PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 1, NO. 9 1 MAY 1970

Dynamic Jahn-Teller Effect of an Impurity in a Spontaneously Distorted Crystal

J. C. SLONCZEWSKI, K. A. MÜLLER, AND W. BERLINGER
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Received 3 November 1969)

The local symmetry of Ti^{4+} sites in $SrTiO_3$ is known to be cubic above 106°K, and tetragonal below. We have investigated the electron-spin-resonance spectrum of substitutional Ni^{3+} in the tetragonal phase of this compound. The components of the g tensor are observed to vary monotonically from $g_\perp = 2.215$ and $g_\parallel = 2.103$ at 4°K, to $g_\parallel = g_\perp = 2.180$ at 106°K. Three models of the dynamical Jahn-Teller effect in the presence of coupling to strain are examined. The magnitude and temperature dependence of $g_\perp - g_\parallel$ are best explained by a model in which the g tensor is given by a Boltzmann average over the two lowest vibronic states. The tunneling splitting appears to exceed by far the maximum spontaneous splitting of these states ($23\ \text{cm}^{-1}$). Our results indicate that the elongation of the nearest-neighbor octahedron is too small to be the principal cause of the g splitting.

I. INTRODUCTION

INVESTIGATION of the Jahn-Teller (J-T) effect[1] in crystalline solids has attracted increasing interest recently. Experimental studies have been carried out using paramagnetic resonance, a technique with which evidence for the existence of the effect was first obtained,[2] as well as optical and ultrasound absorption measurements.[3,4] In the studies so far made, the main variable used was temperature. It has been recognized that more information could be obtained if the systems were investigated as a function of uniaxial strain.[3,4] However, the external application of stress to certain systems has encountered difficulties. Therefore, in this work, use is made of the "built-in" tetragonal strain in $SrTiO_3$ present below the cubic-to-tetragonal phase transition in this compound. Because the transition is of second order starting with vanishing strain at the transition, it increases in a monotonic way on cooling. Thus, although the present study is novel in that the strain is a variable, ultimately again the temperature dependence of a physical quantity is measured.

The choice of the impurity in $SrTiO_3$ was Ni^{3+} substituted for Ti^{4+}. Our analysis of the variation of the EPR g factors with temperature in the tetragonal phase provides information about the J-T effect of this ion. In O_h point symmetry and octahedral coordination, the "low-spin" d^7 configuration of Ni^{3+} is orbitally degenerate, with a ^2E ground state.[3] It will, therefore, undergo a J-T effect of appreciable size, because e-type orbitals are involved.[3,4] If the effect is dynamic, then a single isotropic resonance line should be observed. Such a spectrum was reported by Rubins and Low[5] in the cubic phase of $SrTiO_3$, which exists above 106°K.[6] When the cubic spectrum is followed to temperatures below $T_a = 106°\text{K}$, the isotropic line splits into anisotropic components symmetric about [100]-axes.[5] The behavior of these anisotropic lines is the subject of the present paper. In addition, axial spectra are observed in the cubic phase which result from Ni^{3+} ions with local-charge compensation[5,7] and are of no interest in this context because the e orbitals are not degenerate under the reduced point symmetry.

Recently, understanding of the cubic-to-tetragonal phase transformation in $SrTiO_3$ has been considerably improved.[6,8] This transition was first detected by the axial splitting of cubic EPR spectra of Fe^{3+} impurities

---

[1] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[2] B. Bleaney and D. J. E. Ingram, Proc. Phys. (London) **A63**, 408 (1950); B. Bleaney, K. D. Bowers, R. S. Trenam, Proc. Roy. Soc. (London) **228**, 157 (1958).

[3] For a survey see M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967).

[4] For surveys on J-T effects in magnetic resonance, see K. A. Müller, in *Magnetic Resonance and Relaxation*, edited by R. Blinc (North-Holland Publishing Company, Amsterdam, 1967), p. 192; F. S. Ham, G. E. Report No. 68-C-246 (to be published).

[5] R. S. Rubins and W. Low, in *Proceedings of the First International Conference on Paramagnetic Resonance, 1962* (Academic Press Inc., New York, 1963), p. 59.

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

[7] K. A. Müller, W. Berlinger, and R. S. Rubins, Phys. Rev. **186**, 361 (1969).

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

substitutional for Ti^{4+} ions.[9] From the analysis of the angular dependence of these Fe^{3+} spectra[6,8] as well as those of Gd^{3+} ions substitutional for Sr^{2+},[10] the static properties of the transformation were completely determined. It consists of alternate rotations of near rigid TiO_6 octahedra around Ti^{4+} ionic positions along pseudocubic [100] directions; alternate rotating octahedra have common oxygen corners. The rotation angle has been measured as a function of temperature below T_a. Its relative dependence on reduced temperature T/T_a similar to the one measured in $LaAlO_3$ where the AlO_6 octahedra rotate around [111] axes.[6] It was concluded that the rotation angle ϕ is the order parameter in these structural phase transitions which are characteristic for the perovskite structure.

A simple model Hamiltonian has been introduced to study these transformations.[11] From it the temperature dependence of the rotation angle in the low-symmetry phase was obtained to be proportional to $|T_a-T|^{1/2}$ close to T_a. Assuming rigid octahedra it is easy to show that the c/a ratio of the crystal is given by $c/a=1/\cos\phi$, i.e., for small ϕ, $(c/a)-1\propto\phi^2\propto T_a-T$. A recent careful elastic neutron diffraction study by Alefeld[12] has indeed shown the strain to vary linearly with temperature from T_a to 77°K. However, c/a is not 1.00028 at 77°K as computed from the rotational angle, but 1.0004. This means that the acoustic-optic phonon coupling[11] induces an elongation $(c/a')=1.0001$ of the octahedra along the c axes, where $\frac{1}{2}a'$ is the titanium-oxygen bond length perpendicular to the c axis.

This local strain $(c/a')-1$ and its dependence on temperature is of importance to the present work. A relative measure of the octahedral strain can be gained by the axial splitting of the substitutional Fe^{3+} impurity.[13] However, the linewidth of this spectrum is comparable to the splitting and the scatter in data is considerable.[6,14] There is, however, a second Fe^{3+} spectrum due to an ion next to an oxygen vacancy Fe^{3+}-V_0.[15] The width of this spectrum is smaller than that of the cubic one. Below T_a the axial spectrum splits into a rhombic one whose low field splitting[6] is reproduced in Fig. 1. The relative temperature dependence of this splitting agrees well with the ^2E level splitting of the Cr^{3+} impurity as measured by Stokowski[16] by fluorescence.[17] Using the c/a' ratio of Alefeld[12] between T_a and 77°K and the approximation that the rhombic splittings of Fe^{3+} are proportional to the local strain, the local strain as a function of temperature in the tetragonal phase at the Ti^{4+} cation lattice site is then known.[18]

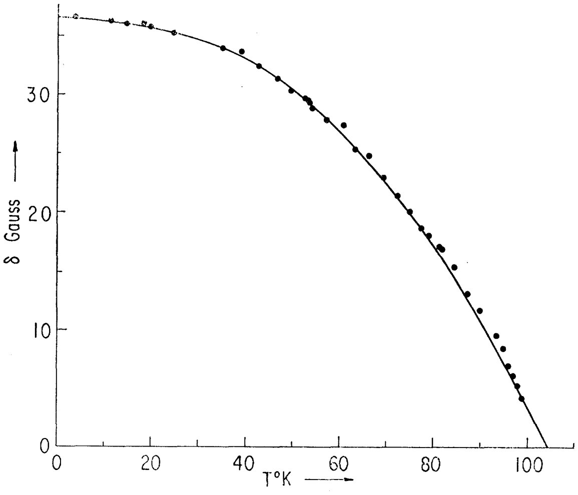

FIG. 1. Local crystal field arising from spontaneous tetragonal distortion of strontium titanate as measured by the rhombic splitting of the tetragonal EPR spectrum of an Fe^{3+}-V_0-complex. Based in part on Ref. 6 and in part on values newly determined by present authors.

Thus it is possible to investigate the dynamical J-T effect of Ni^{3+} as a function of the known natural temperature-dependent strain. The experimental results are given in Sec. II. The theory of g factors of a J-T impurity in the presence of strain is given in Sec. III. Comparison of theory and experiment is made in Sec. IV.

II. Ni^{3+} RESONANCE IN TETRAGONAL PHASE

When the $SrTiO_3$ crystals are cooled below the transition temperature at 106°K, the isotropic Ni^{3+} line is observed to split smoothly into a set of three axially symmetric lines with mutually perpendicular tetragonal axes. They arise from substitutional Ni^{3+} ions in the three possible tetragonal domains of the crystal.[9] Their splitting is much smoother than that of the Fe^{3+} or Gd^{3+} spectra.[6,8,10] This observation was already made by Rubins and Low[5] who measured the axial g values at 77, 22, and 4.2°K, using X band. In order to provide more complete data, a series of K-band

---

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

[10] L. Rimai and G. A. de Mars, Phys. Rev. **127**, 702 (1962).

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

[12] B. Alefeld, Z. Physik **222**, 155 (1969).

[13] In the axial splitting of the rare-earth Gd^{3+} ion at a Sr^{2+} site the point-charge contributions of more distant neighbors may be as important as the one due to the tetragonal strain; see Ref. 8. For the Fe^{3+} transition metal ion the local strain of the octahedron is responsible for up to 90% of the splitting; see R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. **149**, 257 (1966); **155**, 338 (1967); and **171**, 378 (1968).

[14] The observed splitting for $H\|[100]$ is in part due to the axial term b_2^0, and in part due to the rotation of axes by ϕ. An approximate $(T_a-T)^{1/2}$ dependence for this *total* splitting was found in a range from 30 to 80°K in Ref. 6, to which not much significance can be attached.

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

[16] S. E. Stokowski and A. L. Schawlow, Phys. Rev. **178**, 457 (1969).

[17] A comparison of the proportionality of these two splittings is made elsewhere: J. C. Slonczewski and H. Thomas (unpublished). In the latter work the proportionality between ϕ^2 and δ is shown to hold in the whole range below T_a as well.

[18] Extrapolating T_a to 106°K, a linear dependence of the rhombic splitting between 80°K and T_a is observed in good agreement with the work of Alefeld (Ref. 12).

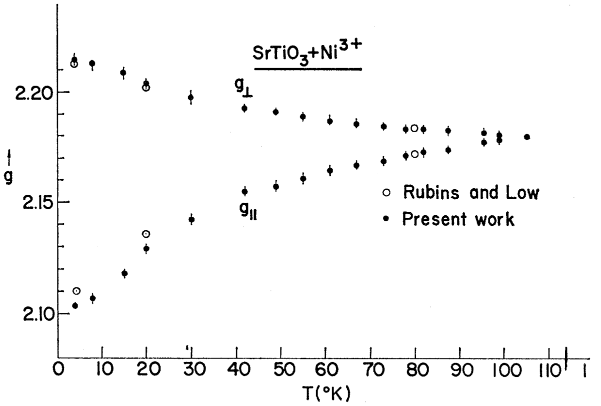

FIG. 2. Experimental g values in SrTiO$_3$:Ni^{3+} for static field parallel ($g_\parallel$) and perpendicular ($g_\perp$) to the tetragonal crystal axis.

measurements at temperatures between 4.2 and 110°K were made. The higher frequency allowed a more accurate determination of the g values. The results are shown in Fig. 2, a certain leveling off of the divergence in the region below 15°K, not apparent in the earlier work, is visible. The mean $\frac{1}{3}(g_\parallel+2g_\perp)$, is 2.179 ± 0.001 at all temperatures. The earlier X-band results of Rubins and Low are also shown in the figure.

III. THEORY

The shift of the Zeeman splitting factors $g_\parallel$ and $g_\perp$ of the dynamical J-T ion Ni^{3+} below the phase transformation at 106°K (see Fig. 2) is very different from the change of the Fe^{3+} rhombic splitting as shown in Fig. 1. The latter is proportional to the tetragonal deformation of the crystal as a function of temperature. We analyze the Ni^{3+} g shift here in terms of the interaction between the tetragonal distortion and the vibronic states of the J-T impurity.

Following O'Brien's[19] theory of the dynamical J-T effect, we write the Hamiltonian for the lower electronic state including the third-order Öpik and Pryce[20] term:

$$H=-(\hbar^2/2M)[(\partial/\partial Q_2)^2+(\partial/\partial Q_3)^2]-A\rho+\tfrac{1}{2}K\rho^2-A_3\rho^3\cos3\theta. \quad (1)$$

Here $Q_2\equiv\rho\sin\theta$ and $Q_3\equiv\rho\cos\theta$ are the vibrational coordinates of the octahedrally coordinated nearest-neighbor ions belonging to the representation E_g, as first described by Van Vleck.[21] The coefficient A measures the strength of the J-T splitting, $K=M\omega^2$ is the harmonic force constant for the E_g modes, and A_3 is the coefficient describing the warping of the energy surface due to Born repulsion of ions[20] and higher-order vibronic coupling.[22]

Equation (1) is adequate for cubic crystal symmetry. We bring into account the additional effect of a constant tetragonal strain ϵ of the nearest-neighbor octahedron without introducing additional adjustable parameters, by a method equivalent to Ham's.[23] This is done by adding to Eq. (1) a term, linear to Q_2 and Q_3, which gives Q_2 and Q_3 the equilibrium values dictated by ϵ when the anharmonic coefficients A and A_3 are set equal to zero. Taking z to be the tetragonal axis, one finds the required values

$$\theta_0=0,\quad \rho_0=2\times3^{-1/2}d\epsilon, \quad (2)$$

where d is the cation-anion distance, and ϵ is given in terms of the tetragonal octahedron parameters a' and c by

$$\epsilon=3(c-a')/(c+2a')\approx(c/a')-1. \quad (3)$$

The additional energy term V_1 required to produce these equilibrium values with $A=A_3=0$ is

$$V_1=-2\times3^{-1/2}Kd\epsilon\rho\cos\theta. \quad (4)$$

Our effective Hamiltonian is

$$H'=H+V_1. \quad (5)$$

According to Bleaney *et al.*,[24] the g factors for fields applied to the x, y, and z axes, respectively, for a d^9 configuration in octahedral coordination, are

$$g_{x,y}=g(\theta\mp\tfrac{2}{3}\pi),\quad g_z=g(\theta)\equiv2+C(1+\cos\theta), \quad (6)$$

where C is a positive constant of the order $|\lambda/V_c|$, where λ is the spin-orbit constant, and V_c is the cubic crystal field splitting. Since, for a certain type of wave function (i.e., $3z^2-r^2$), the sign of the J-T interaction for d^7 is the reverse of that for d^9, one has to replace θ by $\theta+\pi$. This difference arises because the orbital degeneracy of d^9 is due to an e-hole configuration ($\bar{e}\equiv e^3$) and that of d^7 is due to an e-electron configuration (e). The resulting formulas are then correct for the strong field d^7(Ni^{3+}) configuration t^6e if, in addition, a constant term C' is added, as found in the crystal field calculation of Lacroix *et al.*[25] Thus, for d^7 in octahedral coordination, we have

$$g_{x,y}=g'(\theta\mp\tfrac{2}{3}\pi),\quad g_z=g'(\theta)\equiv\bar{g}-C\cos\theta, \quad (7)$$

where $\bar{g}-2-C=C'$.[7,25]

Under the conditions of the dynamical J-T effect, interactions with phonons induce rapid transitions between vibronic states of the impurity, and the observed g factor is a statistical mean over the vibronic states. The mean of g_x, g_y, and g_z is always $\bar{g}$, while the splitting between the g values for fields parallel and perpendicular to the tetragonal axis is for d^7:

$$\Delta g=g_\perp-g_\parallel=g_x-g_z=C\left\langle\left\langle\cos\theta-\cos\left(\theta-\frac{2\pi}{3}\right)\right\rangle\right\rangle, \quad (8)$$

---

[19] M. C. M. O'Brien, Proc. Roy. Soc. **A281**, 323 (1964).

[20] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. **238**, 425 (1957).

[21] J. H. van Vleck, J. Chem. Phys. **7**, 72 (1939).

[22] A. D. Liehr and C. J. Ballhausen, Ann. Phys. **3**, 304 (1958).

[23] F. S. Ham, Phys. Rev. **166**, 307 (1968).

[24] B. Bleaney, K. D. Bowers, and M. H. L. Pryce, Proc. Roy. Soc. **A228**, 166 (1955).

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

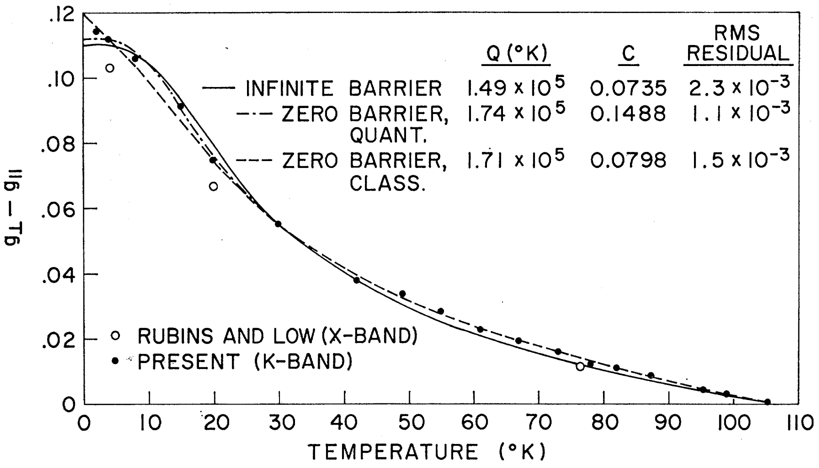

FIG. 3. Anisotropy of the g value for $SrTiO_3:Ni^{3+}$ versus temperature. Theoretical curves are two-parameter fits of the K-band data to three different models. The two curves for zero barrier are indistinguishable for $T>25°K$.

where $\langle\langle\ \rangle\rangle$ means statistical average. Since

$$\langle\langle \sin\theta \rangle\rangle = 0 \tag{9}$$

by symmetry, Eq. (8) reduces to

$$\Delta g = \tfrac{3}{2} C \langle\langle \cos\theta \rangle\rangle , \tag{10}$$

$$\Delta g = \tfrac{3}{2} C \Big[\sum_i \exp(-E_i/kT) \langle\cos\theta\rangle_i\Big] \times \Big[\sum_i \exp(-E_i/kT)\Big]^{-1} , \tag{11}$$

where E_i are eigenvalues and $\langle\ \rangle_i$ are averages over the eigenstates $|\ \rangle_i$ of H'.

We consider three limiting cases:

Case 1: Infinite barrier. We assume A_3 is so large that only the ground states of the system in the wells centered at $\theta=0, \pm\frac{2}{3}\pi$ are occupied. Then, neglecting the amplitude of zero-point oscillation and an additive constant in the energy, we have to first order in V_1, from Eq. (4),

$$\begin{aligned} \langle\cos\theta\rangle_1 &= 1 , & E_1 &= -kQ\epsilon , \\ \langle\cos\theta\rangle_{2,3} &= -\tfrac{1}{2} , & E_{2,3} &= +kQ\epsilon/2 , \end{aligned} \tag{12}$$

where

$$kQ = 2\times 3^{-1/2} K d \rho_0 \tag{13}$$

and where $\rho_0(=A/K)$ minimizes $-A\rho+\frac{1}{2}K\rho^2$. Equation (11) then becomes

$$\Delta g = \tfrac{3}{2} C [\exp(3Q\epsilon/2T) - 1]/[\exp(3Q\epsilon/2T)+2] \quad \text{(infinite barrier)}. \tag{14}$$

Case 2: Zero barrier, quantum limit. We assume $A_3=0$. As is well known from the work of Longuet-Higgins *et al.*,[26] the Schrödinger equation for H is separable and the ground-state angular eigenstates have the form

$$|\ \rangle_1 = \cos\tfrac{1}{2}\theta , \quad |\ \rangle_2 = \sin\tfrac{1}{2}\theta .$$

Neglecting the higher states we have

$$\langle\cos\theta\rangle_{1,2} = \pm\tfrac{1}{2} , \quad E_{1,2} = \mp\tfrac{1}{2} kQ\epsilon , \tag{15}$$

$$\Delta g = \tfrac{3}{4} C [\exp(Q\epsilon/T) - 1]/[\exp(Q\epsilon/T)+1] \quad \text{(quantum limit)}. \tag{16}$$

Case 3: Zero barrier, classical limit. In this limit we neglect the quantization of rotational energy as well as the effect of the barrier. Then H' effectively reduces to V_1 and Eq. (11) becomes

$$\Delta g = \tfrac{3}{2} C f(Q\epsilon/T) \quad \text{(classical limit)} \tag{17}$$

where

$$f(x) = \frac{d}{dx} \ln \int_0^{2\pi} d\theta \exp(x\cos\theta) . \tag{18}$$

Series expanding the exponential in Eq. (18) and integrating term by term, one finds the expression

$$f(x) = \left[\sum_{p=1}^{\infty} (p!)^{-2} p \left(\frac{x}{2}\right)^{2p-1}\right] \Big/ \left[\sum_{p=1}^{\infty} (p!)^{-2} \left(\frac{x}{2}\right)^{2p}\right] , \tag{19}$$

whose sums can be evaluated numerically.

IV. COMPARISON OF THEORY WITH EXPERIMENT

In order to compute Δg according to each of the above models, we require the function $\epsilon(T)$ for the local strain. For reasons given in Sec. I, we write

$$\epsilon(T) = 1.0\times 10^{-4}\, \delta(T)/\delta(77) , \tag{20}$$

where $\delta(T)$ is a third-degree polynomial fitted by least squares to the low field rhombohedral splitting of the Fe^{3+}-V_O-center plotted in Fig. 1.

Figure 3 shows temperature plots of $\Delta g = g_\perp - g_\parallel$ according to experiment and theory as computed electronically.[27] The curves are two-parameter fits of our three models to the K-band data. The best least-

---

[26] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).

[27] Qualitatively similar results have been computed independently by R. Englman and B. Halperin in unpublished work.

TABLE I. Experimental g values of $Ni^{3+}(3d^7)$ and $Pt^{3+}(3d^7)$ in octahedral coordination.

Ion	Host	$\bar{g}$	$g_{\parallel}$	$g_{\perp}$	Reference	$\lvert g_{\parallel}-\bar{g}\rvert$
Ni^{3+}:	$SrTiO_3$ (stable axial)	(2.244)	2.029	2.352	7, 5	0.215
$g_{\perp}>g_{\parallel}$	CaO [a]	(2.2776)	2.0672	2.3828	b, 29	0.2104
	TiO_2 [c] (substitutional)	(2.186)	(2.050)	(2.250)	30	0.136
	Al_2O_3	2.146	2.045		25	0.101
Ni^{3+}:	$SrTiO_3$ (light-induced)	(2.181)	2.375	2.084	7	0.194
$g_{\parallel}>g_{\perp}$	TiO_2 [b] (interstitial)	(2.141)	(2.254)	(2.0845)	30	0.113
Pt^{3+}:	Al_2O_3	2.220	2.011	2.328	d	0.209
$g_{\perp}>g_{\parallel}$	$BaTiO_3$	(2.289)	1.950	2.459	e	0.339
	YAG($Y_3Al_5O_{12}$) [b]	(2.249)	1.962	2.393	f	0.287

[a] Low and Suss assumed the resonance to originate from Ni^+. The reinterpretation in terms of Ni^{3+} is given in Ref. 29.
[b] W. Low and J. T. Suss, Phys. Letters **7**, 310 (1963).
[c] The given values of $\bar{g}$, $g_{\parallel}$, and $g_{\perp}$ are idealizations of the reported orthorhombic ones.
[d] S. Geschwind and J. P. Remeika, J. Appl. Phys. 33, 370 (1962).
[e] E. Šimánek, K. Sroubek, K. Ždánský, J. Kaczer, and L. Novák, Phys. Status Solidi **14**, 333 (1966).
[f] J. A. Hodges, R. A. Serway, and S. A. Marshall, Phys. Rev. **151**, 196 (1966).

square values of Q and C for each model, along with rms residuals, are indicated in the figure. The two curves for "zero barrier" cannot be distinguished for $T>25°K$. Although the curve "zero-barrier, quantum limit" fits best, "zero barrier, classical limit" is almost as good, and "infinite barrier" is not bad. The two limits of zero barrier differ mostly below $T=10°K$, where the classical limit is too steep and the quantum limit is too flat, suggesting that the truth lies in between.

Additional support for "zero barrier, quantum limit" is found in the value of C, which is much larger for this model than for the others. To show this, we have compiled in Table I values of g for $Ni^{3+}(3d^7)$, plus three cases of $Pt^{3+}(5d^7)$, with $S=\frac{1}{2}$ in octahedral coordination, taken from the literature. Measured values of $\bar{g}$ (without parentheses) were obtained from the isotropic spectrum of the dynamical J-T effect and $g_{\parallel}$ and $g_{\perp}$ were obtained either in static axial crystal fields or static J-T distortions. Values of $\bar{g}$ in parentheses were not measured but computed from the other two parameters using the equation

$$\bar{g}=\tfrac{1}{3}(g_{\parallel}+2g_{\perp}), \tag{21}$$

except as noted. In some of the cases shown in Table I, $g_{\perp}$ is greater than $g_{\parallel}$ and smaller in others, showing that both signs of the tetragonal crystal field occur. If a static J-T distortion of an octahedrally coordinated site occurs, then $g_{\perp}>g_{\parallel}$ because it is generally found that $A_3>0$.[4] When a static axial field overrides the J-T effect because of an intrinsic deviation from O_h symmetry or local-charge compensation, either sign of $g_{\perp}-g_{\parallel}$ is possible, depending on the detailed character of the compensating defect.[7,28]

In the limit of a static noncubic crystal field, $\lvert g_{\parallel}-\bar{g}\rvert$ is equal to C; on the other hand, $\bar{g}=2+C+C'$. For sufficiently large values of Dq/B, i.e., well above the ${}^2\Gamma_3-{}^4\Gamma_4$ level crossover at $Dq/B=2.2$, the term C' becomes negligible and $\bar{g}-2$ should be nearly equal to $\lvert g_{\parallel}-\bar{g}\rvert$.[7] In order to test this relation we have plotted in Fig. 4 values of $\bar{g}$ versus C taken from Table I. The linear relation (full line) holds to a certain extent for Pt^{3+}, for which the Dq/B ratios are of the order of 5 or higher; the larger C parameter results from the enhanced spin-orbit coupling as compared to that in Ni^{3+}. For the latter ion, positive departures of $\bar{g}-2$ from the linear relation are expected due to the near low-spin–high-spin crossover, especially for CaO.[29] For both ions dynamical reductions of C may be present. Both effects shift the $\bar{g}-2$ values upwards; the limiting experimental ones have been joined by a dashed line. In addition, large axial crystal fields can split and further admix the ${}^4\Gamma_4$ to the ${}^2\Gamma_3$ level in an as yet unknown way, and thus shift the $\bar{g}-2$ values in either direction from the full line. This effect may be present for Ni^{3+} and Pt^{3+} as well.

Figure 4 also shows the values of C for our case of uncompensated Ni^{3+} in $SrTiO_3$ corresponding to each of the three models of Sec. III. The model, "zero-barrier, quantum limit" ($\square$2), lies well inside the experimental upper limit, whereas the two other models ($\square$1 and $\square$3) are shifted leftwards beyond the dashed limit by nearly 0.1 or 100% of $\bar{g}-2$. This comparison, thus, further supports model 2.

Although we have limited our computation of the quantum limit case ($Qk\epsilon\ll$rotational splitting) to zero barrier, we argue that the magnitude of the barrier height $2A_3\rho_0^3$ bears little on the g shifts as long as it is not too great. The reduction factor $\langle\cos\theta\rangle_1$, which is $\frac{1}{2}$ for zero barrier, actually varies in the narrow range 0.484 to $\frac{1}{2}$ for all values of $2A_3\rho_0^3$ in the absence of strain.[30] Since the only influence of the vibronic wave function on Δg is through the factor $\langle\cos\theta\rangle_1$ (see case 2 above), we conclude that Δg is essentially independent

---

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

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

[30] J. C. Slonczewski, Solid State Commun. **7**, 519 (1969); D. P. Breen, D. C. Krupka, and F. I. B. Williams, Phys. Rev. **179**, 241, 255 (1969); J. R. Fletcher and K. W. H. Stevens, Proc. Phys. Soc. **2**, 444 (1969).

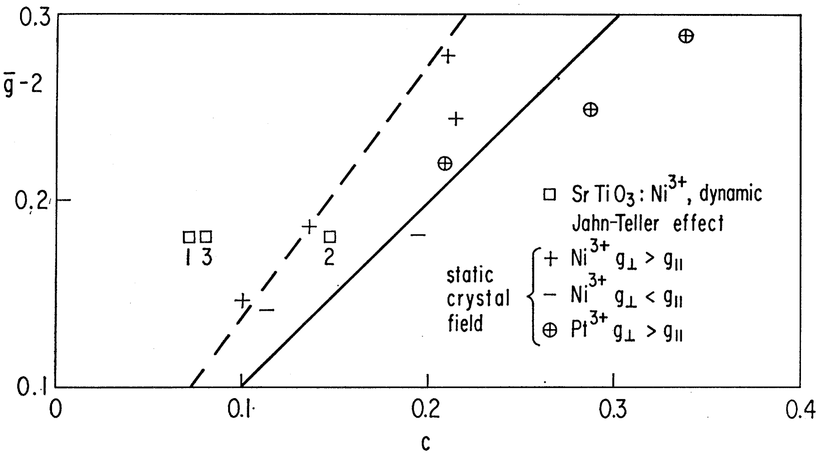

FIG. 4. Mean g value ($\bar{g}$) versus the coefficient of g dependence on orbital state (C): □1 infinite-barrier model; □2 quantum-limit model; □3 classical-limit model. The other points are for comparable Ni^{3+} ($3d^7$)and Pt^{3+}($5d^7$) spectra in which the crystal field at low temperatures is likely nearly static, in which case $C = |g_{\parallel} - \bar{g}|$.

of $2A_3\rho_0{}^3$. In particular, our "zero-barrier–quantum-limit" calculation is even valid when the barrier exceeds the free-rotational level intervals, as long as kT and the level splitting $Qk\epsilon$ are smaller than the excitation energy 3Γ of the first excited singlet which arises from the strain-free tunneling frequency Γ. Of course, if the barrier is sufficiently large, then we will have $3\Gamma \ll Qk\epsilon$, and the "infinite-barrier" model is approached.

Thus, the good fit of "zero-barrier, quantum limit" to the data in all respects down to 4.2°K does not mean that the barrier is inconsequential to the energy levels. It only indicates that our system SrTiO$_3$:Ni^{3+} satisfies the condition $3\Gamma \gg kQ\epsilon(0°\mathrm{K}) = 23$ cm^{-1}. This bound on 3Γ differs markedly from the small value $3\Gamma \approx 1$ cm^{-1} determined by Sturge *et al.*, for the similar system Al$_2$O$_3$:Ni^{3+}, by means of acoustic relaxation measurements,[31] as discussed by Ham.[4] In both cases the Ni^{3+} ion has octahedral coordination with oxygen neighbors, and yet Γ is quite different.

We should also mention in this connection the values $3\Gamma = 15.3$ and 6.5 cm^{-1}, for the excited levels of Eu^{2+} in CaF$_2$ and SrF$_2$, respectively, which were determined optically by Kaplyanskii and Przhevuskii,[32] according to the interpretation given by Chase.[33] Additional support for one of these values is provided by the EPR determination of $3\Gamma = 18 \pm 4$ cm^{-1} for CaF$_2$:Eu^{2+} given by Chase.[33]

Thus, the available data indicate a wide variability in Γ for apparently similar systems. Since Γ depends exponentially on barrier height in the WKB approximation, this circumstance may arise from a narrower variability in anharmonic potential.

We may reason that the good fit of the "zero-barrier, quantum limit" at higher temperatures must be fortuitous in considerable degree. This follows from the fact that the strong coupling theory of the dynamical J-T effect employed here is valid only when the rotational splitting is less in order of magnitude than the vibrational frequency ω which, in temperature units, might be 500°K. At temperatures ranging up to 106°K, higher-rotational states will probably contribute to Δg. Although we have carried out computations involving higher states, we have not included them here because the fits shown in Fig. 3 cannot be meaningfully improved by varying an additional parameter.

As an alternative to our strain-interaction term of Eq. (4) based on displacement of the vibrational equilibrium point, one may consider a strain-dependent crystalline field, described by a coefficient V_2, which has the experimental value $2.4 \pm 1.0 \times 10^4$ cm^{-1} in Al$_2$O$_3$:Ni^{3+}.[31] Ham has shown that these two approaches are physically equivalent[4] with, in our notation,

$$V_2 = kQ. \tag{22}$$

The Q values of our three models vary little, the "zero-barrier–quantum-limit" model yielding $V_2 = 1.2 \times 10^5$ cm^{-1}, which is much larger than the value given above. The fact that the former value of V_2 for Al$_2$O$_3$:Ni^{3+} is reasonable in other respects, according to Ham,[4] suggests that strain of the nearest-neighbor octahedron is not the principal cause of interaction in SrTiO$_3$ as we have assumed. If we had taken the macroscopic strain $\epsilon(77°\mathrm{K}) = 4.0 \times 10^{-4}$ in place of the local strain $\epsilon(77°\mathrm{K}) = 1.0 \times 10^{-4}$ in Eq. (20), our Q would be reduced to give $V_2 = 3.0 \times 10^4$, which is reasonably close to the above value in Al$_2$O$_3$:Ni^{3+}. This result might suggest that the long-range contribution of strain to the crystal field is dominant.

An additional indication of the relative unimportance of the nearest-neighbor strain is provided by the EPR linewidth of SrTiO$_3$:Fe^{3+}, which can be accounted for by *random* local strains (2×10^{-4}) of the same order of magnitude.[34] If the nearest-neighbor strain were the principal splitting agent, the Ni^{3+} resonance lines would

---

[31] M. D. Sturge, J. T. Krause, E. M. Gyorgy, R. C. LeCraw, and F. R. Merritt, Phys. Rev. **155**, 218 (1967).

[32] A. A. Kaplyanskii and A. K. Przhevuskii, Opt. i Spektroskopiya **19**, 597 (1965) [English transl.: Opt. Spectry. (USSR) **19**, 331 (1965)].

[33] L. L. Chase, Phys. Rev. Letters **23**, 275 (1969).

[34] K. A. Müller (unpublished).

not be as sharp as those we have observed ($\delta g/C \approx 0.1$). However, it would be premature to draw a firm conclusion about this point because we should expect that the "soft optic R-corner mode," which becomes statically displaced in the tetragonal phase,[8,11] may also contribute to the local crystal field.

According to the "zero-barrier–quantum-limit" model as well as the "infinite-barrier" model, Δg should level off below 5°K. To test this the g shift at 2.1°K was measured. Interestingly enough, Δg does not level off at 2.1°K (Fig. 3) and the system appears to behave in this region more like the "zero-barrier–classical-limit" model, whereas this is not the case above 5°K. In this connection, a second soft mode in $SrTiO_3$, the Cochran ferroelectric mode may be of importance. In this temperature region, the latter mode has a very low phonon frequency of $\omega < 10$ cm^{-1},[35] which is lower than both rotational modes. Although linear J-T coupling is not possible for vanishing wave vector, such a coupling to this mode, whose frequency obeys the equation

$$\omega^2(q) = \omega_0^2 + \alpha q^2,$$

becomes allowed for $q \neq 0$. The strength of the $q=0$ in the summation is negligibly small as compared to the $q \neq 0$ values. Moreover, quadratic coupling for $q=0$ is allowed. Thus, it is possible that the ferroelectric mode yields such low rotational levels at this temperature that the system behaves more in the classical manner. To clarify this, more data points between 0.3 and 2°K are needed.

ACKNOWLEDGMENTS

The authors are grateful to F. S. Ham and R. S. Rubins for helpful comments and to R. Englman and B. Halperin for communicating unpublished results.

---

[35] P. A. Fleury and J. M. Worlock, Phys. Rev. **174**, 613 (1968).

PHYSICAL REVIEW B VOLUME 1, NUMBER 9 1 MAY 1970

Resonant Cross Section for 14.4-keV Gamma-Ray Absorption in Fe^{57}

Duane P. Johnson

Advanced Materials Research and Development Laboratory, Pratt and Whitney Aircraft, Middletown, Connecticut 06458

(Received 12 December 1969)

The resonant cross section and internal conversion coefficients of the 14.4-keV level in Fe^{57} are determined from Mössbauer absorption spectra of thin polarized iron foils. We obtain a value for the maximum resonant cross section of $(2.56\pm0.05)\times10^{-18}$ cm^2, which leads to a total internal conversion coefficient of 8.19 ± 0.18. This value for the internal conversion coefficient is in excellent agreement with recent results from x–x-ray and x–γ-ray coincident experiments and is nearly 10% lower than the previously accepted value.

I. INTRODUCTION

THERE is some interest in determining the recoilless fraction of resonant absorbers f_a. In order to determine f_a from resonant absorption spectra, it is necessary to secure the maximum resonant cross section σ_0. In the case of the 14.4-keV level in Fe^{57}, many attempts have been made to determine σ_0. After initial very low reported values for σ_0, the value has risen to a generally accepted value[1] of $(2.36\pm0.05)\times10^{-18}$ cm^2. This value is based on the average of several Mössbauer determinations[2–5] $(2.42\pm0.19, 2.39\pm0.15, 2.31\pm0.12, 2.35\pm0.09)\times10^{-18}$ cm^2, and three γ–γ-ray coincidence determinations[1,3,6] $(2.36\pm0.12, 2.31\pm0.12, 2.47\pm0.23)\times10^{-18}$ cm^2. The latter experiments determine the total internal conversion coefficient α_T, which can in turn be used to give the maximum resonant cross section through the expression[7]

$$\sigma_0 = 23.6\times10^{-18}/(1+\alpha_T)\ \text{cm}^2. \qquad (1)$$

Recent x–x- and x–γ-ray coincidence experiments by Rubinson and Gopinathan[8] have led to a significantly smaller value for α_T than is generally accepted. Through Eq. (1), this leads to a significantly larger value for σ_0. Depending upon what auxiliary information is used, they arrive at $\alpha_T = 8.04\pm0.52$, 8.17 ± 0.25, and 8.28 ± 0.21 which in turn leads to $\sigma_0 = (2.61\pm0.14, 2.57\pm0.07, 2.54\pm0.06)\times10^{-18}$ cm^2. Their results are further supported by energy extrapolation of the theoretical values of Rose[9] and by Z extrapolation of the theoretical values of Hager and Seltzer[10] which lead to estimates for α_T of 8.17 and 8.12, respectively.[8]

---

[1] A. H. Muir, K. J. Ando, and H. M. Coogan, *Mössbauer Effect Data Index, 1958–1965* (Interscience, New York, 1966).

[2] S. S. Hanna and R. S. Preston, Phys. Rev. **139**, A722 (1965); **142**, 286(E) (1966).

[3] O. C. Kistner and A. W. Sunyar, Phys. Rev. **139**, B295 (1965).

[4] G. R. Isaak and U. Isaak, Phys. Letters **17**, 51 (1965).

[5] R. H. Nussbaum and R. M. Housley, Nucl. Phys. **68**, 145 (1965).

[6] G. Moreau and G. Ambrosino, Comp. Rend. **261**, 4538 (1965).

[7] This is an evaluation of the expression $\sigma_0 = 2\pi\lambda^2\omega[1/(1+\alpha_T)]$ with $\lambda^2 = 1.88\times10^{-18}$ cm^2, and $\omega = 2$. See, for example, H. Frauenfelder, *The Mössbauer Effect* (Benjamin, New York, 1962).

[8] W. Rubinson and R. P. Gopinathan, Phys. Rev. **170**, 969 (1968).

[9] M. E. Rose, *Internal Conversion Coefficient* (Interscience, New York, 1958).

[10] R. S. Hager and E. C. Seltzer, California Institute of Technology Report No. CALT-63-60, 1967 (unpublished).