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EPR OF Fe^{3+} IN MgO TETRAHEDRAL SITES*

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ABSTRACT

The EPR spectrum of MgO containing iron as an impurity (about .01%) exihbited lines that have been assigned to Fe^{3+} in tetrahedral sites of the lattice. These lines were observed after 24 hrs annealing at 1100°C and quenching to room temperature. The spin Hamiltonian parameters obtained were $g = 1.999 \pm .001$ and $a = (193 \pm 1) \times 10^{-4} cm^{-1}$.

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The EPR spectrum of Fe^{3+} in tetrahedral sites as a substitutional impurity has been studied in a variety of II-IV hosts (1-5). The Fe^{3+} spectrum in interstitial tetrahedral sites has been reported in AgCl (6).

In MgO this ion has been extensively studied by EPR in octahedral symmetry (7-11) and, in one EPR work, the presence of Fe^{3+} in tetrahedral sites has been postulated but no assignment of lines has been made or values of g a reported (12):

In this work we have studied the EPR spectrum of MgO, at $77^{O}K$, containing small amouts of iron (about .01%)and found, besides the well known lines assigned to Fe^{3+} in the MgO octahedral sites, substitutional to Mg^{2+}, lines that can be assigned to Fe^{3+} in tetrahedral sites.

Samples supplied by Materials Research containing, besides iron, chromium and manganese impurities, as seen by EPR, were submitted to annealing at $1100^{O}C$ for 24 hours and quenched to room temperature. Examination by EPR in X Band revealed lines whose angular variation in the (100) plane and, a and g values obtained are coherent with the tetrahedral sites assignment. Fig. 1 shows the observed spectrum, in second derivative, where one can see, besides the regular fine structure octahedral lines, labelled OC, two lines, labelled TE, which we assigned to tetrahedral Fe^{3+}. The angular variation (Fig. 2) of these lines can be followed quite easely up to 17^{O} from the cubic axes. Beyond these points they are masked by the Mn^{2+} spectrum. To these lines we have assigned the fine structure transitions $\pm 3/2 \rightarrow \pm 1/2$. The other fine structure lines could not be observed and assigned due to the spectra of the other impurities which appear superimposed to the region where the angular variation could be informative.

The values $a=(193\pm 1)\times 10^{-4} cm^{-1}$ and $g = 1.999\pm.001$ for the parameters

of the adopted spin Hamiltinian

$$H = g\beta\vec{H}.\vec{S} + (a/6)(S_x^4 + S_y^4 + S_z^4) - (1/5)\, S\,(S-1)(3S^2+3S-1))$$

where retrieved by a least square fit of the data to the theoretically predicted angular variation of these transitions (13). Using results of the well measured octahedral iron (III), which is obtained simultaneously with the tetrahedral spectrum, we could check on the quality on ours results. In this respect it is to be noted that the low field side of the spectrum gives poor results for the octahedral iron angular variation whereas the high field branch gives good agreement with the accepted values of the parameters. So we picked, as the best values for a and g of the tetrahedral sites, those obtained from the high field branch. This condition is attributed to the fact that the formulas for the fine structure angular variation used are derived by perturbation methods (13) assuming $a \ll g\beta H$, condition that, for the low field lines, does not lead to consistent values for a and g.

The ratio of a-octahedral to a - tetrahedral, supposing $a = \alpha V^2$ (14) is 1.16, which, given a value for $a = 212 \times 10^{-4}$ cm^{-1} at 90^{o}K as measured by Griffiths and Orton (15) and confirmed by our measurements, leads to a value of 183×10^{-4} cm^{-1} for the tetrahedral a, smaller than our value by a little more than five per cent. Considering that the presence of the Fe^{3+} in the previously empty tetrahedral site pulls in the doubly negative oxigen ions, one should indeed expect a larger value than that estimated from purely geometrical considerations, as indeed is the case.

Our g-value, also, shows a deviation from what has been measured in other experiments with tetrahedral sites, which provided positive g-shifts

while we obtain negative shifts. This could indicate a delocalization of the Fe^{3+} electrons into the surrounding oxigens (16) with the consequent decrease of spin orbit coupling and an increase of the relaxation time. The narrover tetrahedral lines assigned seem to confirm this.

More detailed measurements are presently under way and will be reported in a later paper. We thank prof. A.P. Guimarães for the computer program for the least square fit. This work has been supported by the Conselho Nacional de Pesquisas of Brazil.

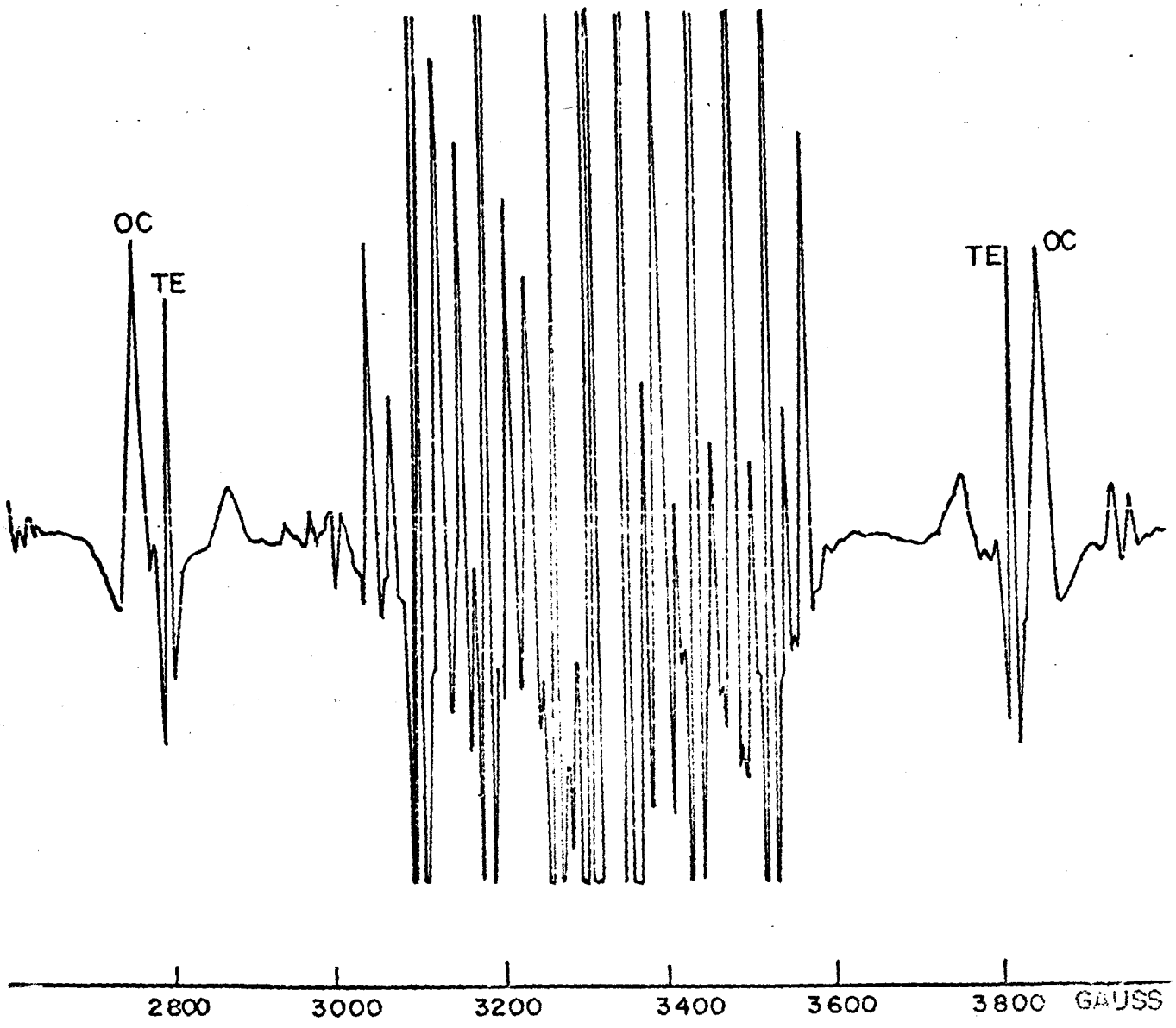

Fig. 1 - Spectrum of Fe^{3+} in MgO octahedral and tetrahedral sites. Only the $\pm 3/2 \rightarrow \pm 1/2$ transitions are labelled. The central part of the spectrum consists of Mn^{2+} and Cr^{3+} lines, besides the central lines of the iron spectrum.

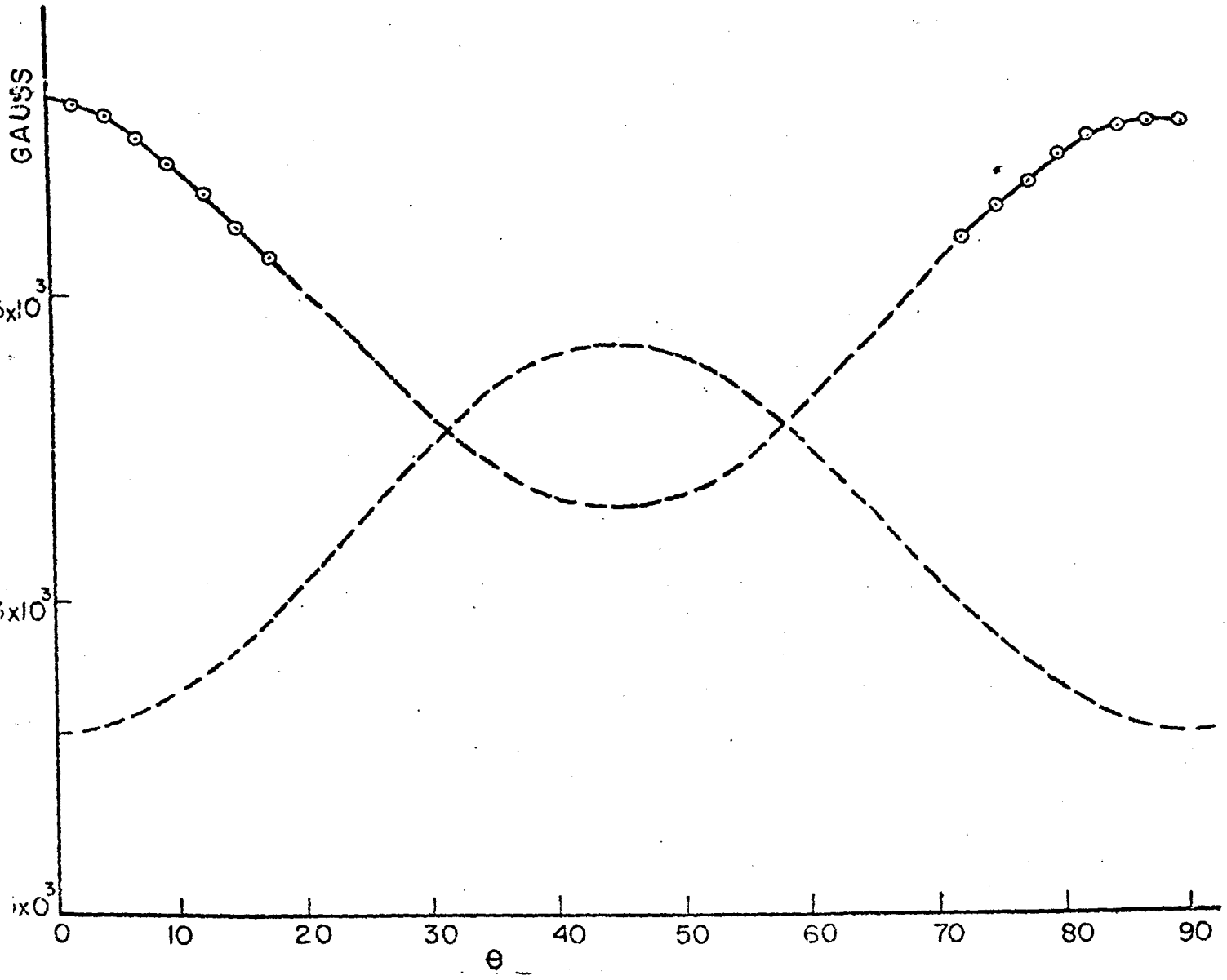

Fig. 2 - Angular variation of the tetrahedral lines in the (100) plane, between the two cubic axes. The circles indicate the experimental points used in the least square fit.

REFERENCES

1. W.H. Walsh, Jr. and L.W. Rupp, Phys. Rev. 126, 952 (1962).
2. J. Lambe, J. Backer and C. Kikuchi, Phys. Rev. Lett., 3, 270 (1959).
3. K. Morigaki and T. Hoshima, J. Phys. Soc. Japan, 21, 842 (1966).
4. H.H. Woodbury and G.W. Ludwig, Bull.Am.Phys.Soc., 6, 118 (1961).
5. T. Hoshima, J. Phys.Soc. Japan, 22, 1049 (1967).
6. W. Hayes, J.R. Pibbrow and C.M. Slifkin, J. Phys. Chem. Sol., 25, 1417 (1964).
7. W. Low, Proc. Phys. Soc. (London), B69, 1169 (1956).
8. E.R. Feher, Phys. Rev., 136, A145 (1964).
9. J.H. Lawford, J.Ch.Phys., 42, 2617 (1965).
10. P.R. Locher and S. Geschwind, Phys. Rev., 139, 1991 (1965).
11. A.M. Stoneham, Sol. Stat. Commun., 10, 1005 (1972).
12. S.L.Blank and J.A. Pask, J. Am. Geram. Soc., 52, 669 (1969).
13. R. de L. Kronig and C.J. Bouwkamp, Physica, 6, 290 (1939).
14. H. Watanabe, Prog. Teor. Phys., 18, 405 (1957).
15. J.H.E. Griffiths and J.W. Orton, Proc.Phys.Soc., 73, 948 (1959).
16. H. Watanabe and H. Kishishita, Prog.Theor.Phys., 46, 1 (1970).

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