Schelling for discussion on dipolar calculations, and G. H. Stauss for helpful comments on the text material. Finally we wish to thank H. W. Greer for assistance in taking the data.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 11 1 DECEMBER 1971

Nuclear-Magnetic-Resonance Line-Shape Calculations for Polycrystalline Materials with bcc and fcc Symmetry*

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(Received 16 June 1971)

The powder free-induction decays for body- and face-centered-cubic lattices of spins are calculated for spin values $I=\frac{1}{2}$ and 1. The powder decays are calculated by a computerized numerical integration of the formula of Lowe and Norberg as extended to include arbitrary spin. Only magnetic dipole-dipole interactions are considered. The powder decays are compared with $e^{(-a^2t^2/2}\sin bt/bt$. The powder absorption curves are also calculated as the cosine transforms of the decay curves.

I. INTRODUCTION

Several formulas exist for the free-induction decay of a single crystal with an arbitrary number of spins fixed in spatial position, which were derived without a restrictive assumption about the form of the decay.[1–6] One of these single-crystal formulas, that of Gade and Lowe for arbitrary spin I, was used in a prior paper to calculate the free-induction decay curves for powders with simple cubic arrangements of the spins and $I=\frac{1}{2}$ and 1.[7] Since in the only case where experimental powder decays are available [CaF_2; simple-cubic lattice (SCL), $I=\frac{1}{2}$], good agreement exists between the theo-

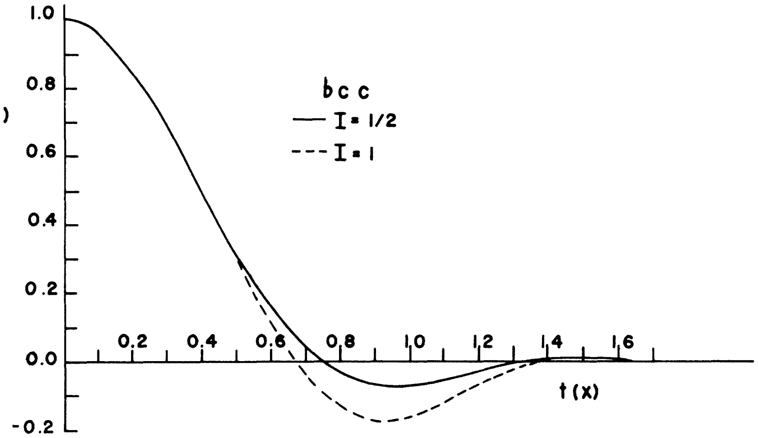

FIG. 1. Free-induction decay shapes for a powder with bcc symmetry and $I=\frac{1}{2}$ and 1. $x=2d^3/3\gamma^2\hbar \times [I(I+1)]^{1/2}$, where d is $2/\sqrt{3}$ times the nearest-neighbor distance.

retical and experimental decays, and since there has been a considerable number of requests for the SCL powder decays, additional powder decays are presented in this paper for materials with body- and face-centered cubic arrangements of spins and $I=\frac{1}{2}$ and 1. The corresponding powder absorption curves were also calculated as the cosine transforms of the free-induction decays and are presented here.

Finally, the simplest analytical expression for the free-induction decay which exhibits the experimentally observed beat effect, namely, $e^{-a^2t^2/2} \times \sin bt/bt$, was evaluated for bcc and fcc powders with $I=\frac{1}{2}$ and 1.[8] These are compared with the decays obtained from the Gade-Lowe formula.

II. METHOD OF CALCULATION OF POWDER FREE-INDUCTION DECAY

The method used for calculating the powder decays is explained in Ref. 7. Briefly, it consists of integrating the free-induction decay for a single crystal over all orientations of the crystal symmetry axes relative to the applied magnetic field. That is, the free-induction decay $F(t)$ for the powder is given by

$$F(t) = (1/4\pi)\int_0^{2\pi}\int_0^{\pi} F(\theta,\phi;t)\,\sin\theta\,d\theta\,d\phi, \qquad (1)$$

where $F(\theta, \phi; t)$ is the free-induction decay for a single crystal with an orientation (θ, ϕ) in the applied magnetic field. Since the θ, ϕ dependence of $F(\theta, \phi; t)$ is extremely complicated, the integration in Eq. (1) cannot be done directly so that $F(t)$ is obtained in functional form. Rather, the powder decays $F(t)$ are obtained in tabular form by means of a computerized numerical integration of Eq. (1). Table I and Figs. 1 and 2 give the powder decays for bcc and fcc symmetries and $I=\frac{1}{2}$ and 1 obtained from Eq. (1) using the Gade-Lowe expansion for

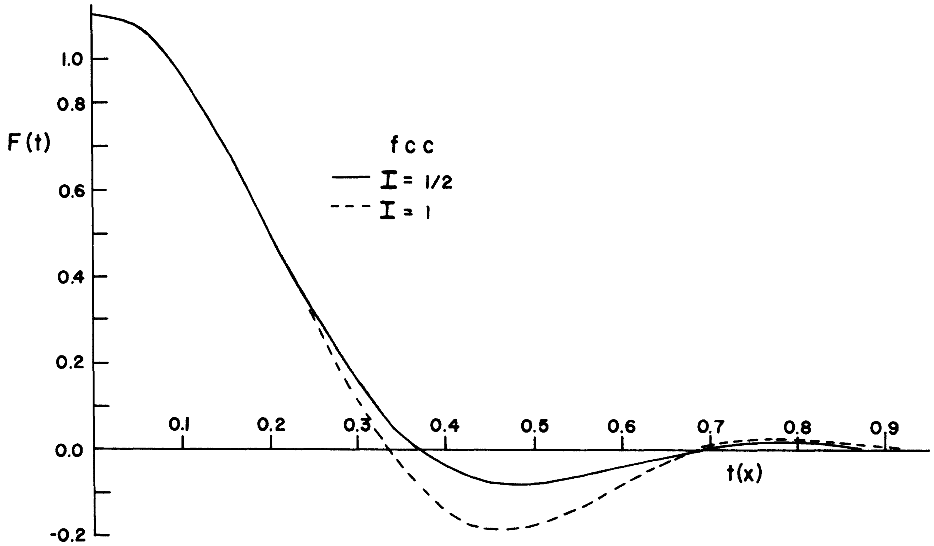

FIG. 2. Free-induction decay shapes for a powder with fcc symmetry and $I=\frac{1}{2}$ and 1. $x=2d^3/3\gamma\,\hbar[I+1)]^{1/2}$, where d is $\sqrt{2}$ times the nearest-neighbor distance.

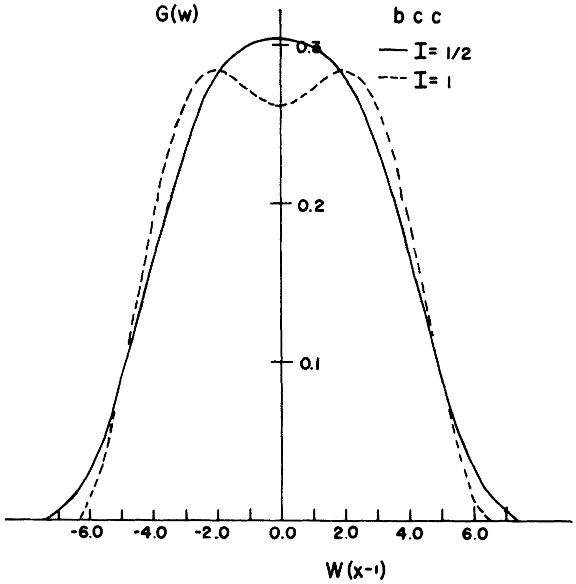

FIG. 3. Absorption curves for a powder with bcc symmetry and $I=\frac{1}{2}$ and 1.

TABLE II. bcc and fcc powder absorption curves for $I=0.5$ and 1.

ω	bcc $G(\omega)$ $I=0.5$	$G(\omega)$ $I=1$	ω	fcc $G(\omega)$ $I=0.5$	$G(\omega)$ $I=1$
0.0	0.303	0.261	0.0	0.151	0.129
0.5	0.302	0.264	1.0	0.150	0.131
1.0	0.298	0.270	2.0	0.148	0.134
1.5	0.291	0.278	3.0	0.145	0.138
2.0	0.278	0.283	4.0	0.139	0.142
2.5	0.260	0.280	5.0	0.131	0.142
3.0	0.234	0.266	6.0	0.119	0.136
3.5	0.202	0.238	7.0	0.103	0.122
4.0	0.166	0.198	8.0	0.084	0.101
4.5	0.127	0.149	9.0	0.064	0.075
5.0	0.090	0.099	10.0	0.045	0.048
5.5	0.058	0.054	11.0	0.028	0.024
6.0	0.032	0.020	12.0	0.015	0.007
6.5	0.015	0.002	13.0	0.007	0.000
7.0	0.005		14.0	0.002	

$F(\theta,\ \phi;\ t)^2$.

III. EVALUATION OF $F(t)$ FOR bcc AND fcc SYMMETRIES

Equation (1) was used to evaluate the powder free-induction decay curves for solids with body- and face-centered cubic symmetries and $I=\frac{1}{2}$ and 1. The interactions among the spins were limited to magnetic dipole-dipole interactions, and $F(\theta, \phi; t)$ for this case is given by Eqs. (13), (14), and (17) in the paper by Gade and Lowe.[2] In evaluating $F(t)$ the same approximations were made as in the evaluation of single-crystal decays of Ref. 2 and the SCL powder decays.[7] These consist of (i) discarding lattice summations containing odd powders of B_{jk}, (ii) assuming identical spins, and (iii) treating exactly 168 and 200 nearest magnetic neighbors, respectively, for bcc and fcc lattices.

The integration in Eq. (1) was performed numerically by computer. Because of the cubic sym-

TABLE I. bcc and fcc powder free-induction decays for $I=0.5$ and 1.

t	bcc $F(t)$ $I=0.5$	$F(t)$ $I=1$	t	fcc $F(t)$ $I=0.5$	$F(t)$ $I=1$
0.00	1.000	1.000	0.00	1.000	1.000
0.10	0.962	0.962	0.05	0.962	0.962
0.20	0.854	0.854	0.10	0.854	0.854
0.30	0.694	0.692	0.15	0.695	0.693
0.40	0.507	0.500	0.20	0.508	0.501
0.50	0.321	0.299	0.25	0.321	0.301
0.60	0.161	0.114	0.30	0.160	0.115
0.70	0.041	−0.034	0.35	0.039	−0.035
0.80	−0.033	−0.130	0.40	−0.036	−0.135
0.90	−0.065	−0.168	0.45	−0.070	−0.179
1.00	−0.066	−0.156	0.50	−0.073	−0.172
1.10	−0.050	−0.113	0.55	−0.057	−0.131
1.20	−0.029	−0.062	0.60	−0.035	−0.077
1.30	−0.011	−0.021	0.65	−0.014	−0.028
1.40	−0.001	0.003	0.70	0.000	0.005
1.50	0.005	0.011	0.75	0.008	0.020
1.60	0.004	0.010	0.80	0.010	0.021
1.70	0.002	0.006	0.90	0.004	0.009

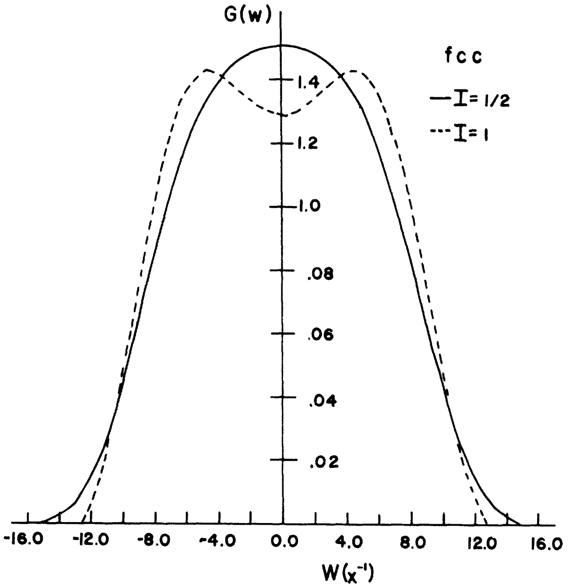

FIG. 4. Absorption curves for a powder with fcc symmetry and $I=\frac{1}{2}$ and 1.

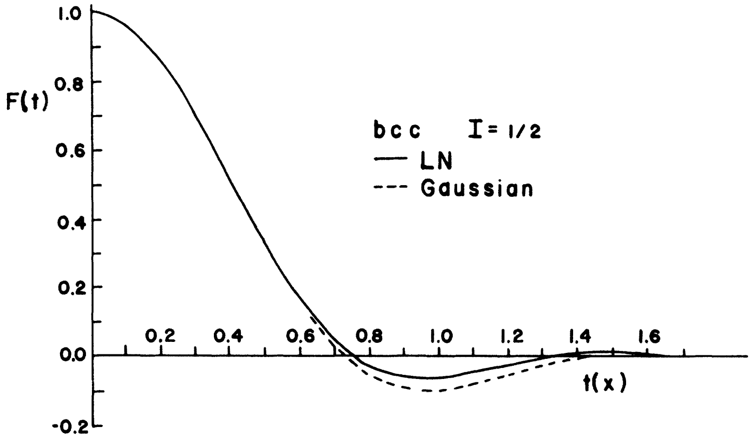

FIG. 5. Comparison of the modified Gaussian and Lowe-Norberg decays for a powder with bcc symmetry and $I=\frac{1}{2}$.

metry it was only necessary to integrate θ from 0° to 90° and ϕ from 0° to 45°. This solid angle was divided into 200 approximately equal sections, and this degree of fineness made the numerical-integration process quite accurate. The decay curves are given as functions of t in units of X, where $X=2d^3/3\gamma^2\hbar[I(I+1)]^{1/2}$. γ is the magnetogyric ratio. d is $2/\sqrt{3}$ times the distance between nearest magnetic neighbors in the bcc lattice and $\sqrt{2}$ times the distance between nearest magnetic neighbors in the fcc lattice.

The magnetic absorption curves in Figs. 3 and 4 and Table II are the cosine transforms of the corresponding powder decays $F(t)$. That is,

$$G(\omega)=(2/\pi)^{1/2}\int_0^\infty F(t)\cos\omega t\,dt. \quad (2)$$

The absorption curves were calculated by a numerical integration of Eq. (2) using Table I for the values of $F(t)$. The absorption curves are given as functions of ω in units of X^{-1}.

IV. DISCUSSION

The free-induction decay curves of Figs. 1 and 2 for $I=\frac{1}{2}$ and 1 are fairly similar and lead to the conclusion that the decays for both symmetries are relatively spin independent. This result was expected because the free-induction decays for single crystals with bcc and fcc symmetries exhibit this small spin dependence.[2] This is a consequence of the fact that the decays are given as functions of t in units of $X=2d^3/3\gamma^2\hbar[I(I+1)]^{1/2}$. This choice of units makes the second moment and the more important parts of the higher moments spin independent.[2,9] Physically, this choice of units makes the magnitude of the magnetic moments spin independent. Then the difference in the decay curves results only from the difference in the number of orientations $(2I+1)$ a spin can assume in a magnetic field. Although the powder decays were not calculated for $I>1$, the single-crystal decays for these symmetries indicate that the $I>1$ curves will be very similar to the $I=1$ curve. In fact, to use an argument of Gade and Lowe,[2] it is reasonable to expect that the difference between the $I=\infty$ (classical magnetic moment) and the $I=1$ powder decays is less than the difference between the $I=1$ and

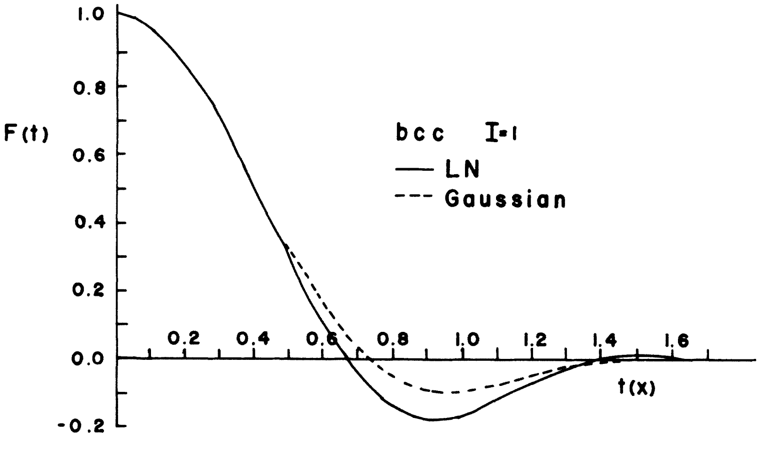

FIG. 6. Comparison of the modified Gaussian and Lowe-Norberg decays for a powder with bcc symmetry and $I=1$.

TABLE III. Parameters used in the modified Gaussian decays of Figs. 5 and 6 for bcc symmetry.

	$M_2(X^{-2})$[a]	$M_4(X^{-4})$[a]	$a^2(X^{-2})$	$b(X^{-1})$
$I=\frac{1}{2}$	7.76	133.45	1.49	4.34
$I=1$	7.76	135.40	1.62	4.29

[a] D. E. O'Reilly and T. Tsang, Phys. Rev. 128, 2639 (1962).

$I=\frac{1}{2}$ powder decays.

The modified Gaussian expression $[e^{-a^2t^2/2} \times \sin bt/bt]$ for the decays is plotted in Figs. 5 and 6 for bcc symmetry along with the powder decays of Fig. 1, obtained from the Lowe-Norberg decay formula. The parameters a and b and the second (M_2) and fourth (M_4) moments used in the evaluation are given in Table III. Figures 5 and 6 show that the modified Gaussian decay is fairly similar to the Lowe-Norberg decay for $I=\frac{1}{2}$ but that the agreement is considerably poorer for $I=1$. The modified Gaussian powder decays were also calculated for fcc symmetry, and their agreement with the Lowe-Norberg decays was very similar to the bcc case, good for $I=\frac{1}{2}$ but considerably poorer for $I=1$.

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[*] Work supported by NSF Institutional Grant for Science No. GU-3820 and Board of Regents of the Wisconsin State University Research Grant No. OSH-15-69.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 11 1 DECEMBER 1971

Study of the Thermal Kinetics of the F'-to-F Conversion in KCl by Electron Spin Resonance[*]

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(Received 20 May 1971)

The temperature dependence of the F'-to-F conversion has been studied in additively colored KCl, at a number of temperatures at which the F' center is thermally unstable. The conversion was monitored by observing the increase of the ESR signal of the F center. The data were analyzed in terms of a kinetics which allowed the electron on leaving the F' center to go to a vacancy to form an F center or to an F center to form another F' center. The results of the analysis indicate that the half-life of the F'center is dependent on the concentration of the F' centers. An activation energy of 0.53 ± 0.05 eV was deduced for low concentrations of F' centers, where it is indicated that the half-life is independent of the concentration of the F' centers.

I. INTRODUCTION

A broad optical absorption on the red side of the F band at about 1.6 eV in KCl has been attributed to two electrons trapped at an anion vacancy. This model of the F' center is supported by Pick's study of the F-to-F' and F'-to-F quantum yields.[1,2] He found that the conversion reaction could be described by $2F \rightleftharpoons F'$ and that the F' optical band could be bleached optically at very low temperatures with a quantum yield of two, indicating that the F' center has no bound excited state. The broadness of the F' optical absorption is attributed to the fact that excitations of the center are to states in the conduction-band continuum. Little attention has been paid to the thermal stability of the center. The broadness of the F' band, which results in it overlapping into the F band, complicates optical studies of the thermal annealing process. However, some studies have been reported and activation energies measured on the assumption that the thermal kinetics is first order.[1,3] More detailed studies have indicated the possibility that the decay is not first order. A simultaneous measurement of the decrease of the F'-band optical absorption and the increase of the F paramagnetic resonance