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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 $\mathcal{J} = \int_0^{\frac{\pi}{2}} I \sin \vartheta \, d\theta \, \vartheta$, where 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 $I = \frac{2 \pi A k}{1 + \pi^2 k^2 (x - c)^2}$ where A is proportional to the number of spins, $k = 2/\pi \Delta x$ and Δx is the line width, and *(b)* the Gaussian $I = 2\pi^{3/2} Ak \exp. [- (x - c)^2 \pi^2 k^2]$ 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 $g^2 = g_\perp{}^2 + (g_{/\!/}{}^2 - g_\perp{}^2) \cos^2 \theta$, and providing that $| g_{/\!/} - g_\perp |$ is small, we may take $c = c_\perp + (c_{/\!/} - c_\perp) \cos^2 \theta$.

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 $| g_{/\!/} - g_\perp |$ 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.

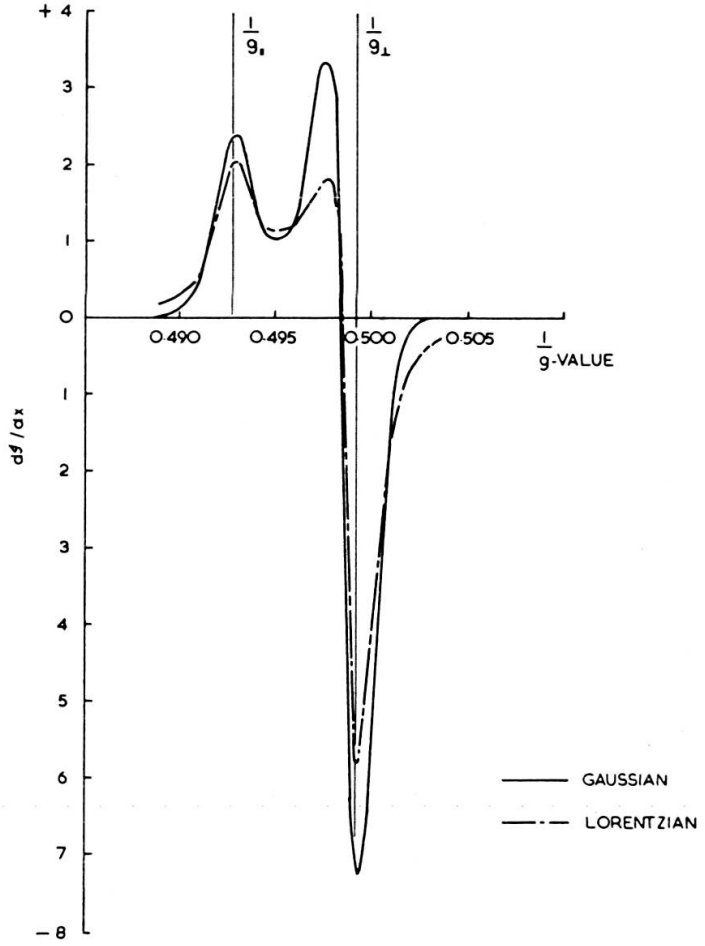

Fig. 1.

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 $\Delta x = \Delta x_{\perp} + (\Delta x_{/\!/} - \Delta x_{\perp}) \cos\theta^2$ 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.

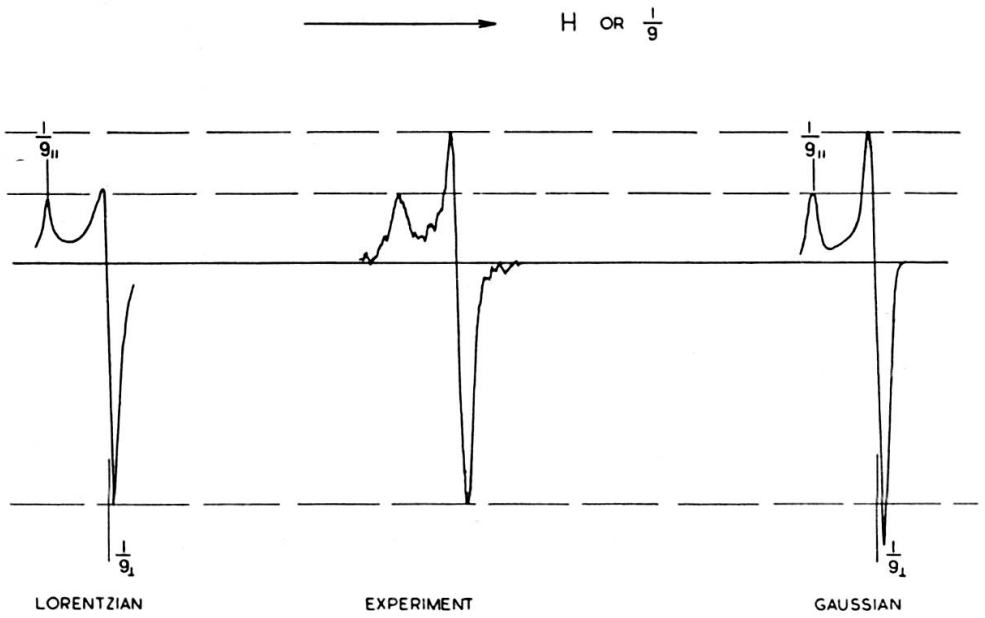

Fig. 2.

Comparison of an experimental E.S.R. first differential recording with curves calculated by g-value anisotropy theory. Experimental curve obtained from 80% D_2O_2 3100Å U.V. irradiated at 90° K, subsequently warmed for 5 minutes at 133.5° K.

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

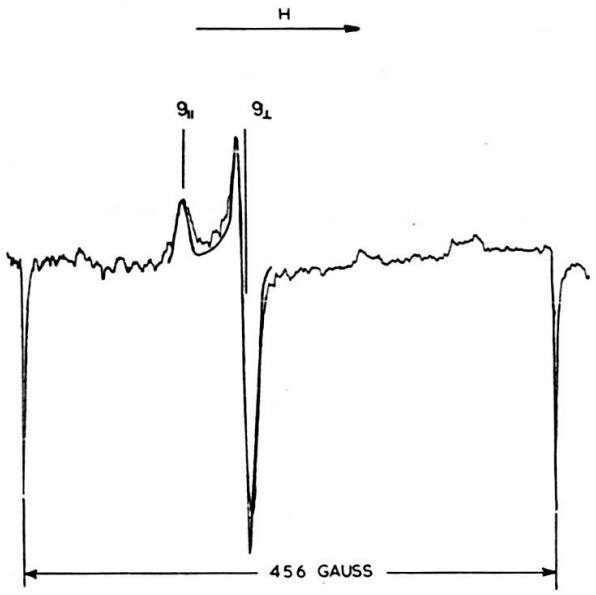

Fig. 3.

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