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Calculations of Line Shape for E.S.R. Absorption in Polycrystalline Substances

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The absorption for a polycrystalline substance is given by $\mathcal{J} = \int_0^\pi \mathbf{I} \sin \vartheta \, d\vartheta$, where \mathbf{I} is the line shape for a single crystal of uniaxial symmetry. We have performed calculations assuming the single crystal line shape to be (a) the Lorentzian $\mathbf{I} = \frac{2 \pi A k}{1 + \pi^2 k^2 (x - c)^2}$ where A is proportional to the number of spins, $k = 2/\pi \Delta x$ and Δx is the line width, and (b) the Gaussian $\mathbf{I} = 2\pi^{3/2} A k \exp. [- (x - c)^2 \pi^2 k^2]$ where A is proportional to the number of spins, $k = \frac{2 (\ln 2)^{1/2}}{\pi \Delta x}$, and Δx is the line width. (The factor $\pi^{1/2}$ is introduced to ensure that the total absorption is the same for (a) and (b).)

If the absorption curve is obtained experimentally by sweeping the frequency ν , $x = \frac{h\nu}{\beta H}$, and $c = g$. If the absorption is obtained by sweeping the magnetic field H , $x = \frac{\beta H}{h\nu}$, and $c = \frac{1}{g}$. Taking a variation of g with θ of $g^2 = g_\perp^2 + (g_\parallel^2 - g_\perp^2) \cos^2 \theta$, and providing that $|g_\parallel - g_\perp|$ is small, we may take $c = c_\perp + (c_\parallel - c_\perp) \cos^2 \theta$.

If the line width and A is assumed constant, \mathcal{J} can be found exactly for the Lorentzian, using the expression for c above [1]; for the Gaussian, approximate numerical methods have to be employed. We have evaluated \mathcal{J} for the Gaussian using a 16 point Gaussian quadrature. The results thus obtained were checked with a 100 point Simpson rule. Figure 1 shows a comparison of typical curves calculated for both line shapes. If $|g_\parallel - g_\perp|$ is not small, both cases must be evaluated numerically. Also when there is considerable anisotropy allowance must be made for the change in transition probability with θ , i.e. in A [2].

We have been able to fit one of these theoretical curves to a spectrum recorded experimentally from U. V. irradiated deuterium peroxide. This fit is shown in figures 2 and 3.

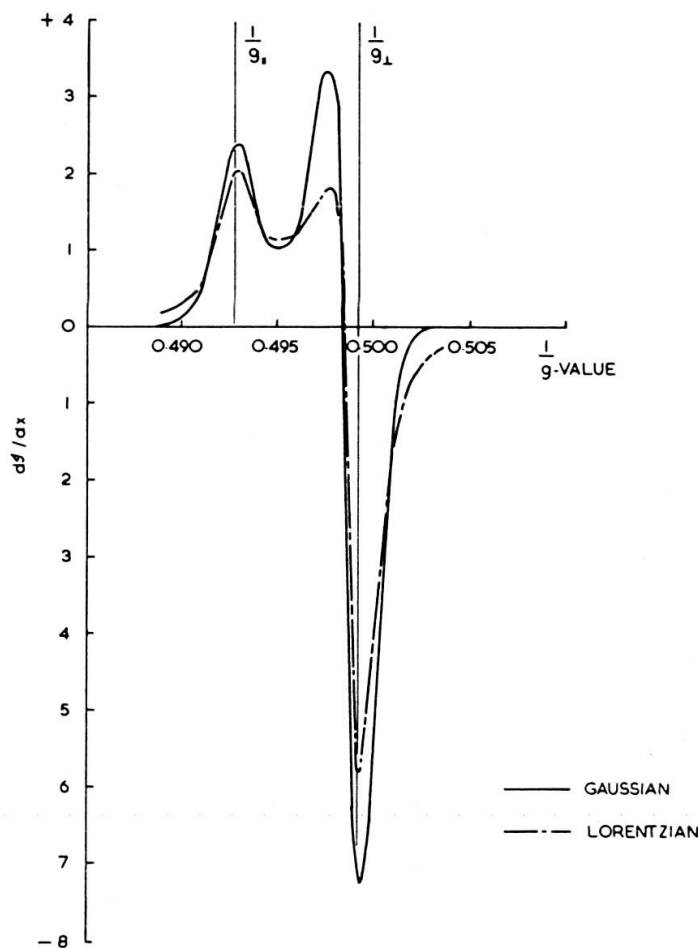


Fig. 1.

First differential of absorption for a polycrystalline substance using $g_{\parallel} = 2.0295$, $g_{\perp} = 2.0034$ and K (for Lorentzian) = 289, calculated for both Lorentzian and Gaussian line shapes.

It is possible to accommodate within these calculations variable line width. If $\Delta x = \Delta x_{\perp} + (\Delta x_{\parallel} - \Delta x_{\perp}) \cos^2 \theta$ for example, it is still possible to evaluate the Lorentzian exactly and the Gaussian numerically. There is, however, a dearth of information of the variation of line width with θ .

¹ SEARL, J.W, R. C. SMITH, S. J. WYARD, 1959, *Proc. Phys. Soc.*, 74, 491.

² BLEANEY, B., 1960, *Proc. Phys. Soc.*, 75, 621.

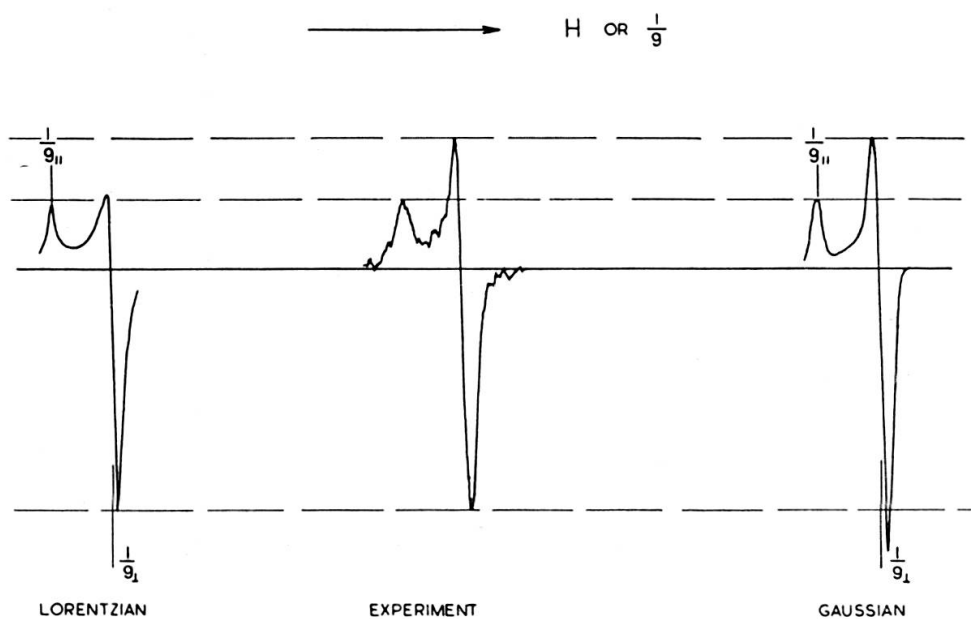


Fig. 2.

Comparison of an experimental E.S.R. first differential recording with curves calculated by g -value anisotropy theory. Experimental curve obtained from 80% $D_2 O_2$ 3100Å U.V. irradiated at 90° K, subsequently warmed for 5 minutes at 133.5° K.

Calculated curves use $g_{||} = 2.039$, $g_{\perp} = 2.006$, line width (in $\frac{1}{g}$) = 0.00168.

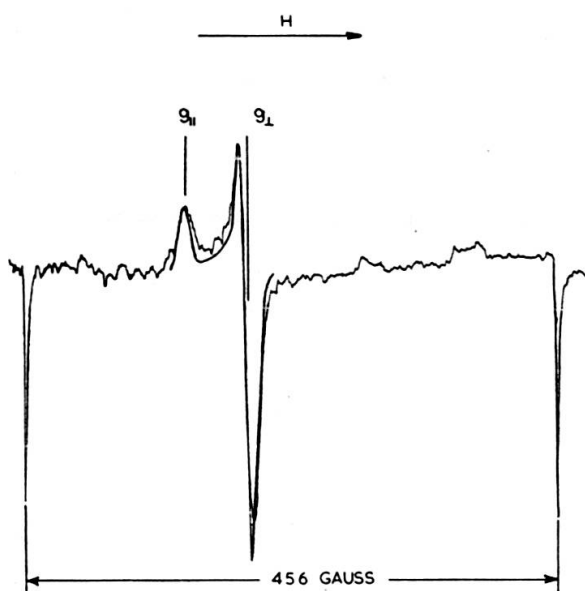


Fig. 3.

From figure 2, fit of Gaussian calculation to experimental curve.