intensity of the N_4^- is increasing while the intensity of the N_2^- is decreasing. The N_4^- reaches its maximum intensity when the N_2^- has just disappeared. When the crystal is now warmed to room temperature for approximately 16 hours, the intensity of the N_4^- spectrum is reduced by one-half. During the annealing studies one of the chromium lines in an oriented sample of Al_2O_3 was used as an intensity standard.

Helpful discussions with C. W. Moeller and R. Schor are gratefully acknowledged. We are indebted to J. E. Mapes and F. B. Otto for the preparation of samples.

Paramagnetic Resonance Absorption of Divalent Nickel in α-Al₂O₃ Single Crystal*

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A paramagnetic resonance absorption spectrum has been observed in single crystals of α-Al₂O₃ having nickel oxide added as an impurity. The spectrum is interpreted as being due to transitions between fine structure states of the divalent nickel ion. Best-fit constants to an axially symmetric spin Hamiltonian are obtained from 4.2°K to 300°K. The spectroscopic splitting factors are found to be nearly constant over this temperature range with average values given by $g_{\shortparallel} = (2.1957 \pm 0.0013)$ and $g_{\perp} = (2.1859 \pm 0.0013)$. The crystal field splitting energy is, on the other hand, found to be temperature dependent following the approximate law $D = -(1.3287 + \alpha T^2)$ cm⁻¹, where $\alpha = 5.2 \times 10^{-7}$ (°K)⁻². The average spin-orbit coupling constant over this temperature range is found to be (-285 ± 30) cm⁻¹.

I. INTRODUCTION

IN recent years, a number of investigations have been reported on the spectra of iron group ions in α-Al₂O₃. As a host, this structure exhibits some properties which make it favorable for the study of magnetic ions. Briefly, these properties include a moderately high coefficient of thermal conductivity, a relatively low dielectric loss factor and a structure containing anions having zero-spin nuclei. In the α-Al₂O₃ structure, local cation sites exhibit the trigonal symmetry of a distorted oxygen octahedron with two nonequivalent cation sites per unit cell. For magnetic ions occupying such sites, the crystallographic nonequivalence produces a magnetic nonequivalence when the magnetic ion spin quantum number is equal to or greater than two. For the divalent nickel ion, $S=1$ so that the crystal should exhibit no magnetic nonequivalence from this source.

Of the various magnetic iron group ions, the magnetic spectra of trivalent chromium,[1] iron[2] and vanadium[3,4] along with divalent manganese,[5] cobalt,[6] vanadium[4] and nickel[7] have been observed in this structure. These spectra are observed to exhibit axial symmetry about the threefold axis of the crystal. From this spectral symmetry and from the fact that trivalent iron and divalent manganese, each with spin $S=\frac{5}{2}$, exhibit spectral characteristics strongly suggesting two magnetically nonequivalent sites, it is concluded that sites occupied by the iron group ions are those of the normal trivalent aluminum ions. In a recent report on the trivalent gadolinium ion in α-Al₂O₃, Geschwind and Remeika reach a similar conclusion and report the additional fact that during the crystal growth process, the gadolinium ion tends to favor one aluminum site over the other.[8] In addition, for the case of divalent ions such as V^{++}, Co^{++} and Mn^{++}, spectra are reported which tend to suggest no local distortion of an extent sufficient to destroy the trigonal symmetry nor any spectral evidence of localized charge compensation.

In this paper, we wish to report the results of an investigation on divalent nickel ion in α-Al₂O₃ single crystals. It is felt that these results will be of interest not only because they have to do with yet another iron group ion in this particular structure, but also because of some rather interesting although as yet unexplained spectral behavior.

II. EXPERIMENTAL PROCEDURE

The magnetic resonance absorption spectrometer used in this investigation is of conventional design making use of superheterodyne detection. Zeeman field was provided by a twelve-inch electromagnet having a 2½ in. pole gap and auxiliary coils for low-frequency field modulation. Microwave power was delivered from a 3 cm wavelength oscillator locked to the specimen cavity.

* This work supported by the Air Force Cambridge Research Laboratories.
[1] J. E. Geusic, Phys. Rev. 102, 1252 (1956).
[2] L. S. Kornienko and A. M. Prokhorov, J. Exptl. Theoret. Phys. (USSR) 33, 805 (1957).
[3] G. M. Zverev and A. M. Prokhorov, J. Exptl. Theoret. Phys. (USSR) 34, 1023 (1958).
[4] J. Lambe and C. Kikuchi, Phys. Rev. 118, 71 (1960).
[5] W. Low and J. T. Suss, Phys. Rev. 119, 132 (1960).
[6] J. E. Geusic, Bull. Am. Phys. Soc. 4, 1260 (1959).
[7] S. A. Marshall and A. R. Reinberg, J. Appl. Phys. 31, 336S (1960).
[8] S. Geschwind and J. P. Remeika, Phys. Rev. 122, 757 (1961).

The specimen, of roughly 0.75 cm³ volume, was placed along the axis of a cylindrical cavity operating in the TE_{011} mode with the crystal [111] direction perpendicular to the cavity axis. With this cavity, having a loaded Q in the neighborhood of 8000, the resonance absorption lines due to divalent nickel were of sufficient strength to be easily observed on an oscilloscope without the aid of phase sensitive detection. Frequency of the microwave power was determined to within a few kc/sec by measuring the difference frequency generated by beating the microwave signal against harmonics from a quartz crystal controlled oscillator. The Zeeman field strengths were determined by making use of the nucleus magnetic resonances of hydrogen and lithium nuclei.

Two aluminum oxide single crystals were used, each obtained from a different boule. One boule was a standard Linde "Golden Sapphire" with four-tenths percent nickel oxide impurity added to the starting mixture, and the second was grown from a mixture having four percent nickel oxide. The magnetic resonance spectra obtained from these two samples were found to be alike except for a slight difference in intensity.

Orientation of the specimens was accomplished by two methods. Preliminary orientation was obtained by observing the rotation of a cross interference figure under a polarizing microscope. This located the crystal [111] direction to within one degree of arc. Final orientation was checked by observing the resonance absorption of trivalent chromium and iron ions which are present as trace impurities. In this manner, the location of the crystal [111] direction was established to within fifteen minutes of arc.

III. RESULTS

Free divalent-nickel ion has a ^3F ground-term designation which is a state of sevenfold orbital degeneracy or of twenty-one-fold degeneracy when electron spin is
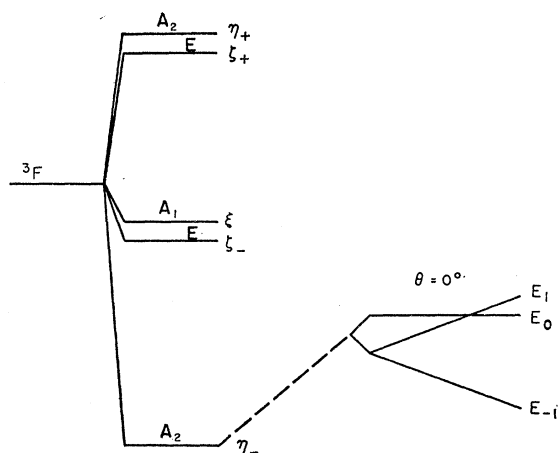

FIG. 1. Energy level diagram for the ^3F state resulting from the combined action of a sixfold coordinated, trigonally symmetric electric field, the spin-orbit potential and the Zeeman field shown for the $\theta=0°$ orientation.

considered. Application of an electric field having sixfold coordinated trigonal symmetry partially lifts this sevenfold orbital degeneracy into three singlets and two doublets of which the ground state is an orbital singlet. The threefold spin degeneracy of the low-lying orbital singlet is further partially lifted by the spin-orbit interaction potential, leaving a spin singlet separated from a spin doublet by an energy of the order of one wave number. The crystalline electric field potential may be described by an expression having the form:

$$V_{cf}=\alpha[3L_z^2-L(L+1)]$$
$$+\beta[35L_z^4-30L(L+1)L_z^2+25L_z^2$$
$$-6L(L+1)+3L^2(L+1)^2]$$
$$+\gamma \cos\delta[L_z(L_+^3+L_-^3)+(L_+^3+L_-^3)L_z]$$
$$-i\gamma \sin\delta[L_z(L_+^3-L_-^3)+(L_+^3-L_-^3)L_z], \quad (1)$$

where the coefficients α, β, γ and the phase angle δ are functions of the local crystal structure parameters and of the second and fourth moments of the magnetic ion radius. Equation (1), which is the crystalline electric field in operator equivalent form, contains only those terms which provide nonvanishing matrix elements within the $L=3$ wave-function manifold. The first order eigenvalues of this potential, calculated within this manifold, are given by

$$\xi=(15\alpha+180\beta),$$
$$\eta_\pm=(\tfrac{3}{2}\alpha+270\beta)\pm9[10\gamma^2+(\tfrac{3}{2}\alpha-10\beta)^2]^{\frac{1}{2}}, \quad (2)$$
$$\zeta_\pm=-[(9/2)\alpha+180\beta]\pm3[10\gamma^2+(\tfrac{3}{2}\alpha-80\beta)^2]^{\frac{1}{2}}.$$

To justify the singlet character of the lowest orbital level, it is assumed that the divalent nickel ion causes no local structure distortion, that the averages $\langle r^2 \rangle$ and $\langle r^4 \rangle$ over the magnetic ion wavefunctions can be approximated from calculations based upon free ion radial wavefunctions,[9] and that the magnetic ion interactions are with nearest neighbors only. Upon making these assumptions, it is found that the state η_- lies lowest with the state η_+ highest and nearly coincident with the twofold degenerate level ζ_+. This ordering of energy levels for the α-Al_2O_3 magnetic ion complex is in qualitative agreement with that given for the sixfold coordinated, trigonally symmetric, cubic field case.[10] Further use of the crystal field potential in predicting the magnetic resonance absorption spectra characteristics of the divalent nickel ion proved to be difficult in view of the above stated assumptions and in view of the fact that no optical transitions could be observed which correlated with the divalent state of nickel. This is not to say that the nickel oxide doped α-Al_2O_3 crystal exhibits no optical absorption but that such absorptions as do occur appear to be unrelated to the divalent nickel ion magnetic resonance absorption as has been shown by observing both the magnetic and optical absorptions before and after heat treating the crystals at 1800°C in a vacuum

[9] R. E. Watson, Phys. Rev. 119, 1934 (1960).
[10] B. Bleaney and K. W. H. Stevens, Reports on Progress in Physics (The Physical Society, London, 1953), Vol. 16, p. 108.

furnace for two to three hours. After such treatment, the optical absorptions of the crystals greatly diminish while the magnetic resonance absorption intensities remain essentially unchanged.

Application of the spin-orbit interaction potential $\lambda \mathbf{L} \cdot \mathbf{S}$ and a Zeeman field remove the final degeneracy due to electron spin in the lowest orbital level. The energy level scheme is shown in Fig. 1, where no effort has been made at accurate scaling. From the fact that the lowest orbital level is only spin degenerate and separated by the order of 10^4 cm^{-1} from the first excited orbital level, it is expected that this lowest level should be well relaxed at room temperature and accurately described as a spin triplet. For the case of axial symmetry, the ground level spin Hamiltonian takes the form

$$\mathcal{K} = D[S_z{}^2 - \tfrac{1}{3}S(S+1)] + g_{||}\beta H S_z \cos\theta$$
$$+ \tfrac{1}{2}g_\perp\beta H \sin\theta[S_-e^{i\varphi} + S_+e^{-i\varphi}], \quad (3)$$

where the terms have their normal spectroscopic meaning.[11]

The secular equation obtained by evaluating the matrix elements of $\mathcal{K}$ in the spin states representation is given by

$$E^3 - [\tfrac{1}{3}D^2 + g^2\beta^2H^2]E$$
$$+ \tfrac{1}{3}D\{(2/9)D^2 + g^2\beta^2H^2[1 - 3(g_{||}{}^2/g^2)\cos^2\theta]\} = 0, \quad (4)$$

where $g^2 = g_{||}{}^2 \cos^2\theta + g_\perp{}^2 \sin^2\theta$. The roots to this equation at $\theta = 0°$ and $\theta = 90°$ are given by

$$E_{\pm 1}(0°) = \tfrac{1}{3}D \pm g_{||}\beta H,$$
$$E_0(0°) = -\tfrac{2}{3}D, \quad (5)$$

and

$$E_{\pm 1}(90°) = -\tfrac{1}{6}D \pm [(\tfrac{1}{2}D)^2 + (g_\perp\beta H)^2]^{\frac{1}{2}},$$
$$E_0(90°) = \tfrac{1}{3}D, \quad (6)$$

where the subscripts on the roots refer to their strong field limit.

At a microwave energy of 0.315 17 cm^{-1}, two fine-structure resonance absorption lines are observed. These lines, uncomplicated by nuclear hyperfine interactions and having full widths between inflection points of 35 and 40 oersteds, occur, respectively, at 10 347 oe for $\theta = 0°$ and at 7151 oe for $\theta = 90°$ at room temperature. No low-field resonance lines having comparable widths and intensities are observed at either orientation. This suggests that the crystal field splitting energy is greater than the microwave energy. Assuming this to be the case, one can see that only the low-field component of the $E_0 \leftrightarrow E_1$ transition can account for the 10 347 oe line at $\theta = 0°$. At $\theta = 90°$, there seems to be very little question that the 7151 oe line is due to the $E_{-1} \leftrightarrow E_0$ transition. For the $\theta = 0°$ orientation, the nature of the energy levels is conveniently checked since E_0 is a field-independent level and consequently serves as an arbi-
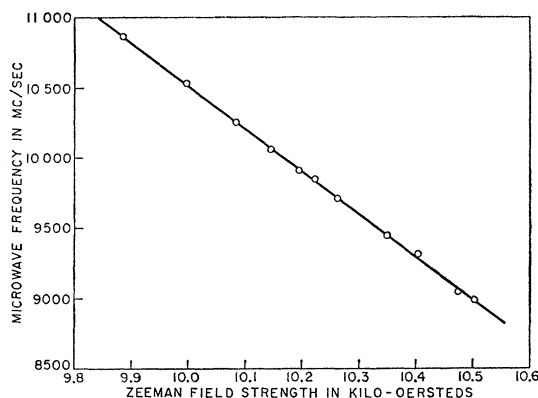
[11] D. J. E. Ingram, *Spectroscopy at Radio and Microwave Frequencies* (Butterworth Scientific Publications, New York, 1955).

FIG. 2. Microwave frequency vs Zeeman field strength relation for the $\theta = 0°$ orientation low-field $E_0 \leftrightarrow E_1$ transition.

trary reference. The resonance condition for this transition should exhibit a linear relation between the Zeeman field strength and the microwave energy. Such a relation is shown in Fig. 2 from which approximate values of D and $g_{||}$ are obtained.

The resonance observed at $\theta = 90°$, as stated previously, is due to $E_{-1} \leftrightarrow E_0$ transition. If this resonance is followed from $\theta = 90°$ to $\theta = 0°$, an iso-frequency relation can be established between the Zeeman resonance field strength and the polar angle. In addition, if one imposes the conditions that the sum of the roots to Eq. (4) vanish and that $\Delta E = h\nu$, then the resulting equation can be used to solve for the field strength required for resonance. This H vs θ relation is shown in Fig. 3, where the points are experimental and the solid curve is calculated.

Another characteristic of this spectrum, which serves to strengthen the argument for divalent nickel, is the ratio of relative intensities of the fine structure resonance lines. At $\theta = 0°$, the nonvanishing terms in Eq. (3) contain only commuting operators so that the eigenfunctions are given by the unmixed spin vectors corresponding to the states $S_z = 0, \pm 1$. At $\theta = 90°$, the situation is slightly complicated by noncommuting operators and the large crystal field splitting energy. Once eigenvalues are determined, the state functions can be developed in the spin states representation. These functions are given by

$$\Psi_{-1} = (0.65)\psi_1 - (0.40)\psi_0 + (0.65)\psi_{-1},$$
$$\Psi_0 = (0.71)\psi_1 \qquad - (0.71)\psi_{-1}, \quad (7)$$
$$\Psi_{+1} = (0.28)\psi_1 + (0.92)\psi_0 + (0.28)\psi_{-1},$$

where the states involved in the $\theta = 90°$ transition are Ψ_{-1} and Ψ_0. Transition probabilities are determined, using these eigenfunctions, by calculating matrix elements of the magnetic dipole moment operator and weighted by the appropriate microwave magnetic field strengths to account for the finite dimensions of the specimen. Using Eqs. (7), an intensity ratio $I(0°)/I(90°) = 4.0$ is obtained which compares favorably with the
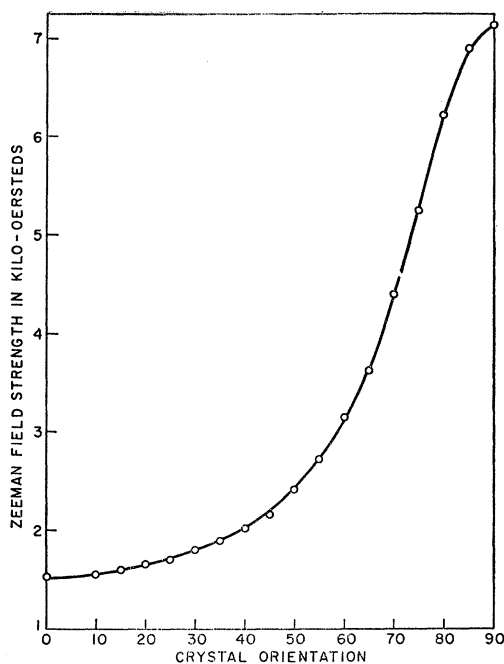
FIG. 3. Iso-frequency relation for H vs θ starting with the $E_{-1} \leftrightarrow E_1$ transition at $\theta=0°$ and ending with the $E_{-1} \leftrightarrow E_0$ transition at $\theta=90°$. The points are experimental and the solid curve is predicted from the determined values of $g_{||}$, $g_\perp$ and D.

experimentally determined ratio of 4.2. Best-fit constants to the Hamiltonian given by Eq. (3) are obtained from 4.2° to 300°K by observing resonance absorptions at several orientations and solving the simultaneous equations resulting from Eq. (4). The spectroscopic splitting factors, which are observed to be rather insensitive to temperature are given by $g_{||}=(2.1957 \pm 0.0013)$ and $g_\perp=(2.1859 \pm 0.0013)$. The sign of the crystal field splitting energy is found to be negative by comparing relative integrated intensity ratios of the $\theta=0°$ and $\theta=90°$ resonance absorptions at $T=1.5°$ and $T=77°K$. In addition, the spin-orbit coupling constant λ is found to be, within ten percent error, fairly insensitive to temperature with its average value given by (-285 ± 30) cm^{-1}. This value compares favorably with those for the divalent nickel ion in magnesium oxide[12,13] and in the Tutton salts.[14] The negative sign of the crystal field splitting energy is consistent with the inequality $g_{||}>g_\perp$ and with the sign of the spin-orbit coupling constant. Measurements made at points between 4.2° and 300°K show that the crystal field splitting energy follows a temperature dependence given by

$$D= -(1.3287+\alpha T^2) \text{ cm}^{-1}, \qquad (8)$$

where $\alpha=5.2\times10^{-7}$ (°K)$^{-2}$ (see Fig. 4). This dependence is not surprising in view of results reported by

[12] W. Low, Bull. Am. Phys. Soc. 1, 398 (1956).
[13] W. Low, Phys. Rev. 109, 247 (1958).
[14] J. H. E. Griffiths and J. Owen, Proc. Roy. Soc. (London) A213, 459 (1952).

Holden, Kittel, and Yager[15] and by Penrose and Stevens[16] on nickel fluosilicate and by Cross and Terhune[17] on the trivalent chromium ion in α-Al$_2$O$_3$.

If either of the two fine-structure resonance absorption lines is followed as the Zeeman field is rotated with respect to the crystal [111] direction, the linewidths are found to change. Unfortunately, the $\theta=0°$ line at 10 347 oe could not be followed for more than eight degrees due to field strength limitations of our electromagnet. On the other hand, the $\theta=90°$ line at 7151 oe could be followed to $\theta=0°$, as shown in Fig. 3. Recorder tracings of this resonance were taken from $\theta=0°$ to $\theta=90°$. Linewidths between points of inflection taken from these recordings are found to vary from 7 oe at $\theta=0°$ to 40 oe at $\theta=90°$ with a maximum width of 57 oe at $\theta=75°$. After having accounted for linewidth variations due to the derivatives of the eigenvalues of Eq. (4) with respect to the Zeeman field, it is found that the variation of linewidth with orientation can be correlated with the slope of the iso-frequency plot shown in Fig. 3. This suggests that the linewidth variation is either wholly or in part due to a slight but random distribution (mosaic effect) of the impurity ion site [111] direction about the mean crystal [111] direction. For the $E_{-1} \leftrightarrow E_1$ transition at $\theta=0°$, one would expect no linewidth contribution due to such a distribution. Thus, the 7 oe width at $\theta=0°$ would represent that width due to such effects as unresolved nuclear hyperfine interactions with next-nearest neighbor aluminum nuclei and interactions with lattice vibrations. Assuming the local mosaic effect to follow a Gaussian distribution and assuming further that the resonance absorption shapes are
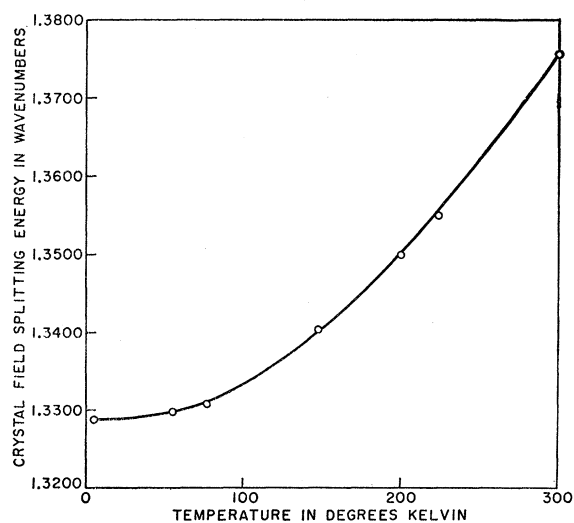

FIG. 4. Temperature dependence of the crystal field splitting energy.

[15] A. N. Holden, C. Kittel, and W. A. Yager, Phys. Rev. 75, 1443 (1949).
[16] R. P. Penrose and K. W. H. Stevens, Proc. Roy. Soc. (London) A63, 29 (1949).
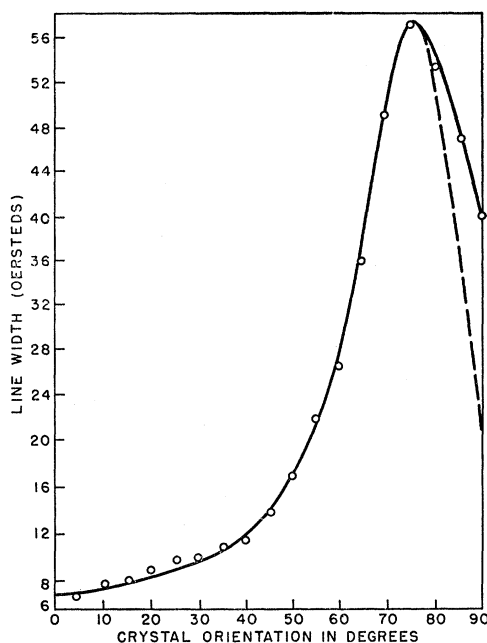[17] L. Cross and R. W. Terhune, Bull. Am. Phys. Soc. 3, 371 (1958).

FIG. 5. Resonance absorption linewidth variation with orientation of Zeeman field with respect to the crystal [111] direction.

Gaussian, which they very closely approximate, one can use the iso-frequency plot to generate resonance absorption linewidths which are proportional to the slope of this plot and to the width of the mosaic distribution. This relationship of linewidth to orientation is shown in Fig. 5 and is fitted with the data, $\Delta H_0 = 7$ oe (the orientation-independent resonance absorption linewidth) and $\Delta\theta = 0.3°$ (the width of the mosaic distribution) obtained from values of ΔH_1 (the magnetic resonance absorption linewidth due to the mosaic distribution taken at several orientations). The relation assumed between the total resonance absorption line width ΔH and the two widths ΔH_0 and ΔH_1 is given by $(\Delta H)^2 = (\Delta H_0)^2 + (\Delta H_1)^2$. This linewidth behavior is found to be reproduced within experimental error for a specimen cut from a second boule of nickel-oxide-doped $\alpha-Al_2O_3$. It is thus concluded that the linewidth vs orientation behavior is not a peculiarity of one particular specimen but is a consequence of the nature of the impurity center and the rather large value of the crystal field splitting energy. Why the excess line width does not vanish at $\theta = 90°$, as one might expect since the slope of the iso-frequency plot at this orientation vanishes, is not clearly understood. A similar behavior is observed for the $\theta = 0°$ resonance at 10 347 oe. This residual line width could arise from a number of sources such as a random distribution of crystal field splitting energies about a mean or perhaps a distribution of charge compensators partially locallized on the oxygen ions of the magnetic complex.

To check the width of the mosaic distribution, a similar set of observations were made on the trivalent iron ion resonance absorption. In particular, the reso-

nance corresponding at $\theta = 0°$ to the $E_{-\frac{5}{2}} \leftrightarrow E_{-\frac{3}{2}}$ transition was followed at constant frequency from $\theta = 0°$ to $\theta = 90°$. Recorder tracings were taken at eleven orientations which provided resolved lines of the iron ion resonance doublets. A linewidth vs orientation analysis of these tracings yielded a mosaic distribution width in the neighborhood of $0.3°$ which is considered to be in agreement with the analysis carried out for the divalent nickel ion. The uncertainty in both $\Delta\theta$ measurements is estimated to be $\pm0.03°$ from the data spread.

The $E_{-1} \leftrightarrow E_1$ transition at $\theta = 0°$ exhibits a rather interesting, although as yet unexplained behavior. This transition is, strictly speaking, forbidden. That it is observed at all, even though its intensity is two orders of magnitude below the $E_{-1} \leftrightarrow E_0$ transition at $\theta = 90°$, suggests that a mixing of states occurs either through a slight misorientation of the crystal or a slight orthorhombic distortion to the local structure. The weakness of the transition and the fact that the specimen dimensions are finite, causing some of the specimen to occur in regions where the microwave magnetic field has components parallel to the Zeeman field, makes this question difficult to resolve. At $T = 300°K$, this transition consists of a single resonance absorption, well isolated from resonances due to the trivalent iron and chromium ions. As the temperature is lowered, a satellite resonance is observed to grow in intensity at a field strength of roughly twenty oersteds above the main resonance. It first becomes noticeable at $T = 200°K$ and at $T = 77°K$ the satellite has an intensity comparable to that of the main line (see Fig. 6). The separation between the two lines is found to be almost invariant as the Zeeman field orientation is changed. At orientations of $\theta = 50°$ and above, the lines are no longer resolved partially because of the increase in widths and perhaps because of a possible crossover or merging of the lines.

Two pieces of information strongly suggest that the satellite is due to the $E_{-1} \leftrightarrow E_1$ transition of the divalent nickel ion and not to some other impurity whose strength increases as the temperature is lowered. First, the satellite faithfully follows the iso-frequency plot up to the $\theta = 50°$ orientation at which point it is no longer resolved from the main resonance. It remains roughly 20 oe above the main resonance with a width between
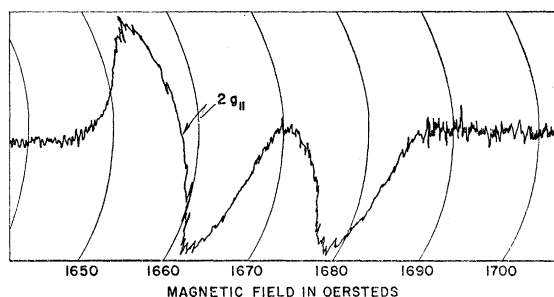

FIG. 6. First derivative recorder tracing of the satellite due to the $E_{-1} \leftrightarrow E_1$ transition taken at the $\theta = 0°$ orientation and $T = 77°K$.
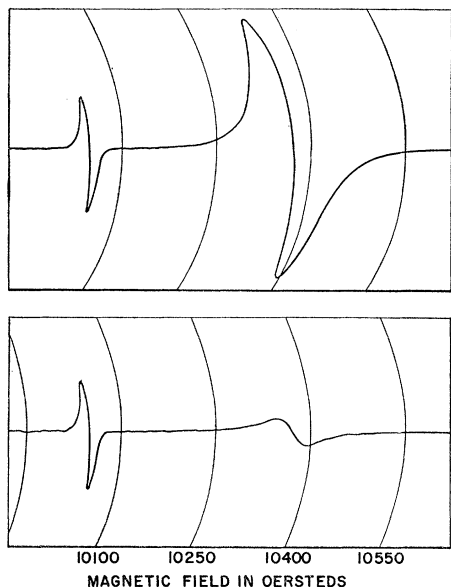
FIG. 7. Effect of x-ray irradiation on the magnetic resonance absorption of the divalent nickel ion. Tracings are for the low-field $E_0 \leftrightarrow E_1$ transition. Top tracing is for an unirradiated crystal and below it, the same crystal after irradiation. The resonance at the left is due to the $E_{-\frac{5}{2}} \leftrightarrow E_{-\frac{3}{2}}$ transition of the trivalent iron ion.

inflection points of 6.5 oe at $\theta = 0°$. The second piece of information results from the behavior of the nickel ion resonance absorption when the crystal is exposed to x irradiation. Under such irradiation, this resonance absorption is observed to diminish to a degree dependent upon the total irradiation dosage.

Irradiation of our two samples for 8 hr with 50 kv silver anode x rays showed a resonance intensity diminution of roughly an order of magnitude. The process is found to be reversible upon heating the crystals for a few hours at temperatures of 1000 to 1200°C. Recorder tracings of this effect are shown in Fig. 7 for the low-field $E_0 \leftrightarrow E_1$ transition at $\theta = 0°$, which also shows the $E_{-\frac{5}{2}} \leftrightarrow E_{-\frac{3}{2}}$ transition of trivalent iron which is known to be only slightly, if at all, affected by irradiation with x rays. When this x-ray irradiation is applied to the crystal, it is found that for the $E_{-1} \leftrightarrow E_1$ transition, both the satellite line and main line intensities changed commensurately.

The occurrence of the satellite at low temperatures cannot be accounted for by crystal twinning or by a local orthorhombic distortion. To begin with, twinning can be dismissed since the satellite does not cross over from the high to the low field side of the main line as the Zeeman field direction is rotated through the $\theta = 0°$ orientation. Such behavior would be required if twinning were the cause of the satellite. Furthermore, the same satellite behavior is observed in a specimen cut from a second boule and the probability of duplication of twin angle and twin-size ratios seems not too likely. The possibility of a local orthorhombic distortion would of course explain the nonvanishing resonance absorption

intensity at $\theta = 0°$ for this transition. If this were the case, the twenty-oersted satellite separation at a microwave energy of 0.315 17 cm^{-1} could be used to determine the crystal field energy separation between the two states E_{-1} and E_{+1}. This separation would have to amount to roughly 0.030 cm^{-1} and would be sufficient in magnitude to be checked by varying the microwave energy by, say, ten percent. Resonance absorption measurements made at 0.340 00 cm^{-1} show that if the states E_{-1} and E_1 are separated, the separation cannot amount to more than 0.003 cm^{-1}.

As the temperature is lowered further, the satellite resonance becomes more intense and at $T = 52°K$, its strength is roughly 90% of the main resonance. At this temperature, two more satellites are observed with intensities of roughly ten and thirty percent of the main line. The low intensities of these satellites make them difficult to follow beyond the $\theta = 20°$ orientation. At $\theta = 0°$, they are unresolved from the stronger satellite which may account for the peculiar shape of the resonance absorption first derivative tracing shown in Fig. 6.

IV. CONCLUSION

Although there exist as yet several unexplained features to this magnetic resonance absorption spectrum, there seems to be good evidence for identifying it with the divalent state of nickel. Aside from the fact that the spectrum fits into the scheme of a well-isolated orbital singlet ground level having threefold spin degeneracy, the values of spin-orbit coupling constant, the spectroscopic splitting factors, and the temperature dependence of the crystal splitting energy are in good agreement with the constants observed for the divalent nickel ion in other hosts.[12–16] The three principal features that remain in question are (i) the calculated values of the spectroscopic splitting factor, (ii) the calculated temperature dependence of the crystal splitting energy and (iii) the onset at $T = 220°K$ of a satellite due to the $E_{-1} \leftrightarrow E_1$ transition at the $\theta = 0°$ orientation. These unexplained features are sensitive to our choice of a model for the magnetic ion complex. This model choice may be unrealistic, and yet there seem to be few alternatives to choose from for the following reasons: (i) no optical absorptions are available which can be unambiguously identified with the divalent state of nickel, (ii) the positive-ion vacancies of the α-Al_2O_3 structure do not easily accommodate the divalent nickel ion, and (iii) the onset of localization of a charge compensator can cause a complicated alteration of local symmetry, which should manifest itself in the observed spectrum. Despite the fact that the first two features are compared with the results of other investigations and then used as arguments for identifying the source of this spectrum, these features are at considerable variance with calculations based on the α-Al_2O_3 structure parameters. For example, the experimentally observed con-

stants to the spin Hamiltonian exhibit the inequalities $g_{||}>g_{\perp}$ and $D<0$, while calculations based on the crystalline electric field potential given by Eq. (1), the α-Al_2O_3 structure parameters and the assumption that $\lambda = -285$ cm^{-1}, reverse these inequalities and yield values of $(g-2)$ which are in the neighborhood of 300% greater than those determined experimentally. In a similar manner, a calculation of $(1/D)\partial D/\partial t$ based upon the room temperature thermal expansion coefficient for α-Al_2O_3 yields a value which is 200 to 300% smaller than the value observed at this temperature.

It thus appears that if a satisfactory explanation to these two behaviors and the appearance of the satellite resonance absorption is forthcoming, the simple model must of necessity be modified to take account of distortions produced by the large divalent nickel ion, the localization of charge compensators and the interaction with ions outside the oxygen octahedron.

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Knight Shift in Silver Base Solid Solutions

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This paper describes an experimental investigation of some primary substitutional solid solutions of silver. Nuclear magnetic resonance was used to detect the charge density at the solvent nuclei in these alloys, and the results are compared with theory. Solutes chosen for the study were Cu, Zn, Ga, Ge, As, Cd, In, Sn, Sb, Au, and Tl. Insertion of a few percent of any of these caused a decrease in the Knight shift of silver in rough proportion to both solute concentration and valence. Also the normally narrow silver absorption became very broad under the influence of a few percent solute. This severe broadening serves as the major basis for an argument concerning the distribution of charge density around the solute atoms. It is shown that dipolar and indirect exchange broadening are not sufficient to account for the observed line-widths; subsequently the absorption is analyzed in terms of the long-range oscillations in the conduction electron density thought to be present in the vicinity of the solute atoms. The comparison with theory indicates that the line shift and width are equally well explained by the presence of long-range oscillations. If the shift were much greater than that observed it would suggest another source of shift not included by the present mechanism. It is concluded that the theory of Blandin, Daniel, and Friedel is applicable to these alloys and explains the data satisfactorily. It is not possible to test the theory quantitatively unless one knows the exact phase shifts to describe the scattering process underlying this theory.

I. INTRODUCTION

THE purpose of this paper is to describe the results of an investigation of the nuclear magnetic resonance of Ag^{109} in an extensive group of silver base solid solutions. Early work directed at determining the dependence of the Knight shift on the constitution of solid solutions failed in that objective because of the dominant effect of quadrupole perturbations on the resonance in the systems considered. When it was recognized that localized conduction electron charge redistribution was responsible for these quadrupole interactions[1] the prospect of studying localized charge distributions by means of the Knight shift became attractive. It was also necessary to establish with certainty the dominant features to be associated with the effect of the Knight shift in alloys in order to consider their role in the analysis of the quadrupole interaction studies.[1] For the work reported here Ag^{109}

was chosen for attention primarily because it has no nuclear electric quadrupole moment. Of course it was also advantageous that numerous solutions could be formed using silver as solvent. The electron distribution suggested and developed by Friedel and co-workers[2-4] will be used to analyze the data after it has been shown that other interactions distinct from the electron-nuclear contact interaction responsible for the Knight shift are relatively unimportant.

The major characteristics of the results are a very rapid broadening of the absorption with increased impurity content, coupled with a shift of the absorption. The shift is roughly proportional to the excess valence of the solute and is in every case decreased from its value in the pure metal; it is proportional to solute concentration within experimental error. These characteristics are consistent with the presence of the long-

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