltonian may be written

$$\mathcal{H} = D(S_z^2 - \tfrac{1}{4}) + g_{||}\beta H S_z \cos\theta + g_{\perp}\beta H S_x \sin\theta.$$

The factor $-\frac{1}{4}$ is included in the crystal field term in order to make this term zero for the $S_z = \pm\frac{1}{2}$ doublet.

In computing the Zeeman splitting to the third order, only $S_z = \pm\frac{1}{2}$ and $S_z = \pm\frac{3}{2}$ levels need be considered, as there are no matrix elements between $S_z = \pm\frac{1}{2}$ and higher S_z states. The matrix elements within the $S_z = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$ levels are then as shown below.

	$\vert\frac{1}{2}\rangle$	$\vert-\frac{1}{2}\rangle$	$\vert\frac{3}{2}\rangle$	$\vert-\frac{3}{2}\rangle$
$\vert\ \frac{1}{2}\rangle$	A	B	C	0
$\vert-\frac{1}{2}\rangle$	B	$-A$	0	C
$\vert\ \frac{3}{2}\rangle$	C	0	$2D+3A$	0
$\vert-\frac{3}{2}\rangle$	0	C	0	$2D-3A$

[5] R. S. Rubins and W. Low, *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962* (Academic Press Inc., New York, 1963), p. 59.
[6] K. A. Müller and R. S. Rubins (to be published).

with

$$A = \tfrac{1}{2}g_{||}\beta H \cos\theta,$$
$$B = \tfrac{1}{2}mg_{\perp}\beta H \sin\theta, \quad m = [S(S+1) + \tfrac{1}{4}]^{1/2},$$
$$C = \tfrac{1}{2}ng_{\perp}\beta H \sin\theta, \quad n = [S(S+1) - \tfrac{3}{4}]^{1/2},$$

and $D \gg A, B, C$.

We begin by neglecting second-order effects and diagonalizing the 2×2, $S_z = \pm\frac{1}{2}$ matrix. The first-order solutions are:

(1) for the energy levels

$$W = \pm(B^2 + A^2)^{1/2};$$

(2) for the wave functions

$$\vert\gamma\rangle = \alpha\vert+\tfrac{1}{2}\rangle + \beta\vert-\tfrac{1}{2}\rangle, \quad \vert\delta\rangle = \alpha\vert-\tfrac{1}{2}\rangle - \beta\vert+\tfrac{1}{2}\rangle,$$

where

$$\alpha = \left(\frac{(A^2+B^2)^{1/2}+A}{2(A^2+B^2)^{1/2}}\right)^{1/2}, \quad \beta = \left(\frac{(A^2+B^2)^{1/2}-A}{2(A^2+B^2)^{1/2}}\right)^{1/2}.$$

Using $\vert\gamma\rangle$ and $\vert\delta\rangle$ as basis vectors the matrix given above transforms to

	$\vert\gamma\rangle$	$\vert\delta\rangle$	$\vert\frac{3}{2}\rangle$	$\vert-\frac{3}{2}\rangle$
$\vert\gamma\rangle$	$(A^2+B^2)^{1/2}$	0	αC	βC
$\vert\delta\rangle$	0	$-(A^2+B^2)^{1/2}$	$-\beta C$	αC
$\vert\frac{3}{2}\rangle$	αC	$-\beta C$	$2D+3A$	0
$\vert-\frac{3}{2}\rangle$	βC	αC	0	$2D-3A$.

Terms obtained from second-order perturbation theory do not split the $\vert\gamma\rangle$ and $\vert\delta\rangle$ levels further. The relevant third-order terms are contained in the expression

$$\sum_{n(\neq m)}' \frac{\vert\mathcal{H}_{mn}\vert^2}{(E_m - E_n)^2}[\mathcal{H}_{nn} - \mathcal{H}_{mm}],$$

where m is the ground level.

For the $\vert\gamma\rangle$ level they give an energy shift

$$\Delta W = \frac{3AC^2}{(2D)^2}(\alpha^2 - \beta^2) - \frac{C^2}{(2D)^2}(A^2+B^2)^{1/2}$$

and for the $\vert\delta\rangle$ level $-\Delta W$. The experimental g value is then obtained by means of the equation

$$g^e\beta H = 2(W + \Delta W).$$

The factor $(\alpha^2 - \beta^2)$ simplifies to $A(A^2+B^2)^{1/2}/(A^2+B^2)$, so that

$$g^e\beta H = 2(A^2+B^2)^{1/2}\left[1 - \frac{C^2}{(2D)^2}\left(\frac{B^2-2A^2}{B^2+A^2}\right)\right].$$

The general expression for g^e may now be written. This is

$$g^e = [g_{||}^2 + (m^2 g_{\perp}^2 - g_{||}^2)\sin^2\theta]^{1/2}\left[1 - \frac{n^2}{4}\frac{(g_{\perp}\beta H)^2}{(2D)^2}F(\theta)\right],$$

where

$$F(\theta)=\sin^2\theta\left[\frac{(m^2g_\perp+2g_{||})\sin^2\theta-2g_{||}}{(m^2g_\perp-g_{||})\sin^2\theta+g_\perp}\right].$$

As $g_{||}$ and $g_\perp$ are in general nearly equal in systems with $S\geqslant\frac{3}{2}$, they may be equated in the expression for $F(\theta)$ which simplifies to

$$F(\theta)=\sin^2\theta\left[\frac{(m^2+2)\sin^2\theta-2}{(m^2-1)\sin^2\theta+1}\right].$$

If $S=\frac{3}{2}$, then $m=2$ and $n=\sqrt{3}$; and the expression for $g^e(\theta)$ reduces to that derived by Geusic et al.[7] For $S=\frac{5}{2}$, $m=3$ and $n=2\sqrt{2}$, and for $S=\frac{7}{2}$, $m=4$ and $n=(15)^{1/2}$.

If in the general expression for $g^e(\theta)$ one replaces $(g_\perp\beta H)^2$ by $(h\nu/m)^2$, which is allowed for large enough D's, and again assumes $g_\perp=g_{||}$, g^e reduces, noting that $m=S+\frac{1}{2}$, for $\theta=0°$, to $g_{||}{}'$, and for $\theta=90°$ to $g_\perp{}'$, as given in Eq. (5.6) by Ludwig and Woodbury.[8]

III. EXPERIMENTAL RESULTS

Axial lines were observed in samples cut from a crystal of $SrTiO_3$ grown by the Verneuil process with 0.03% Fe_2O_3 added to the feed. By the use of x rays, alignment was achieved by machining the sample faces to within 0.3° of the (100) plane. Except for a $g_\perp{}^e$ value determination at the Ku-band using a balanced bolometer reflection spectrometer, the measurements were made at 3.2-cm wavelength and room temperature on a superheterodyne spectrometer. Apart from the intense cubic spectrum of Fe^{3+}, which has been reported in detail by Müller,[9] a spectrum was observed consisting of three axially symmetric lines with mutually perpendicular tetragonal axes. The intensities of the axial lines were about 0.15 times that of the central ($S_z=-\frac{1}{2}\leftrightarrow S_z=+\frac{1}{2}$) transition of the cubic spectrum. Measurements were made with the constant magnetic field parallel to a (100) plane of the crystals as a function of the angle. The effective g values of the axial lines are plotted in Fig. 1. The solid lines refer to the theoretical curve (see below).

Introducing into the general expression for $g^e(\theta)$ derived in Sec. II $S=\frac{5}{2}$ ($m=3$; $n=2\sqrt{2}$), one obtains

$$g^e(\theta)=[g_{||}{}^2+(9g_\perp{}^2-g_{||}{}^2)\sin^2\theta]^{1/2}\left[1-\frac{2(g_\perp\beta H)^2}{(2D)^2}F(\theta)\right]$$

$$F(\theta)=\sin^2\theta\cdot\left[\frac{(9g_\perp+2g_{||})\sin^2\theta-2g_{||}}{(9g_\perp-g_{||})\sin^2\theta+g_\perp}\right],$$

for

$$\theta=0 \quad g_{||}{}^e=g_{||} \quad \text{and for} \quad \theta=90° \quad g_\perp{}^e=3g_\perp\left[1-\frac{2(g_\perp\beta H)^2}{(2D)^2}\right].$$
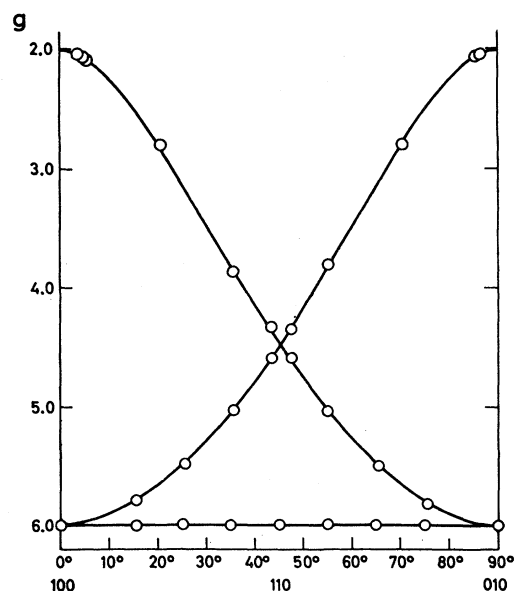

FIG. 1. The behavior of the three lines of the axial Fe^{3+} spectrum in strontium titanate on rotation of the magnetic field in a (100) plane of the crystal. Circles represent the experimental points, and the theoretical curves are given by the solid lines. The measurements were made at room temperature and 9091 Mc/sec.

Therefore, by measuring $g_\perp{}^e$ ($H\perp Z$) at two different resonance magnetic fields H_1 and H_2, i.e., at two different frequencies (X- and Ku-band) $g_\perp$ and $|2D|$ can be obtained. Let $\alpha=g_\perp{}^e(1)/g_\perp{}^e(2)$ and $\delta=(H_1/H_2)^2$, then

$$g_\perp=\frac{g^e_\perp(1)}{3}\frac{1}{\alpha}\left(\frac{\alpha-\delta}{1-\delta}\right)$$

and

$$|2D|=g_\perp\beta\left(\frac{2(\alpha H_2{}^2-H_1{}^2)}{\alpha-1}\right)^{1/2}.$$

From these formulas one sees that in order to obtain a value of a large Stark splitting (several cm^{-1}) with an accuracy of some percent, the ratio $\alpha\simeq1+\epsilon$ of the two effective g values $g_\perp{}^e$ (1) and $g_\perp{}^e$ (2) has to be determined precisely. Their absolute values or $g_\perp$ can be known with moderate precision, i.e., the microwave frequency need not be known with the same accuracy as α.

We determined this quantity in the following way: The klystrons at X- and Ku-band were locked to the sample cavities. Then the ratio of the resonance magnetic fields of the axial line H(ax) ($g\sim6$) and the cubic $M=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ Fe^{3+} line H(cub) were measured by proton resonance.[10] The effective g factor of the latter line is independent of the microwave frequency to second order for H parallel to the cube edges of $SrTiO_3$.[9] With the ratios obtained in the two bands, α was obtained

[7] J. E. Geusic, M. Peter, and E. O. Schulz-du Bois, Bell System Tech. J. 38, 291 (1959).

[8] G. W. Ludwig and H. H. Woodbury, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 261.

[9] K. A. Müller, Helv. Phys. Acta 31, 173 (1958).

[10] The stability of the microwave frequency was controlled by periodic H(cub) measurements.

from their ratio, i.e.,

$$\alpha = \frac{H_1(\text{ax})/H_1(\text{cub})}{H_2(\text{ax})/H_2(\text{cub})} .$$

With this method we get

$$|2D| = (2.85 \pm 0.15)\text{cm}^{-1} \text{ and } g_\perp = 2.0106 \pm 0.0008.$$

As $g_{||}$ and $g_\perp$ were found to differ less than 1%, the theoretical curve in Fig. 1 was computed by putting $g = g_\perp = g_{||}$, i.e.,

$$g(\text{eff}) = g(1 + 8 \sin^2\theta)^{1/2}\left[1 - \frac{2(g\beta H)^2}{(2D)^2}F(\theta)\right],$$

$$F(\theta) = \sin^2\theta\frac{(11 \sin^2\theta - 2)}{(8 \sin^2\theta + 1)},$$

was used and in fact all the experimental points fell well within 1% of the theoretical values (see Fig. 1).

The same axial Fe^{3+} spectra were observed in $SrTiO_3$ after two different types of treatment. In the first experiments nickel- and chromium-doped crystals, which both showed cubic Cr^{3+} [2,11] and Fe^{3+} spectra, were heated in the dark at various temperatures. After about fifteen minutes heating at or above 80°C, axial Fe^{3+} and cubic Mn^{4+} [12] spectra were observed. The Cr^{3+} spectrum decreased in intensity by a factor of 2 in the crystals doped with 0.05% Cr^{3+}, and vanished completely in the nickel-doped crystals, in which the Cr^{3+} intensity was an order of magnitude smaller. The axial Fe^{3+} lines were in these experiments an order of magnitude less intense than the central cubic Fe^{3+} line. Prolonged heating produced no further changes in the spectra. After several minutes' exposure to daylight, the new spectra vanished and the Cr^{3+} spectrum was restored to its initial intensity.

In a second experiment, a reddish-brown transparent nickel-doped crystal, which showed a cubic Fe^{3+} spectrum about three times as intense as an axial Ni^{3+} spectrum,[6] was heated in a hydrogen atmosphere at 1000°C for three hours, until it became opaque blue-grey and semiconducting.[13] It was then heated in air for 30 min at 700°C, after which it became yellower than the untreated crystal, and fairly transparent. This treatment caused the disappearance of the axial Ni^{3+} spectrum and brought strong axial Fe^{3+} spectra, in which the intensity of each axial line was a quarter that of the central cubic Fe^{3+} line.

Finally, mention should be made in this section of previously unreported "forbidden" $\Delta M = 3$ transitions which were observed in the cubic Fe^{3+} spectrum of the iron-doped crystals. When the magnetic field was directed parallel to the [011] axis, a weak line was observed 18 G below the line of the axial spectrum (at

$g = 5.993$) isotropic in the (100) plane (see Fig. 1). From Kronig and Bouwkamp's calculation[14] for the parameters of the spin Hamiltonian for Fe^{3+} in a cubic field, the three possible $\Delta M = 3$ transitions occur at the following fields:

$$\left(+\frac{5}{2} \leftrightarrow -\frac{1}{2}\right) \quad H = \frac{H_0}{3} + \frac{1}{6}(1 - 5\phi)\frac{a}{g\beta}$$

$$-\frac{5}{144}(3 - 72\phi + 287\phi^2)\frac{a^2}{(g\beta)^2}H^{-1},$$

$$\left(+\frac{3}{2} \leftrightarrow -\frac{3}{2}\right) \quad H = \frac{H_0}{3} - \frac{5}{48}(1 + 22\phi - 75\phi^2)\left(\frac{a}{g\beta}\right)^2 H^{-1},$$

$$\left(+\frac{1}{2} \leftrightarrow -\frac{5}{2}\right) \quad H = \frac{H_0}{3} - \frac{1}{6}(1 - 5\phi)\frac{a}{g\beta}$$

$$-\frac{5}{144}(3 - 72\phi + 287\phi^2)\left(\frac{a}{g\beta}\right)^2 H^{-1},$$

where $\phi = \sin^2\theta \cos^2\theta$ if $H||$ to a (100) plane and $a/g\beta = 206$ G, the published value obtained from the $\Delta M = 1$ transitions.[9]

The lowest of these, the $+\frac{5}{2} \leftrightarrow -\frac{1}{2}$ line, should be found 17 G lower in the field than the axial line when H is parallel to the [011] axis. The other two lines lie 5 and 17 G higher, and are totally obscured by the intense axial line. The intensities of the lines decrease as the magnetic field is rotated away from the [011] axis.

Most of the possible "forbidden" transitions in cubic Fe^{3+} have been observed by Weaver.[15,16] The line assigned by him to the $(+\frac{3}{2} \leftrightarrow -\frac{3}{2})$ transition appears to be in fact the axial line isotropic for rotations in the (001) plane. The two axial lines he reported with g^e varying from 6 to 2.2 and 2.0 would appear to be the other two lines of the axial Fe^{3+} spectrum, the extreme value of 2.2 being due to slight misalignment of the crystal.

IV. DISCUSSION

In the previous sections we have shown that the spectrum we observed must be due to a center having a total spin $S = \frac{5}{2}$ in a strong axial field. No hfs is observed, and as the spin lattice relaxation time is long, the only possible assignment which can be made is the S-state ion Fe^{3+}. This is consistent with the fact that in all the crystals investigated, a cubic Fe^{3+} spectrum was present, and that the intensity of the axial spectrum was greatest in the samples with the largest iron doping.

A stronger axial Fe^{3+} spectrum has been observed

[11] K. A. Müller, Arch. Sci. (Geneva) 11, 150 (1958).
[12] K. A. Müller, Phys. Rev. Letters 2, 341 (1959).
[13] A. Linz, Phys. Rev. 91, 753 (1953).

[14] R. de L. Kronig and C. J. Bouwkamp, Physica 6, 290 (1939).
[15] H. E. Weaver, Internal Quarterly Varian Report, 1959 (unpublished).
[16] $\Delta M = 3$ and $\Delta M = 4$ forbidden lines of Fe^{3+} at cubic sites of MgO have been observed as well [I. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) 73, 948 (1959)].
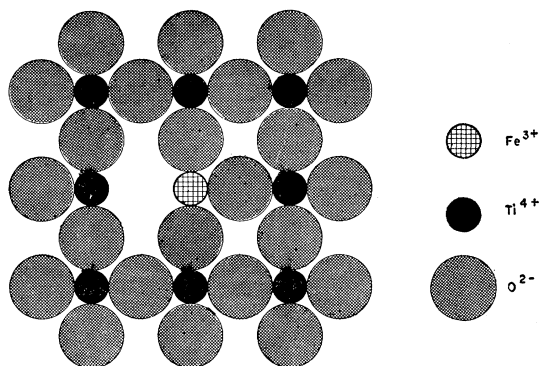
FIG. 2. Schematic diagram of the (100) plane of the cubic perovskite structure ($SrTiO_3$) containing a Fe^{3+}-oxygen vacancy pair. The relative size of the ionic radii of the ions has been taken into account.

only in hemoglobin[17] in which the Fe^{3+} is surrounded by five nitrogen ions at nearly octahedral sites, the sixth site being occupied by a molecule such as CO_2 or H_2O. The measured g values of this spectrum are $g_\perp{}^e = 6.0$ and $g_{||}{}^e = 2.0$, and the zero-field splitting $|2D|$ has been estimated to be greater than 10 cm^{-1}.

A tetragonal Cr^{3+} spectrum observed by Wertz and Auzins[18] in MgO with $2D = 0.164$ cm^{-1} has been attributed to charge compensation produced by a next nearest Mg^{2+} vacancy. The magnitude of the zero-field splitting Δ of Cr^{3+} in *tetragonal* fields has always been found to be similar or greater than that of Fe^{3+}; for example, in rutile (TiO_2), $\Delta = 1.44$ cm^{-1} for both Cr^{3+} [19,20] and Fe^{3+},[21] and in $MgWO_4$, $|2D| = 1.59$ cm^{-1} for Cr^{3+},[22] and 1.34 cm^{-1} for Fe^{3+}.[23] As the zero-field splitting of Fe^{3+} in $SrTiO_3$ is more than 10 times larger than that of Cr^{3+} in MgO, we conclude that charge compensation must occur nearer in the titanate, and this can only be at a nearest oxygen site. As no super-

hyperfine structure has been observed, it is improbable that charge compensation is achieved by a monovalent ion replacing an O^{2-} ion. (Compensation by an O^- ion is excluded by the fact that this ion would show an EPR line.) Therefore, it is most probable that local charge compensation is produced by an oxygen vacancy. In Fig. 2 an oxygen vacancy next to a substitutional Fe^{3+} ion is shown for a (100) plane of the cubic perovskite structure where the relative size of the different ions has been taken into account. The presence of the axial Fe^{3+} spectrum after heat treatment is most likely due to a hole trapped at a neutral complex containing an Fe^{2+} ion and an O^{2-} vacancy (instead of a tetravalent titanium ion without a vacancy).

It was mentioned in the introduction that the attraction of defects and impurity ions in crystals having a high dielectric constant should be low. We have shown here that local charge compensation at nearest-neighbor ions does exist, but no evidence has so far been found for defects lying on next-nearest neighbors.[24] This indicates that charge compensation centers are indeed poorly attracted to the impurity ions at the diffusion temperature, but once they are at a nearest site tend to form a stable complex, probably the neutral $Fe^{2+} - O^{2-}$ vacancy pair, which does not dissociate.

While this paper was being prepared for publication, D. J. A. Gainon[25] informed us that he has observed a strong axial spectrum at 8.8 Gc/sec due to Fe^{3+} in ferroelectric tetragonal $PbTiO_3$ with $g_{||} = 2.009 \pm 0.005$ and $g_\perp{}^e = 5.97 \pm 0.02$. Due to the rather large uncertainty in $g_\perp{}^e$ we are unable to compute $|2D|$ from his results (assuming $g_\perp = 2.00$) and therefore compare it with our case.

[17] J. E. Bennet, J. F. Gibson, and D. J. E. Ingram, Proc. Roy. Soc. (London) A240, 67 (1957).

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[19] J. Sierro, K. A. Müller, and R. Lacroix, Arch. Sci. (Geneva) 12, 122 (1959).

[20] H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. P. Wittke, Phys. Rev. Letters 2, 153 (1959).

[21] D. L. Carter and A. Okaya, Phys. Rev. 118, 1485 (1960).

[22] V. A. Atsarkin, E. A. Gerasimova, I. G. Matveeva, and A. V. Frantsesson, Zh. Eksperim. i Teor. Fiz. 43, 1272 (1962) [English transl.: Soviet Phys.—JETP 16, 903 (1963)].

[23] M. Peter, Phys. Rev. 113, 801 (1959).

[24] In $SrTiO_3$ doped with gadolinium and aluminum, J. Sierro [Helv. Phys. Acta 34, 404 (1961)] observed nearest cation neighbor charge compensation of a $Gd^{3+} \rightarrow Gd^{3+}$ ion (at a Sr^{2+} site) by an Al^{3+} ion (at a Ti^{4+} site).

[25] D. J. A. Gainon, Phys. Rev. 134, A1300 (1964).