

Paramagnetic Resonance Line Shapes and Magnetic Parameters of Polycrystalline Substances

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A closed-form expression for the paramagnetic resonance line shape of a polycrystalline substance is derived on the assumption of axial symmetry, a crystallite line shape that is Lorentzian, random orientation of the crystallites, and a spin Hamiltonian that consists of Zeeman, dipolar and exchange terms only. Some representative line shapes are evaluated from this expression and are compared with previous, approximate calculations. An iterative procedure for the derivation of magnetic parameters from polycrystalline spectra is described. As an example of this procedure the magnetic parameters of polycrystalline potassium perchromate are derived.

INTRODUCTION

PARAMAGNETIC resonance absorption line shapes of polycrystalline substances have been studied by many authors¹⁻¹⁰ in an attempt to understand the unusual shapes and to determine the magnetic parameters in the absence of single crystals. Calculations of the line shapes have involved either the drastic approximation of a delta function for the line shape of each crystallite or the assumption of small anisotropy of the g tensor (Table I). Derivation of the magnetic parameters

TABLE I. Summary of line-shape calculations.

g tensor	Crystallite line shape	Reference	Comments
axial	delta	1	
axial	delta	2,6,7	axial hfs included.
anisotropic	delta	3	
isotropic	delta and Gaussian	4	anisotropic hfs included.
isotropic	delta	5	anisotropic hfs included.
isotropic	delta	8	zero field ($S=3/2$) included.
axial	Lorentzian	9	expression valid only for small anisotropy.
anisotropic	Lorentzian	10	assumes small anisotropy; closed-form expression given for axial symmetry only; expression identical with 9.
axial	Lorentzian	present work	

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¹ B. Bleaney, Proc. Phys. Soc. (London) **A63**, 407 (1950); Phil. Mag. **42**, 441 (1951); Proc. Phys. Soc. (London) **A75**, 621 (1960).

² R. H. Sands, Phys. Rev. **99**, 1222 (1955).

³ F. K. Kneubühl, J. Chem. Phys. **33**, 1074 (1960).

⁴ S. M. Blinder, J. Chem. Phys. **33**, 748 (1960).

⁵ H. Sternlicht, J. Chem. Phys. **33**, 1128 (1960).

⁶ R. Neiman and D. Kivelson, J. Chem. Phys. **35**, 156 (1961).

⁷ H. R. Gersmann and J. D. Swalen, J. Chem. Phys. **36**, 3221 (1962).

⁸ L. S. Singer, J. Chem. Phys. **23**, 379 (1955).

⁹ J. W. Searl, R. C. Smith, and S. J. Wyard, Proc. Phys. Soc. (London) **A74**, 491 (1959).

¹⁰ A. K. Chirkhov and A. A. Kokin, J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 1381 (1960) [translation: Soviet Phys.—JETP, **12**, 964 (1961)].

from polycrystalline spectra has involved simply the comparison of these approximate line shapes with the experimental curves.

The Lorentzian line shape for a crystallite has been justified theoretically in the common case of paramagnetic ions with exchange; in the less common case of no exchange, the Gaussian line shape is appropriate.¹¹⁻¹⁴ The delta function is not a realistic approximation to the line shape of an individual crystallite. Let us assume that there is no fine or hyperfine interaction. Then, in order to study line shapes of polycrystalline substances one would like a closed-form expression based on a Lorentzian line shape of an individual crystallite and on complete anisotropy. We have not been able to obtain such an expression. On the other hand, we give here for axial symmetry and a Lorentzian line shape a closed-form expression for the paramagnetic absorption line of a polycrystalline substance. Since axial or near axial symmetry is common, this expression should be a more useful one for the study of line shapes than has been given previously.

In order to derive reliable magnetic parameters from polycrystalline spectra, particularly when there is appreciable anisotropy, it is necessary to carry out a detailed comparison of a physically realistic calculated line shape with the experimental line shape. An iterative procedure, applicable to any line shape, is described here for doing this. As an example, the magnetic parameters of potassium perchromate, K_2CrO_8 , for which a Lorentzian line shape is justified, are derived by this procedure.

ABSORPTION LINE SHAPE

Let us assume that

(a) each ion has axial symmetry, i.e.,

$$g_x = g_y = g_{\perp}, \quad g_z = g_{\parallel}, \quad \text{and} \quad g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta, \quad (1)$$

where θ is the azimuthal angle¹;

¹¹ C. J. Gorter and J. H. Van Vleck, Phys. Rev. **72**, 1128 (1947).

¹² J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹³ J. H. Van Vleck, Suppl. Nuovo cimento **6**, 993 (1957).

¹⁴ P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 269 (1953).

(b) the shape $f(H)$ of the resonance absorption line of an individual crystallite is Lorentzian, i.e.,

$$f(H) \propto [(H-H')^2 + b^2]^{-1}, \quad (2)$$

where b is the half-width at half power and H' is the resonance field;

(c) the linewidth from a single crystallite is independent of the orientation of the crystallite;

(d) the crystallites are randomly oriented;

(e) the absorption coefficient K for a linearly polarized rf field and a polycrystalline sample is proportional to¹

$$K \propto g_1^2 [(g_{11}/g)^2 + 1];$$

and

(f) the spin Hamiltonian consists of the Zeeman, dipolar, and exchange terms only.

Then the paramagnetic resonance absorption line shape of a polycrystalline substance can be written as²

$$I(H) \propto \int_0^{\pi/2} K f(H) \sin \theta d\theta. \quad (3)$$

With the resonance condition

$$h\nu = g\beta H \quad (4)$$

and the definitions

$$H_1 = h\nu/g_1\beta \quad \text{and} \quad H_{11} = h\nu/g_{11}\beta, \quad (5)$$

we obtain, upon changing the variable of integration

and taking into account Eq. (1), the integrals

$$I(H) \propto \int_{H_1}^{H_{11}} \frac{(1+H_{11}^{-2}H'^2)dH'}{[(H-H')^2+b^2]H'^2(H'^2-H_1^2)^{1/2}} \quad \text{for } H_{11} > H_1 \quad (6a)$$

and

$$I(H) \propto - \int_{H_{11}}^{H_1} \frac{(1+H_{11}^{-2}H'^2)dH'}{[(H-H')^2+b^2]H'^2(H_1^2-H'^2)^{1/2}} \quad \text{for } H_1 > H_{11}. \quad (6b)$$

It apparently had not been realized before that the evaluation of (6a) and (6b) is straightforward. Let us take (6a) as an illustration. Make the substitution $t = H - H'$ to obtain

$$I(H) \propto \int_{H-H_{11}}^{H-H_1} \frac{[(H-t)^{-2} + H_{11}^{-2}]dt}{(t^2+b^2)(t^2-2Ht+H^2-H_1^2)^{1/2}}. \quad (7a)$$

Note that

$$[(H-t)^{-2} + H_{11}^{-2}](t^2+b^2)^{-1} = A(t^2+b^2)^{-1} + Bt(t^2+b^2)^{-1} + C(H-t)^{-1} + D(H-t)^{-2}, \quad (8)$$

where

$$A = (H^2 - b^2)(H^2 + b^2)^{-2} + H_{11}^{-2}, \quad B = C = 2H(H^2 + b^2)^{-2}, \quad \text{and} \quad D = (H^2 + b^2)^{-1}. \quad (9)$$

The substitution of (8) into (7a) leads to an expression for $I(H)$ involving four integrals, all of which may be found in standard tables.¹⁵ In this way we obtain

$$I(H) \propto \frac{A\beta_2 - Bb\beta_1}{2bP} L_1 + \frac{A\beta_1 + Bb\beta_2}{bP} T_1 + \frac{B}{H_1} \left(\sin^{-1} \frac{H_1}{H_{11}} - \frac{\pi}{2} \right) + D \frac{(H_{11}^2 - H_1^2)^{1/2}}{H_1^2 H_{11}} \quad \text{for } H_{11} > H_1, \quad (10a)$$

$$I(H) \propto \frac{A\beta_1 + Bb\beta_2}{2bP} L_2 + \frac{-A\beta_2 + Bb\beta_1}{bP} T_2 - \frac{B}{H_1} \ln \frac{H_{11}}{H_1 - (H_1^2 - H_{11}^2)^{1/2}} - D \frac{(H_1^2 - H_{11}^2)^{1/2}}{H_1^2 H_{11}} \quad \text{for } H_1 > H_{11}, \quad (10b)$$

where

$$P = +[(H^2 - H_1^2 - b^2)^2 + 4H^2 b^2]^{1/2},$$

$$\beta_1 = +[\frac{1}{2}P + \frac{1}{2}(H^2 - H_1^2 - b^2)]^{1/2},$$

$$L_1 = \left[\ln \frac{t^2 + b^2}{\theta_1^2 + \Phi_1^2} \right]_{t=H-H_{11}}^{t=H-H_1},$$

$$T_1 = [\tan^{-1}(b/t) + \tan^{-1}(\Phi_1/\theta_1)]_{t=H-H_{11}}^{t=H-H_1},$$

$$\theta_1 = \gamma_1 t + \delta_1 - (t^2 - 2Ht + H^2 - H_1^2)^{1/2},$$

$$\theta_2 = \gamma_2 t + \delta_2 + (-t^2 + 2Ht + H_1^2 - H^2)^{1/2},$$

$$\gamma_1 = (b\beta_2 - H\beta_1)/P, \quad *$$

$$\delta_1 = [-Hb\beta_2 + (H^2 - H_1^2)\beta_1]/P,$$

$$\beta_2 = -[\frac{1}{2}P - \frac{1}{2}(H^2 - H_1^2 - b^2)]^{1/2},$$

$$L_2 = \left[\ln \frac{t^2 + b^2}{\theta_2^2 + \Phi_2^2} \right]_{t=H-H_{11}}^{t=H-H_1},$$

$$T_2 = [\tan^{-1}(b/t) - \tan^{-1}(\Phi_2/\theta_2)]_{t=H-H_{11}}^{t=H-H_1},$$

$$\Phi_1 = \gamma_2 t + \delta_2,$$

$$\Phi_2 = \gamma_1 t + \delta_1,$$

$$\gamma_2 = (b\beta_1 + H\beta_2)/P,$$

$$\delta_2 = [-Hb\beta_1 - (H^2 - H_1^2)\beta_2]/P.$$

In the evaluation of $I(H)$ proper account must be taken of the branch points of arctan and arcsin.¹⁶

Equations (10a) and (10b) for various values of H_{11} , H_1 , and b have been readily evaluated on an IBM 7090

computer. The problem was coded in FORTRAN, a symbolic language that is particularly well suited for the various substitutions involved here. Typical line shapes for a series of half-widths and $H_{11} = 3600$ G, $H_1 = 3300$ G are given in Fig. 1. The maximum values

¹⁵ See, for example, W. Gröbner and N. Hofreiter, *Integraltafel-Erster Teil-Unbestimmte Integrale* (Verlag-Julius Springer, Berlin, 1961), integrals 231.23a, 231.23b, 231.10, 231.9.

¹⁶ We are indebted to Dr. G. Gioumoussis of these laboratories for a discussion of this point.

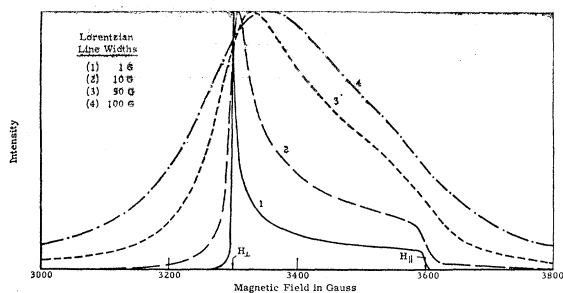


FIG. 1. Calculated EPR (electron paramagnetic resonance) line shapes. $H_{11}=3600$ G, $H_1=3300$ G.

of the curves have been set at unity; the relative values of the true maxima are 963:35:3:1 for b of 1:10:50:100. It is not surprising that the curve for $b=1.0$ G closely resembles the curve based on a delta function for the crystallite shape.

Comparisons can be made with the calculations of Searl, Smith and Wyard⁹ and with those of Chirkhov and Kokin.¹⁰ Both of these groups assumed that

$$g = g_1 + (g_{11} - g_1) \cos^2 \theta, \quad (11)$$

a form which may be derived from (1) on the assumption of small anisotropy, i.e.,

$$|g_{11} - g_1|/g \ll 1. \quad (12)$$

These groups assumed K to be constant [for their work preceded Bleaney's (1960) paper], but this causes negligible errors at anisotropies consistent with (12). Closed-form expressions are given by both groups for the case of a Lorentzian line shape and axial symmetry. These expressions are identical, although Chirkhov and Kokin fail to so note. Chirkhov and Kokin point out that $I(H)$ in their case is a function only of $(H - H_0)/b$ and of $(H_{11} - H_1)/b$. In Fig. 2 we reproduce the curve given by Chirkhov and Kokin for $(H_{11} - H_1)/b = 24$, and also give two curves of our own. (All three curves have been normalized to unity.) Agreement with their work is poor, not only because of the striking differences, particularly at high field, between their curve and ours, but also because our curves do not superimpose, as is required in their formulation. As $|H_{11} - H_1|$ is decreased, our curves for various linewidths are more nearly identical and the agreement with the curves of Chirkhov and Kokin is improved because under these conditions Eq. (12) is more nearly satisfied. There is very good agreement between our calculation and that of Searl *et al.* for $b=0.51$ G, $H_{11}=8508$ G, $H_1=8504$ G, a case of very small anisotropy, although even here agreement is poorer at the high field side.

ITERATION SCHEME FOR THE DERIVATION OF MAGNETIC PARAMETERS

From Fig. 1 it is obvious that except in those cases where the crystallite linewidth is very narrow, it is impossible to derive reliable magnetic parameters

directly from the positions of the maximum and the inflection point of the absorption curve. It is necessary, at the very least, to compare in detail the experimental curve with curves based on a physically reasonable crystallite line shape and calculated for a series of parameters. Although reliable parameters can be derived by such a trial-and-error procedure, an iteration scheme is to be preferred. The simplest, and in many ways most easily justified, iteration scheme is a least-squares procedure in which one minimizes

$$\sum_H w(H) [I_{\text{calc}}(H) - I_{\text{exp}}(H)]^2, \quad (13)$$

where the weight $w(H)$ is taken inversely proportional to the variance of the experimental point at H . An important advantage of this procedure over the trial-and-error procedure is that estimates of the errors in the derived parameters are obtained. Since $I(H)$ is not a linear function of H_{11} , H_1 , and b , one solves not for the magnetic parameters directly, but rather for the changes in these parameters from initially chosen values. Sufficiently reliable initial values can usually be obtained with the delta function approximation.

The iteration scheme, of course, can be applied not only to the intensity curves, but also to the derivative curves, if desired. This is frequently a better procedure, for the experimental derivative curve is recorded directly in most experiments and is thus subject to fewer errors than is the absorption curve, derived from it by numerical or electronic means.

Clearly, the iteration procedure requires numerical computation, preferably on an electronic computer. Then since $I(H)$, or its derivative, can be evaluated numerically for any form of the g tensor and for any crystallite line shape, no restrictive approximations are necessary. In fact, one of the problems is the proper choice of the crystallite line shape. In the following example of potassium perchromate we first justify the choice of a Lorentzian line shape, and then demonstrate the usefulness of the iteration scheme for the derivation of reliable magnetic parameters.

MAGNETIC PARAMETERS OF POTASSIUM PERCHROMATE

Exchange-narrowed resonance lines have been shown by Anderson and Weiss¹⁴ to be of Lorentzian shape in

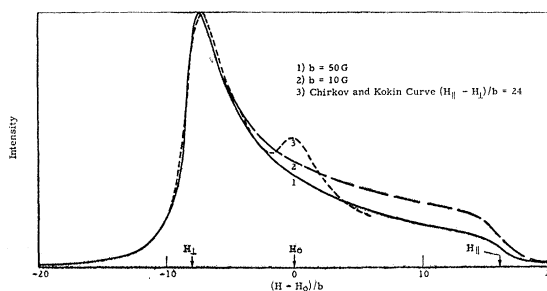


FIG. 2. EPR line shapes reduced by the linewidth. For curves 1 and 2 $H_0=3400$ G.

TABLE II. Magnetic parameters of K_3CrO_8 in gauss.

Parameter	Initial guess	Cycle 1	Cycle 2
H_{11}	3508	3512.2	3511.9 ± 1.2
H_1	3424	3429.7	3429.7 ± 0.3
b	30	23.8	23.5 ± 0.4

the center but to transform to Gaussian shape in the neighborhood of the exchange field. They show that

$$\langle \Delta H^2 \rangle = bH_e, \quad (14)$$

where $\langle \Delta H^2 \rangle$ is the second moment and H_e the exchange field. The rigid-lattice second moment for polycrystalline K_3CrO_8 is found from the expression of Van Vleck¹² to be approximately 1.27×10^5 G², on the assumption of an isotropic g . An approximate value of b of 30 G was obtained by inspection of the experimental absorption curve. A value of 4200 Oe for H_e thus follows from these values and Eq. (14). Since this exchange field is very large compared with the linewidth of the resonance line from K_3CrO_8 , it follows that each crystallite must have a Lorentzian line shape. This exchange field corresponds to a Curie-Weiss constant of (1 ± 1) °K, in excellent agreement with the value of (0 ± 2) °K obtained by Meisenheimer¹⁷ from static magnetic susceptibility measurements.

The experimental derivative and absorption curves from a polycrystalline sample of K_3CrO_8 are given in Figs. 3 and 4. The derivative curve was obtained on a Varian V4500 EPR spectrometer at room temperature with a modulation frequency of 100 kc/sec and an amplitude of less than 0.1 G. The absorption curve was obtained from the derivative curve by electronic integration with a Philbrick UPA-2 amplifier with capacitance feedback. There was a phase lag during elec-

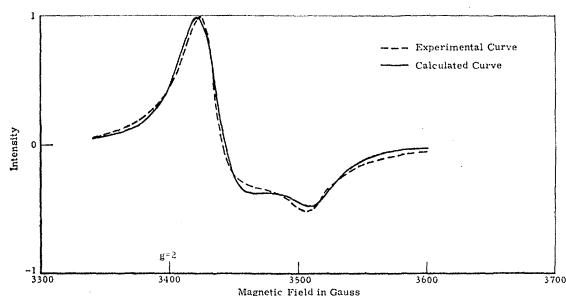


FIG. 3. EPR signal from K_3CrO_8 at 20°C. $H_{11} = 3511.9$ G, $H_1 = 3429.7$ G, and $b = 23.5$ G.

¹⁷ Unpublished work by R. Meisenheimer of these laboratories.

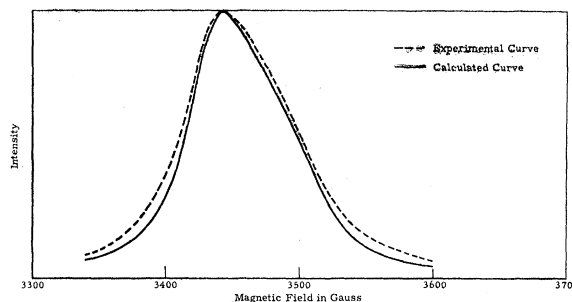


FIG. 4. Integral of EPR signal of K_3CrO_8 .

tronic integration; therefore the absorption curve has been adjusted in field so that its maximum occurs at the field where the derivative curve is zero. The magnetic field was calibrated with an NMR probe. A g value of 2.000 corresponds to a field of 3400 G.

Magnetic parameters were obtained from the derivative curve by the least-squares procedure described above. The derivative curve was read at 5 G intervals; the 50 points so obtained were weighted equally. Values of $I(H)$ were calculated from (10a), and values of $dI(H)/dH$ were calculated from $I(H)$ on the IBM 7090 with the use of central difference formulas.¹⁸ Table II illustrates the course of the refinement. The initial values were obtained from the delta-function approximation and from inspection of the absorption curve. The final values, even in this case of small anisotropy, differ significantly from these initial values.

The agreement between calculated and experimental derivative curves (Fig. 3) is very good. The agreement between calculated and experimental absorption curves (Fig. 4) is not as good, both because of errors inherent in electronic integration and because the iteration procedure was not applied in this case.

We feel that this good agreement between theory and experiment justifies the approach described here. Elsewhere¹⁹ we shall show that the derived g values for K_3CrO_8 together with ligand field calculations lead to an understanding of the bonding in this unusual compound.

Note added in proof.—Recently J. W. Searl, R. C. Smith, and S. J. Wyard [Proc. Phys. Soc. (London) **A78**, 1174 (1961)] have evaluated the integral (6b) numerically for some specific cases.

¹⁸ A closed-form expression for $dI(H)/dH$ can, of course, be obtained by differentiation of Eq. (10). However, sufficient accuracy was achieved on the computer with the use of central difference formulas.

¹⁹ J. D. Swalen and J. A. Ibers, J. Chem. Phys. (to be published).