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Detection of $Al_2O_3:Fe^{2+}$ by Acoustic Paramagnetic Resonance

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We have observed acoustically a spin-resonance line that we believe is due to the ground state of Al_2O_3: Fe^{2+}. This spin system has not previously been detected by resonance techniques. The transition has a $g_{\parallel}$ of 3.40±0.04, and its variation with magnetic field direction suggests that a singlet level is also present, at an energy, when the field is parallel to the c axis, of not less than 6 cm^{-1} above the ground doublet. From the intensity of the line, it was estimated that the magneto-elastic coefficient $[\frac{1}{4}(G_{11}-G_{12})^2+G_{16}^2]^{1/2}$ has a value of not less than 15 cm^{-1} (unit strain)$^{-1}$. These results are consistent with recent calculations by Stevens and Walsh.

During acoustic paramagnetic resonance (APR) experiments[1] performed on a crystal of Al_2O_3 which had been doped nominally with 0.05% Fe^{3+}, an additional line was observed that could not be fitted into the Fe^{3+} energy level scheme. Not only was the magnetic field at which the line occurred incompatible with this ion, but also its intensity was at least an order of magnitude greater than that of the regular Fe^{3+} transitions. Our further investigations suggest that the resonance is attributable to Fe^{2+}, an ion that has not previously been observed in Al_2O_3 by either acoustic or electron paramagnetic resonance.

The experiments were carried out at 4.2°K and utilized a conventional pulse-echo system[2] operating initially at a fixed frequency of 9.37 GHz. The longitudinal acoustic waves propagated along the a-axis of the Al_2O_3, a twofold symmetry axis and therefore a pure-mode and acoustic-energy-flux axis. At this frequency, and with the magnetic field parallel to the c axis, the resonance line of interest occurred at 985±10 Oe (Fig. 1). From the manner in which its position varied with the direction of the magnetic field, the line was at first mistaken for the $\langle\frac{5}{2},-\frac{5}{2}|\leftrightarrow|\frac{5}{2},+\frac{3}{2}\rangle$ transition on the Fe^{3+} effective-spin energy scheme.[3] This is a $\Delta S_c=\pm4$ transition, however, and as such is forbidden by the usual quadrupolar selection rules for APR.[2] Furthermore, decreasing the acoustic frequency also decreased the magnetic field position of the line, in contradiction to the expected behavior of the Fe^{3+} $\Delta S_c=\pm4$ transition. From the magnetic field position of the experimental line with the field parallel to the c axis, and from its dependence on the change in frequency, we were able to infer a parallel g factor of 6.80±0.08. This value, together with the large magnitude of the resonance absorption and its asymmetric line shape, led us to the conclusion that we were observing the $\Delta S_z=\pm2$ transition of $Al_2O_3:Fe^{2+}$. The reasoning is summarized below.

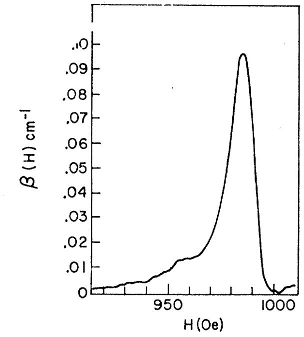

FIG. 1. $\Delta S_z=\pm2$ transition of $Al_2O_3:Fe^{2+}$ observed by APR [APR absorption coefficient $\beta(H)$ and magnetic field H] at a frequency of 9.37 GHz and with $\mathbf{H}$ parallel to the c axis. The much weaker line occurring at 955 Oe is due to Fe^{3+}.

(a) An asymmetric line shape with a sharper high-field edge is particularly characteristic of a strain-broadened transition between two states of the type $|\mathbf{S},+S_z\rangle$ and $|\mathbf{S},-S_z\rangle$. It arises as follows.[4] The effect of a symmetric distribution of static strains on a spin system is represented by a spin-lattice Hamiltonian of which the dominant term under most circumstances is the quadrupolar $\mathbf{S}\cdot\mathbf{d}\cdot\mathbf{S}$. Here $\mathbf{d}$ is related to the applied strain $\boldsymbol{\varepsilon}$ at an individual site by the tensor-relation $\mathbf{d}=\mathbf{G}\cdot\boldsymbol{\varepsilon}$, where $\mathbf{G}$ is the magneto-elastic tensor. The first-order changes in the eigenvalues of $|\mathbf{S},+S_z\rangle$ and $|\mathbf{S},-S_z\rangle$ are $\langle\mathbf{S},+S_z|\mathbf{S}\cdot\mathbf{d}\cdot\mathbf{S}|\mathbf{S},+S_z\rangle$ and $\langle\mathbf{S},-S_z|\mathbf{S}\cdot\mathbf{d}\cdot\mathbf{S}|\mathbf{S},-S_z\rangle$. These matrix elements are directly proportional to $\boldsymbol{\varepsilon}$ and are identically equal. In second order, however, shifts are obtained that are proportional to $\boldsymbol{\varepsilon}^2$ and are not equal. Hence, the total

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[1] J. Lewiner and Paul H. E. Meijer (to be published).

[2] For example, see W. I. Dobrov, Phys. Rev. **134**, A734 (1964).

[3] Details of the electron paramagnetic resonance of $Al_2O_3:Fe^{3+}$ have been given by G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. (London) **73**, 531 (1959).

[4] D. H. McMahon, Phys. Rev. **134**, A128 (1964).

inhomogeneously broadened $\langle \mathbf{S}, +S_z|\leftrightarrow|\mathbf{S}, -S_z\rangle$ transition is asymmetric with a sharp high-field edge. One of the few resonances to which the discussion can be applied is the $\langle 1, +1|\leftrightarrow|1, -1\rangle$ line of Fe^{2+}. This asymmetric transition has been observed in a number of host crystals.[5–7]

(b) If the observed line in Al_2O_3 is indeed $\Delta S_z=\pm 2$, then the g factor $g_{\parallel}$ becomes 3.40 ± 0.04. The value is close to the g factor of Fe^{2+} that has been observed in other hosts.[5–7] It has been found that the spin resonances of most other $3d$ ions in Al_2O_3 may be satisfactorily represented by the effective-spin Hamiltonian

$$\mathcal{H}=\beta[g_{\parallel}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)]+D[S_z^2-\tfrac{1}{3}S(S+1)],$$

with $g_{\parallel}$ always equal to $g_{\perp}$ to within 1%.[8] This is because the crystal electric field at the site of the paramagnetic ion, which replaces an Al^{3+} ion, is mainly cubic with a smaller trigonal field superimposed. We therefore attempted to fit the $Al_2O_3:Fe^{2+}$ transition that we observed to a Hamiltonian of this type, with the effective spin $S=1$. Unfortunately, the observed dependence of the resonance field $\mathbf{H}$ on the angle θ between the magnetic field and the crystal c axis (shown in Fig. 2) did not allow an unambiguous determination of the parameters $g_{\perp}$ and D. A perturbation treatment of the Hamiltonian yielded $(D\gg g\beta H)$

$$h\nu=2g_{\parallel}\beta H\cos\theta\,\{1+\tfrac{1}{8}\tan^2\theta.[(g_{\perp}/g_{\parallel})^2\sin^2\theta-4\cos^2\theta]\times(g_{\parallel}\beta H/D)^2\}$$

to second order in $g\beta H/D$, while the experimental curve fitted

$$h\nu=2g_{\parallel}\beta H\cos\theta.$$

With the assumption that $g_{\parallel}=g_{\perp}$, a lower limit of 6 cm^{-1} for $|D|$ could be inferred from the observational error. On the basis of this figure, and the additional observation that the APR absorption increased on lowering the temperature, we concluded that the doublet states $|1, +1\rangle$ lie lower in energy than the singlet $|1, 0\rangle$, and therefore that the sign of D is negative.

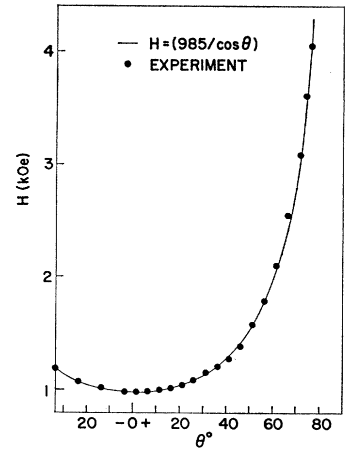

FIG. 2. Dependence of the magnetic field magnitude H at which the $\Delta S_z=\pm 2$ transition of $Al_2O_3:Fe^{2+}$ occurs, on the angle θ between the magnetic field direction and the crystal c axis.

It is now clear why $Al_2O_3:Fe^{2+}$ has never been observed by electron-spin resonance. The only transition that occurs in low magnetic fields is the $\Delta S_z=\pm 2$, which is forbidden for electromagnetic radiation. Even if a field of (at least) 40 kOe, were used in an attempt to reach the lower $\Delta S_z=\pm 1$ transition, $\langle 1, 0|\leftrightarrow|1, +1\rangle$, both these states would be depopulated by a factor of $e^{-2g\beta H/kT}$—that is, by approximately 10^{-2} at helium temperatures.

(c) The Fe^{2+} ion in a cubic crystal field has an orbitally degenerate ground state which is very strongly coupled to lattice vibrations.[7,9] If Fe^{2+} in Al_2O_3 does indeed take up the predominantly cubic Al^{3+} site, then it might be expected to have a correspondingly large spin-phonon interaction. For this site, the quadrupolar magnetoelastic tensor has the form

$$\mathbf{G}=\begin{bmatrix} G_{11} & G_{12} & -\frac{1}{2}G_{33} & G_{14} & G_{15} & G_{16} \\ G_{12} & G_{11} & -\frac{1}{2}G_{33} & -G_{14} & -G_{15} & -G_{16} \\ -(G_{11}+G_{12}) & -(G_{11}+G_{12}) & G_{33} & 0 & 0 & 0 \\ G_{41} & -G_{41} & 0 & G_{44} & G_{45} & G_{46} \\ -G_{46} & G_{46} & 0 & -G_{45} & G_{44} & G_{41} \\ -G_{16} & G_{16} & 0 & -G_{15} & G_{14} & \frac{1}{2}(G_{11}-G_{12}) \end{bmatrix}.$$

It should be noted that there are two magnetically nonequivalent Al^{3+} sites. The magneto-elastic tensors for the two sites differ in sign in some of the off-diagonal elements.[10] With the magnetic field parallel to the c axis and acoustic strain along the a axis, the $\Delta S_z=\pm 2$ matrix element of the spin-lattice Hamiltonian is proportional to $\frac{1}{2}(G_{11}-G_{12})\pm iG_{16}$. Because the concentration of the Fe^{2+} ions was unknown, we were not able to make a quantitative evaluation of $[\frac{1}{4}(G_{11}-G_{12})^2+G_{16}{}^2]^{1/2}$. However, we could again set a lower limit by assuming that the total iron concentration of the

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[5] W. Low and M. Weger, Phys. Rev. **118**, 1130 (1960).

[6] A. J. Shuskus, J. Chem. Phys. **40**, 1602 (1964).

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[8] For example, see S. Geschwind and J. P. Remeika, J. Appl. Phys. Supp. **33**, 370 (1962); S. A. Marshall, T. T. Kikuchi, and A. R. Reinberg, Phys. Rev. **125**, 453 (1962).

[9] N. S. Shiren, Phys. Rev. **128**, 2103 (1962).

[10] T. G. Phillips, R. L. Townsend, Jr., and R. L. White, Phys. Rev. **162**, 382 (1967).

crystal was doubly ionized, with no Fe^{3+} present. This is probably a gross overestimate of the Fe^{2+} concentration, since Fe^{3+} is the charge-allowed state and its APR is observed. It is known, though, that reduction to Fe^{2+} may occur in Al_2O_3 if the material is heated in vacuum to 1200°C,[11] and possibly our crystal was partially reduced during its growth or annealing. With this assumption we estimate that $[\frac{1}{4}(G_{11}-G_{12})^2+G_{16}^2]^{1/2}$ is not less than 15 cm^{-1} (unit strain)$^{-1}$.

Note added in manuscript. Since preparing the present article, we have seen a recent paper by Stevens and Walsh[12] in which the nature of the $Al_2O_3:Fe^{2+}$ ground state is suggested, and the magnitude of its spin-lattice interaction calculated. Our results are not inconsistent with their conclusions that the ground state should be a non-Kramers doublet separated by ~ 100 cm^{-1} from the lowest excited states, and that the Fe^{2+} ion is more weakly coupled to the lattice in Al_2O_3 than in a purely cubic environment such as MgO.

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Jahn-Teller Effects in the Far-Infrared, EPR, and Mössbauer Spectra of MgO:Fe^{2+}

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Measurements by Wong of the far-infrared absorption spectrum of the Fe^{2+} ion at undistorted cubic sites in MgO have revealed that the first excited spin-orbit level (evidently comprising both the Γ_{3g} and Γ_{4g} states) lies 105 cm^{-1} above the Γ_{5g} ground state, in contrast to the value ~ 200 cm^{-1} predicted by crystal-field theory. A calculation has been made to determine if this reduced spin-orbit splitting can reasonably be attributed to a dynamic Jahn-Teller effect without leading to inconsistencies with other EPR and Mössbauer data for MgO:Fe^{2+}. It is concluded that this reduction is indeed predominantly the result of the Jahn-Teller coupling, that this reduction is consistent with the strength of Jahn-Teller coupling indicated by strain data for the Γ_{5g} level, and that significant Jahn-Teller corrections occur also in other parameters which characterize the EPR and Mössbauer spectra, such as the g factor, hyperfine field, and nuclear quadrupole coupling coefficients of the Γ_{5g} level. These Jahn-Teller corrections are calculated using the strength of the Jahn-Teller coupling to both E_g and T_{2g} vibrational modes as parameters, which are adjusted to give the observed spin-orbit reduction, and the resulting values are compared with estimates of corrections resulting from covalency. The calculations are carried out by treating the Jahn-Teller interaction by perturbation methods, and the calculation is formulated both for coupling with discrete vibrational modes and also for coupling with the continuum of lattice phonons.

I. INTRODUCTION

THE low-energy electronic states of the Fe^{2+} ion in cubic symmetry and octahedral coordination, as given by crystal-field theory,[1] result from the splitting of the $^5T_{2g}$ term by the spin-orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$. The first excited states, a doublet Γ_{3g} and a triplet Γ_{4g}, are predicted to lie at an energy approximately $-2\lambda \simeq 200$ cm^{-1} above the ground-state triplet Γ_{5g} (the predicted separation of Γ_{3g} and Γ_{4g} being a few cm^{-1}). Wong[2] has recently measured the far-infrared absorption spectrum of Fe^{2+} in MgO, and he has found that the only absorption line in the range 10-220 cm^{-1} which can be attributed to isolated Fe^{2+} ions is a single line at 105 cm^{-1} (with a width ~ 9 cm^{-1} at 20.3°K). If this line is attributed to one or both of the magnetic-dipole-allowed transitions $\Gamma_{5g}\rightarrow\Gamma_{3g}$ and $\Gamma_{5g}\rightarrow\Gamma_{4g}$, the excitation energy of these states is thus found to be only half of that predicted by crystal-field theory. Although one expects that effects of covalency[3] may reduce λ in the crystal by perhaps some 20% compared with the free-ion value $\lambda\simeq -100$ cm^{-1}, a 50% reduction is too large to be reasonably attributed to this cause. However, Wong's result that Fe^{2+} in MgO has an excited level very much lower in energy than expected on the basis

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