ENDOR MEASUREMENTS IN $^{57}Fe^{3+}$ IN CALCIUM OXIDE*

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The hyperfine constant and the nuclear magnetic moment of $^{57}Fe^{3+}$ in CaO has been measured by the ENDOR technique.

The ENDOR (electron-nuclear double resonance) technique [1,2] has been used in this work to measure the hyperfine coupling constant and the nuclear magnetic moment of the isotope 57 of Fe^{3+} in cubic positions of the CaO lattice. We used an undoped sample provided by Semi-Elements, Inc. (USA), where the iron is a natural impurity. At 1.2°K, the EPR spectra has a very narrow $M_S = -\frac{1}{2} \rightarrow \frac{1}{2}$ fine structure transition (0.1 gauss) where the hyperfine structure of the 57 isotope ($I = \frac{1}{2}$, natural abundance 2%) is resolved. We observed the ENDOR lines that correspond to this fine structure transition with linewidths of only 5 kHz. The data were fitted with the spin Hamiltonian used by Locher and Geschwind [3] for $^{57}Fe^{3+}$ where high order hyperfine terms are considered.

The value we obtained for the nuclear magnetic moment, $\mu_I = (0.090\,36 \pm 0.000\,15)$ nm is in very good agreement with the value of the nuclear magnetic moment of ^{57}Fe measured by Locher and Geschwind [3] in MgO. It was not possible from our data to separate the values of the hyperfine coupling constants A and U. Our value of $A' = A - \frac{1}{5}U[3S(S+1) - 1] = (-29.811 \pm \pm 0.002)$ MHz is smaller than previous data [3,4] obtained by the less accurate EPR techniques. In addition, we looked for shifts of the ENDOR lines when a uniaxial stress was applied to the sample. No shifts were observed within an upper limit of $\Delta A/A \leqslant 0.6 \times 10^{-7}$ for a stress of 1 kg/cm^2 along the [110] direction. It is of interest to note that this upper limit for $\Delta A/A$ of $^{57}Fe^{3+}$:CaO under uniaxial stress is of the same order of magnitude as the value for Mn^{2+}:MgO under the same amount of hydrostatic stress [5].

Our value of A' for $^{57}Fe^{3+}$:CaO should be compared with the value $A' = (-30.1474 \pm 0.0005)$ MHz for Fe^{3+}:MgO [3]. Because the U term (S^3I contribution to the hyperfine coupling) is small, the change of A' between Fe^{3+}:CaO and Fe^{3+}:MgO should be attributed to a chan[illegible] A and not to U [6].

The large variations of A for Fe^{3+} (and Mn^{2+}) in different structures of ligands has been explained by Henning [7]. However, to explain the smaller changes which appear when the dimensions of the octahedron of oxygen ligands changes (the lattice parameter varies from 2.4 Å for CaO to 2.1 Å for MgO), more detailed calculations are needed. Two kinds of contributions could be important: the first one produces a change of A because of the different covalent and overlap contributions when the distance of the ligands changes [7,8]. The second appears when the lattice vibrations are considered; they produce a decrease of A proportional to the mean value of the square of the vibration amplitude [9]. At low temperatures the zero point phonons contribute mainly to this effect [10]. No calculations of these contributions exist for Fe^{3+} and estimations for the isoelectronic Mn^{2+} in oxide lattices are not conclusive about the predominant mechanism [8].

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More data on the change of A with hydrostatic stress should be helpful in further understanding the problem.

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References

1. G. Feher, Phys. Rev. 103 (1956) 834.
2. S. Geschwind, in Hyperfine interactions (Academic Press, Inc., New York, 1967), p. 225.
3. P. R. Locher and S. Geschwind, Phys. Rev. 139 (1965) A991.
4. W. Low and R. S. Rubins, Proc. First Intern. Conf. in Paramagnetic resonance, Jerusalem (Academic Press, Inc., New York, 1962), p. 79.
5. W. M. Walsh Jr., Phys. Rev. 122 (1961) 762.
6. The difference could be accounted for only by assuming U varies by a factor of ten which seems unreasonable within the mechanisms proposed by Locher and Geschwind [3].
7. J. C. M. Henning, Phys. Letters 24A (1967) 40.
8. E. Simanek and Z. Sroubek, Covalent effects in E. P. R. spectra-hyperfine interactions, to be published.
9. E. Simanek and R. Orbach, Phys. Rev. 145 (1966) 191.
10. R. Orbach and E. Simanek, Phys. Rev. 156 (1967) 383.

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