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Paramagnetic Resonance Absorption of Divalent Nickel in Sapphire*

S. A. MARSHALL, T. T. KIKUCHI AND A. R. REINBERG
Physics Division, Armour Research Foundation
Chicago 16, Illinois, U.S.A.

The paramagnetic resonance absorption lines of divalent nickel in sapphire single crystals have been studied at various orientations of the Zeeman field with respect to the crystal [111] direction. Widths of the absorption lines, measured at points of inflection, are found to vary in a manner which strongly suggests that the local structure symmetry directions are randomly distributed about the mean crystal [111] direction. The full width of this distribution is estimated to be $\Delta\theta = 0.30$ degrees. Similar results are obtained from paramagnetic resonance absorption lines due to the trivalent ions of chromium and iron in the same specimen.

The magnetic resonance absorption spectrum of divalent nickel in α-Al_2O_3 can be characterized as being due to a three-fold spin degenerate ground state with the spectroscopic constants $g_{\parallel} \cong g_{\perp} \cong 2.2$ and $D \cong 1.4$ cm^{-1}. This spectrum consists of three fine structure resonance absorption lines, one located at 10347 oersteds with an image resonance at 16500 oersteds for the $\theta = 0°$ orientation and another located at 7151 oersteds for the $\theta = 90°$ direction when the microwave energy is 0.315 cm^{-1}. These lines correspond to the $E_0 \leftrightarrow E_1$ and $E_{-1} \leftrightarrow E_1$ transitions, where the energy nomenclature refers to the high Zeeman field limit.[1]

If the resonance at 7151 oersteds is followed as the Zeeman field direction is varied, an isofrequency relation can be established between the polar angle θ and the strength of the Zeeman field necessary for resonance absorption. At the $\theta = 0°$ orientation, this resonance corresponds to a transition between the two states E_{-1} and E_1 which are degenerate in the absence of a Zeeman field. In observing the divalent nickel ion resonance absorption along this isofrequency curve, see Fig. 1, it is found that the line width varies from 7 oersteds at $\theta = 0°$ to 40 oersteds at $\theta = 90°$ with a maximum of 58 oersteds at $\theta = 75°$.[2] To a first approximation, this line width behavior is found to be correlated to the derivative $(\partial H / \partial \theta)$ of the isofrequency curve which exhibits a maximum at the $\theta = 75°$ direction and minima at the parallel and perpendicular orientations.

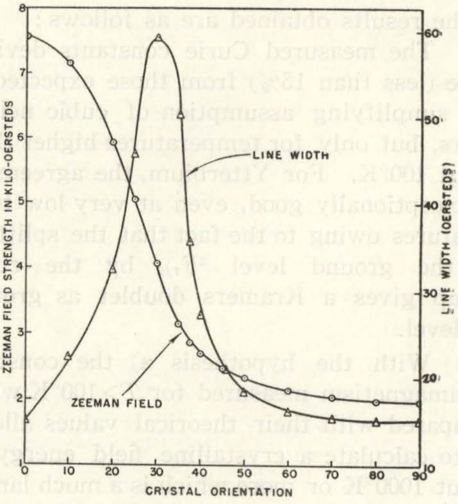

Fig. 1. Isofrequency plot and the variation in line width as a function of crystal orientation for the divalent nickel ion in α-Al_2O_3.

In an attempt to understand this line width variation, two classes of broadening are considered. The first, (ΔH_1) the residual line width, is assumed to be due to such effects as unresolved nuclear hyperfine interactions with next-nearest aluminum ion neighbors, frequency fluctuations in the microwave energy, interactions with lattice vibrations and variations in the relative slopes of the Zeeman field dependent energy levels (vertical broadening). The second, (ΔH_2), takes into consideration the random distributions of the local magnetic ion [111] directions with respect to the mean crystal [111] direction which will be referred to as the mosaic effect and a randomness in crystalline field parameters.

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The relation between (ΔH_τ) the total line width, and the two contributions just mentioned is given by

$$(\Delta H_\tau)^2=(\Delta H_1)^2+(\Delta H_2)^2 \tag{1}$$

where

$$\Delta H_1=(\Delta\nu)\left(\frac{\partial\nu}{\partial H}\right)^{-1} \tag{2}$$

and where the more important contributions to (ΔH_2) are given by

$$(\Delta H_2)^2=\left(\frac{\partial H}{\partial\theta}\right)^2(\Delta\theta)^2+\left(\frac{\partial H}{\partial D}\right)^2(\Delta D)^2 \tag{3}$$

where D is the crystalline field splitting energy.

In Eq. (2), $(\Delta\nu)$ is just the width in the frequency spectrum of the resonance absorption. At $\theta=0°$, the line width ΔH_1 due to the $E_{-1}\leftrightarrow E_1$ transition is, incidentally, not affected by the mosaic or variations in the crystal field splitting energy, and the derivatives $\partial\nu/\partial H$ take account of broadening due to the rates at which the energy levels diverge. The terms in Eq. (3) are just those due to the mosaic effect and to the random distribution of the crystalline field splitting energy. In deriving the expression for (ΔH_τ) it is assumed that the basic line shape can be given by an expression having the form

$$S(\nu,\nu_0)=S_0\exp\left\{-\left(\frac{\nu-\nu_0}{\alpha}\right)^2\right\} \tag{4}$$

where ν is the radiation source frequency, ν_0 is some resonance frequency characterized by specific values of the angle θ, the crystal field splitting energy D and the Zeeman field, and α is a line width parameter in the frequency spectrum. Equation (4) is then converted from the frequency spectrum to the Zeeman field spectrum through a straight forward substitution. The variations in θ and D are accounted for by first assuming that both the θ and D distributions are gaussian in character and by performing summations on these distributions. The final result of this, is another Gaussian distribution with the Zeeman field as the variable and with a line width parameter given by Eq. (1).

If the difference between $(\Delta H_\tau)^2$ and $(\Delta H_1)^2$ is plotted against $(\partial H/\partial\theta)^2$, a straight line should result whose intercept is zero and whose slope is just $(\Delta\theta)^2$, the square of the width of the mosaic distribution, assuming of course, that the first component to (ΔH_2) is predominant. For this particular sequence of transitions, it can be shown that the variations in the crystal field splitting energy cause no significant line broadening. The best estimate for the mosaic distribution width obtained from this data is given by $\Delta\theta=0.30$ deg. A similar result is obtained from the widths of the line due to the $E_0\leftrightarrow E_1$ transition which was followed from $\theta=0°$ to $\theta=20°$.

At $\theta=0°$ the divalent nickel ion exhibits two resonance absorptions. One occurs at $2g_\parallel$ and corresponds to the forbidden transition $E_{-1}\leftrightarrow E_1$. As stated previously, this transition is independent of both the mosaic and crystalline field distributions since the slope of the isofrequency plot is zero at this orientation and since in the absence of a Zeeman field these two levels are degenerate. The second resonance occurs at 10345 oersteds and corresponds to the permitted $E_0\leftrightarrow E_1$ transition. Although this transition too is independent of the mosaic distribution, it very definitely depends on the value of the crystalline field. The measured width of this transition is 35 oersteds and its residual width (ΔH_1) is probably just twice that of the transition at $2g_\parallel$ as a consequence of vertical broadening. Using Eqs. (1), (2), and (3) and the resonance condition for this transition given by

$$h\nu=D-g_\parallel\beta H\,, \tag{5}$$

the width ΔD of the crystalline field distribution is estimated to be $3\times10^{-3}\,\mathrm{cm}^{-1}$.

In order to verify the source of this unexpectedly large line width variation as being due to the local ion mosaic and also, to see whether this effect is exhibited by other paramagnetic impurity ions, the spectra of trivalent chromium and iron ions were studied. These two ions were singled out because they exhibit spectra with no nuclear hyperfine complications and because they occur as trace impurities in the nickel doped sapphire specimen in amounts sufficient to be observed without undue difficulty. In this way, three different ions could be studied in the same specimen. The isofrequency plots and line width variations for these two ions are given in Figs. 2 and 3. In the case of the trivalent iron ion, special care had to be taken in measuring line widths because of the doublet nature of its spectrum. At $\theta=90°$, a good line width measurement is possible; however, for the particular transition chosen, no data was taken between $\theta=90°$ and $\theta=50°$ because the spectrum exhibits unresolved doublets. Beyond $\theta=0°$, the doublets resolve; however, between $\theta=27.5°$ and $\theta=0°$ vertical broadening becomes overwhelming. As a consequence of these two effects, data for these transitions could be obtained over only a limited range of orientations. All the other iron ion transition sequences exhibit less favorable vertical broadening over a much wider region of the polar angle. The mosaic angle obtained for the trivalent iron ion is found to be $\Delta\theta=0.40$ degrees. No crystalline field splitting energy variation data was obtained because of the insensitivity to this effect of the particular sequence of transitions studied.

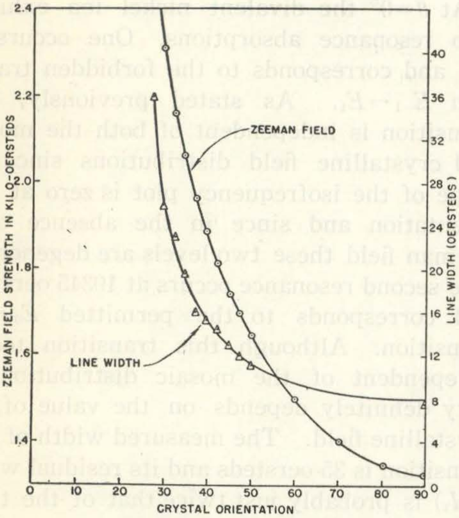

Fig. 2. Isofrequency plot and variation in line width as a function of crystal orientation for the trivalent iron ion in α-Al_2O_3.

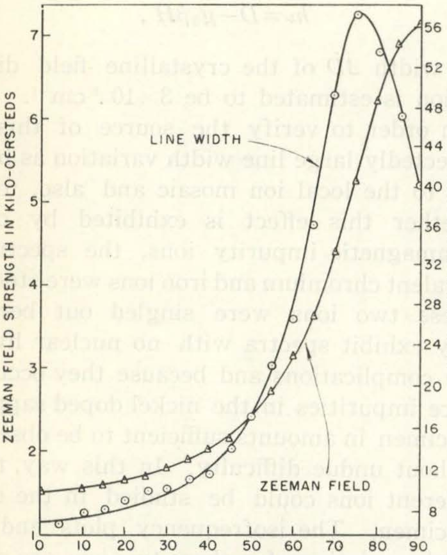

Fig. 3. Isofrequency plot and variation in line width as a function of crystal orientation for the trivalent chromium ion in α-Al_2O_3.

In the case of the trivalent chromium ion, for the $E_{-3/2}\leftrightarrow E_{-1/2}$ transition, difficulty in interpretation arises because of a large vertical broadening effect at $\theta=30°$ which is also the orientation at which $(\partial H/\partial\theta)$ experiences a maximum. This broadening coincidence is undoubtedly the cause of the unusual peaking in the line width data at $\theta=30°$. At both $\theta=0°$ or $\theta=90°$ the resonance absorptions of this ion exhibit line widths of the order of 15 oersteds and an analysis of the energy levels shows no vertical broadening in excess of twenty percent. It is therefore concluded that variations in the crystalline field splitting energy cause no significant line broadening. This is not unexpected in view of the fact that this crystalline field splitting energy is of the order of $0.2\,\mathrm{cm}^{-1}$, and a variation in this energy which is commensurate with that measured for the divalent nickel ion would probably go undetected. An analysis of the chromium ion data which ignores variations in the crystalline field splitting energy yields a mosaic angle of $\Delta\theta=0.37$ degrees.

Finally, an analysis based on x-ray diffraction data from the sample used in the paramagnetic resonance absorption study showed the mosaic angle to be 0.04 degrees. This angle, which is an order of magnitude smaller than that measured by variations in the paramagnetic resonance absorption line widths is far more in keeping with what one might expect for a nearly perfect single crystal. It thus appears, provided the line width data interpretation is not grossly in error, that whereas the α-Al_2O_3 crystal structure appears to be nearly perfect, the sites at which the impurity ions are accommodated exhibit a large and random local symmetry axis distortion. Whether this means that during the crystal growth process, the structure accepts impurities only at those sites which, for one or more reasons, are imperfect or that the impurity ion itself causes a local structure distortion, is not known. It is interesting to note however, that if the latter were the case, then an interpretation would be required which would predict essentially the same mosaic angle for ions having widely varying ionic radii and for divalent as well as trivalent ions. Work along these lines is currently in progress at this laboratory.

In conclusion, the authors would like to express their indebtedness to Mr. Alfred Attard for his x-ray diffraction analysis.

References

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DISCUSSION

W. Low: Dr. D. Shaltiel and I have measured the anisotropy in the line width of gadolinium in thorium oxide. We have analysed these data along the lines of Dr. Marshall and in the particular crystal we found a deviation of 0.17° using a Gaussian distribution.

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Spin Resonance Properties of ZnTe : Mn and of Other $A_{II}B_{VI}$ Compounds

C. KIKUCHI AND G. H. AZARBAYEJANI

Department of Nuclear Engineering, the University of Michigan
Ann Arbor, Michigan, U.S.A.

The cubic field splittings $3a$ for ZnTe:Mn and CdSe:Mn are reported. The ground state splittings in ZnTe and CdTe, whose lattice parameters are 6.10 and 6.48Å, are 88.9 and $83.1\times10^{-4}\,\mathrm{cm}^{-1}$, respectively. On the other hand, for CdSe, for which the lattice parameter is 6.05Å, the cubic field splitting is $46.3\times10^{-4}\,\mathrm{cm}^{-1}$. It is suggested that the impurity Mn^{++} ions produce local dilatations such as to be under compression in the zinc $A_{II}B_{VI}$ compounds and under tension in the corresponding cadmium compounds.

These investigations were motivated by the results of measurements of the Mn^{++} ions in the $A_{II}B_{VI}$ compounds reported earlier.[1)2)] Baker, Bleaney, and Hayes[3)] noted that the cubic field splitting $3a$ for ZnS:Mn is in contradiction to Watanabe's theory[4)], whereas the results for Mn^{++} in MgO and CaF_2 appeared to be consistent with the theoretical predictions. Subsequent measurement of $3a$ for CdTe:Mn showed that the experimental results cannot be reconciled with Watanabe's theory, or with the more refined calculations by Powell, Gabriel, and Johnson[5)]. In this paper, we report the results for ZnTe:Mn and CdSe:Mn.

The surprising result is that $3a$ for Mn^{++} ions in both ZnTe and CdTe are very nearly equal, as are the hfs coupling constants A, despite the marked difference in the lattice parameters. On the other hand, the lattice parameters for CdSe and ZnTe are very nearly equal; yet the cubic field splitting $3a$ for CdSe is almost one half of that of ZnTe. As a tentative explanation of these observed results, we propose that the impurity Mn^{++} ions produce local distortions so as to produce the nearest neighbor environment that is almost independent of the host crystal.

The experimental procedures used in the determination of the spin Hamiltonian para-