ANGULAR VARIATION OF THE EPR LINEWIDTH OF Ni^{2+} IN CaO

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We measured the angular variation of the EPR linewidth of Ni^{2+} in CaO. The data is used to estimate the distribution of internal stresses in the sample.

The study of the linewidths and lineshapes of the electron paramagnetic resonance (EPR) lines of impurities in crystals is a powerful method for studying qualitatively and quantitatively the distribution of internal stresses in the host lattice [1-3]. Because of the simplicity of its EPR spectra, Ni^{2+} is one of the best ions for this purpose. In cubic crystals the spectra consist mainly of one line ($\Delta M_S = 1$) which can be described by the Hamiltonian

$$\mathcal{H}_c = g\beta \boldsymbol{H}\cdot S \qquad (1)$$

where $g = 2.32$ for Ni^{2+}: CaO [4] is the gyromagnetic factor, β the Bohr magneton, $\boldsymbol{H}$ the external magnetic field and the fictitious spin $S = 1$.

When the cubic symmetry around the ions is removed an additional term [2]

$$\mathcal{H}_{nc} = \sum_{ij} D_{ij} S_i S_j \qquad (2)$$

is added to the Hamiltonian of eq. (1) and the EPR line splits in two. Small distortions of the cubic symmetry could appear due to internal random stresses in the sample: crystal impurities, dislocations, etc. Because of the random character of these non cubic distortions, each paramagnetic ion will have a slightly different value of $\mathcal{H}_{nc}$ of eq. (2) and the EPR transition will be inhomogeneously broadened.

We have measured the angular dependence of the EPR linewidths and lineshapes of Ni^{2+} in CaO at 1.4 K and 9.3 GHz in the (110) plane; the sample contained about 0.1% of Ni^{2+} and was supplied by Semi Elements Inc. U.S.A. The EPR lineshape was Lorentzian and the observed linewidths $\Delta H_{1/2}$ measured between points of half intensity of the line are shown in fig. (1). A good fit of the experimental data is obtained with the function

$$\Delta H_{1/2} = [a(1-3F) + bF]^{1/2} \qquad (3)$$

represented by a solid line in fig. (1), where $F = \sin^2\theta - \frac{3}{4}\sin^4\theta$; a least square analysis gives $a = 10.3 \times 10^4$ gauss^2, and $b = 8.6 \times 10^4$ gauss^2; θ is the angle between the magnetic field and the [001] axis. Eq. (3) was obtained by Feher [2] assuming that the broadening is due to a Gaussian distribution of internal stresses. In our case, where a Lorentzian line-shape is observed, the same formulation remains valid when the second moment of the line δH^2 is used. The ratio $K\cdot\delta H^2 = \Delta H^2_{1/2}$, where $K = 8/7$ was obtained using the experimental errors as a criterium for the cut-off magnetic field at the wings of the line and the formulas given by Poole [5] for the cutt-off Lorentzian line.

If $\epsilon_{001} = 2\epsilon_{33} - \epsilon_{11} - \epsilon_{22}$, and $\epsilon_{111} =$

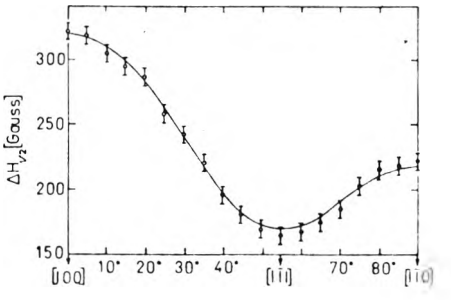

Fig. 1. Angular dependence of the EPR linewidth of Ni^{2+} in CaO measured at 1.4 K and 9.3 GHz in the (110) plane. The solid line is the dependence predicted by eq. (3) for $a = 10.3 \times 10^4$ gauss^2 and $b = 8.6 \times 10^4$ gauss^2.

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$\epsilon_{12} + \epsilon_{13} + \epsilon_{23}$, it is found from eq. (2)

$$\Delta H = \left\{\frac{8}{7}\left[\frac{9}{16} G_{11}^2 \langle \epsilon_{001}^2 \rangle (1-3F) + 3 G_{44}^2 \langle \epsilon_{111}^2 \rangle F\right]\right\} \quad (4)$$

where the values for the spin-lattice coefficients $G_{11} = (110 \pm 5)\,\mathrm{cm}^{-1}$ and $G_{44} = (42 \pm 5)\,\mathrm{cm}^{-1}$ have been reported [6] for Ni^{2+} in CaO under the approximation that the elastic constants of the crystal are not changed at the position of the impurity. $\langle \epsilon_{001}^2 \rangle$ and $\langle \epsilon_{111}^2 \rangle$ should be understood as mean values taken over the distribution of strains.

Comparing eqs. (3) and (4) we found

$$(\langle \epsilon_{001}^2 \rangle)_{\mathrm{CaO}}^{1/2} = (4.5 \pm 0.3) \times 10^{-4} ,$$

$$(\langle \epsilon_{111}^2 \rangle)_{\mathrm{CaO}}^{1/2} = (4.0 \pm 0.5) \times 10^{-4} .$$

Smaller values of $(\langle \epsilon_{001}^2 \rangle)^{1/2}$ and $(\langle \epsilon_{111}^2 \rangle)^{1/2}$ are found for Ni^{2+} in MgO using the values of the EPR linewidths of Ni^{2+} in MgO given by Lewis and Stoneham [7] for the [001] and [111] directions, together with eq. (4):

$$(\langle \epsilon_{001}^2 \rangle)_{\mathrm{MgO}}^{1/2} = 1.01 \times 10^{-4}$$

$$(\langle \epsilon_{111}^2 \rangle)_{\mathrm{MgO}}^{1/2} = 0.66 \times 10^{-4} .$$

The origin of the differences in the strain distributions found in both lattices could be discussed in terms of the theory given by Stoneham [3]; the Lorentzian lineshape observed for Ni^{2+} in CaO suggest that the broadening is due to point defects or dislocations. Besides Ni^{2+}, Mn and Fe impurities were identified in our CaO sample and are probably the origin of the inhomogeneous broadening. A precise analysis of the relative influence of the point and line defects could be obtained only with a complete knowledge of the history and composition of the sample.

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