resonator which first aroused our interest in the technique, to Professor D. Langreth for finding an error in our calculation, to A. Gynn, M. Moskowitz, and S. Wolf for much useful advice on the art of making thin films, and to R. Longo for experimental assistance.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 3 1 FEBRUARY 1971

Effect of Brownian Motion on the Mössbauer Line Shape

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A general theoretical expression for the resonance-absorption cross section of γ rays by particles in liquids is worked out. The treatment takes into account the general solution of the Langevin equation, thereby revealing the important role played by the characteristic time of the liquid. While the line shape predicted by Singwi and Sjölander takes care of atomic motion, it is inadequate for the motion of particles in liquids. When composite particles are used, the nuclear lifetimes of the Mössbauer isotopes may be compared with the characteristic time of the liquid. It is shown that, under certain conditions, narrowing of the Singwi-Sjölander line can be considerable.

I. INTRODUCTION

It has been long recognized that the resonance absorption of γ rays, otherwise known as the Mössbauer technique, could be used to investigate the nature of diffusive motion in liquids. Singwi and Sjölander,[1] using the space-time correlation function of van Hove, have derived an expression for the resonance-absorption cross section. They have predicted a diffusive broadening of the resonance line proportional to the diffusion coefficient of the liquid and the square of the γ-ray energy.

In this laboratory, some experiments have been conducted using a composite particle containing two Mössbauer isotopes. An $FeSnO_3$ suspension in machine oil was used, and the line broadenings of ^{119}Sn and ^{57}Fe were compared. The ratio should have been the ratio of the squares of the two γ-ray

energies on the basis of the Singwi-Sjölander expression. However, the ratio obtained was different from this. Furthermore, the observed line broadening for both the ^{57}Fe and the ^{119}Sn lines is less than that predicted by Singwi and Sjölander. There are other experimental papers[2–6] which report deviations from the Singwi-Sjölander expression. In view of this, we felt the need to look into the theoretical derivation of the absorption cross section afresh, and investigate the diffusive broadening of the Mössbauer line. We felt that, while the Singwi-Sjölander expression takes care of atomic motion, it is inadequate for the motion of particles in a liquid. The characteristic time, or the relaxation time of the liquid, plays an important role in determining the diffusive broadening when particles are considered. This time can be included in the analysis only by considering the general solution of the Langevin equation.

II. GENERAL LANGEVIN DISTRIBUTION

Following Chandrasekhar,[7] one can write the general Langevin distribution function for a free particle as

$$W(r, t) \simeq \frac{1}{[2\pi\rho(|t|)]^{3/2}} \exp\left(-\frac{|r - r_0|^2}{2\rho(t)}\right) , \qquad (1)$$

where $|r - r_0|^2$ is the mean-square displacement of the particle and

$$\rho(t) = (2k_B T/m\beta^2)[\beta t - 1 + \exp(-\beta t)]$$
$$= (2D/\beta)[\beta t - 1 + \exp(-\beta t)] , \qquad (2)$$

where D is the diffusion coefficient of the liquid; k_B, the Boltzmann constant; m, the mass of the particle; and $\beta = 6\pi a\eta/m$. The quantity β^{-1} has the dimensions of time and is called the characteristic time or the time of relaxation.

The use of $\rho(t)$ implies that the Langevin probability distribution is a valid description of the diffusion of a particle in a liquid for all time intervals $t \ll \beta^{-1}$ as well as $t \gg \beta^{-1}$. For atomic motion β^{-1} is very small, of the order of 10^{-12}–10^{-20} sec. When particles are considered, β^{-1} could well be of the order of lifetime of the nucleus in the excited state, or even greater, and it is necessary to take the general form of $\rho(t)$ as given by Eq. (2).

III. ABSORPTION CROSS SECTION

Singwi and Sjölander have shown that the absorption cross section per nucleus for a γ ray of energy E is given by

$$\sigma_a(\omega) = \frac{\sigma_0\Gamma}{4} \exp\left(\frac{\hbar\omega}{2k_B T} - \frac{\hbar^2\kappa^2}{8mk_B T}\right)$$
$$\times \int_{-\infty}^{\infty} \exp\left[i(\vec{\kappa}\cdot\vec{r} - \omega t) - \frac{\Gamma}{2}|t|\right] F_s^c(\vec{r}, t)\, d\vec{r}\, dt , \qquad (3)$$

where $F_s^c(r, t)$ is the classical self-diffusion function, $\hbar\omega = E - E_0$, and Γ is the natural width. Substituting

$$F_s^c(r, t) = \frac{1}{[2\pi\rho(|t|)]^{3/2}} \exp\left(-\frac{|r - r_0|^2}{2\rho(t)}\right)$$

and taking the space Fourier transform, we get

$$\sigma_a(\omega) = \tfrac{1}{4}\sigma_0\Gamma A \int_{-\infty}^{\infty} \exp(-i\omega t - \tfrac{1}{2}\Gamma|t|)$$
$$\times \exp\{-\alpha[\beta t - 1 + \exp(-\beta t)]\}\, dt , \qquad (4)$$

where

$$A = \exp\left(\frac{\hbar\omega}{2k_B T} - \frac{\hbar^2\kappa^2}{8mk_B T}\right) , \quad \alpha = \frac{\kappa^2 D}{\beta} .$$

α is a dimensionless number connecting the γ-ray energy with the relaxation time of the liquid and the diffusion coefficient for the particle.

It is readily seen that

$$\sigma_a(\omega) = (\sigma_0\Gamma/2\beta)A \int_0^1 \exp(\alpha x)\,(1 - x)^{s-1} dx ,$$

where

$$s = \frac{\Gamma}{2\beta} + \alpha + \frac{i\omega}{\beta} = p + iq ,$$

say

$$\mathrm{Re}\, s > 0, \quad \arg s < \pi - \epsilon \quad (\epsilon > 0) .$$

This is the integral representation of the confluent hypergeometric function of Kummer[8] and can be written as a power series:

$$\sigma_a(\omega) = \frac{\sigma_0\Gamma A}{2\beta} \cdot \frac{\Gamma(s)}{\Gamma(1 + s)} \Phi(1, s + 1, \alpha) , \qquad (5)$$

where $\Gamma(s)$ is the γ function. The general relation for all values of α is

$$\frac{\sigma_0\Gamma A}{2\beta} \sum_{n=1}^{\infty} \alpha^{n-1} \frac{\Gamma(s)}{\Gamma(n + s)} . \qquad (6)$$

When $\alpha \ll 1$ and β is very large, only the first term really matters, and we get the Singwi-Sjölander result, viz.,

$$\sigma_a(\omega) = \frac{\sigma_0\Gamma}{4} A \frac{\Gamma + 2\alpha\beta}{\omega^2 + \frac{1}{4}(\Gamma + 2\alpha\beta)^2} . \qquad (7)$$

When $\alpha < 1$, we can transform $\Phi(1, s + 1, \alpha)$ in Eq. (5) by Kummer's formula

$$\Phi(1, s + 1, \alpha) = \exp(\alpha)\Phi(s, s + 1, -\alpha) , \qquad (8)$$

which gives

$$\sigma_a(\omega) = \frac{\sigma_0\Gamma}{4} A \exp(\alpha) \sum_{n=0}^{\infty} (-1)^n$$
$$\times \frac{\Gamma + 2\alpha\beta + 2n\beta}{\omega^2 + \frac{1}{4}(\Gamma + 2\alpha\beta + 2n\beta)^2} \frac{\alpha^n}{n!} , \qquad (9)$$

a result obtained by Singwi and Sjölander[9] for neutron scattering where $\Gamma = 0$. Our general relation, viz.,

$$\sigma_a(\omega) = \frac{\sigma_0\Gamma A}{2\beta S} \left(1 + \frac{\alpha}{s + 1} + \frac{\alpha^2}{(s + 1)(s + 2)} + \cdots\right) , \qquad (10)$$

clearly reveals that the Singwi-Sjölander Lorentzian gets modulated by the terms in the parentheses. The intensity is increased however small α might be, with a corresponding reduction in the linewidth. Taking only the first two terms in Eq. (10), the linewidth is given by

$$\Delta \simeq (\Gamma + 2\alpha\beta)\left[\left(\frac{\Gamma + 2\alpha\beta}{\Gamma + 2\alpha\beta + 2\beta}\right)^2 + 1\right]^{-1/2}. \qquad (11)$$

In Table I, we give the broadening that may be expected for a particle of radius 0.5 μ, diffusing in a liquid with coefficient of viscosity $\eta = 1$ P. Along with this, the broadening as expected by the Singwi-Sjölander expression is also given. It is seen that the correction is appreciable in the case of ^{127}I for which $\alpha = 1.28$ and β is nearly 0.10 times the natural width. It is of interest to see the ratio of the broadening ^{127}I line to the ^{57}Fe line and also of ^{119}Sn line to ^{57}Fe line for the same particle. According to the corrected formula $\Delta_{127_I}/\Delta_{57_{Fe}} = 10.94$, $\Delta_{119_{Sn}}/\Delta_{57_{Fe}} = 2.509$ as against the values of 16.0 and 2.754 expected on Singwi-Sjölander expression. This quantity provides a check on the validity of the expression derived.

We took a composite particle of $FeSnO_3$ enriched to 85% by ^{57}Fe and ^{119}Sn and observed the broadening caused by the diffusive motion of this particle in machine oil with viscosity $\eta = 1$ P. The suspension in the machine oil was prepared by stirring the compound and the oil together in an agate mortar. That the mixture was left to stay for 2–3 days enabled the big particles to settle down. Only the upper part of the suspension was used. The linewidths for both ^{57}Fe and ^{119}Sn lines were measured while the particles were in suspension. After this, the linewidths for the same particles without the oil were measured. The average particle size was determined using an electron microscope. T The additional broadening caused because of diffusive broadening was thus computed for both a 14.4-keV line of ^{57}Fe and a 23.9-keV line of ^{119}Sn. Figure 1 shows the spectra for 23.9 γ rays for the bulk sample and for particles in the suspension. It was found that the ratio of the additional broadening caused because of diffusion was 2.6 as opposed to 2.509 predicted by our formula and 2.754 predicted by the Singwi-Sjölander expression. We realize that the ^{57}Fe and ^{119}Sn combination does not provide the real test. Experiments are in progress with composite particles containing iron and iodine.

With neutrons, α is always less than 1 and consequently in neutron scattering we will invariably get a width of the coherent elastic peak equal to $2\alpha\beta = 2\kappa^2 D$. However, when one uses γ rays as the probe, since κ for γ rays is large, there is a possibility of α being greater than 1, particularly so for particles.

When $\alpha > 1$ the root mean square displacement is greater than the wavelength of a γ ray. Under these conditions γ rays will be able to bring out the finer details of the motion of the particles in liquid. $\alpha > 1$ satisfies the condition of space resolution.

When $\alpha > 1$, the series in Eq. (6) approaches the series

$$\frac{2}{\beta}\Gamma(s)\alpha^{-s}\sum_m \frac{\alpha^m}{m!} = \frac{2}{\beta}\Gamma(s)\alpha^{-s}\exp(\alpha), \qquad (12)$$

$$\sigma_a(\omega) = (\sigma_0\Gamma/2\beta)A\exp(\alpha)\alpha^{-s}\Gamma(s). \qquad (13)$$

Using the asymptotic expansion of $\Gamma(s)$, we obtain

$$\begin{aligned}|\Gamma(s)| &= (2\pi)^{1/2}(p^2+q^2)^{p/2-1/4} \\ &\quad \times \exp(-p)\cdot\exp(-q\,\tan^{-1}(q/p)) \\ &= (2\pi)^{1/2}(p^2+q^2)^{p/2}\exp(-p)\exp(-q^2/p),\end{aligned} \qquad (14)$$

since $\tan^{-1}(q/p) \simeq q/p$ and $\frac{1}{4}$ is not of any consequence in comparison with $\frac{1}{2}p$. $\Gamma(s)$ has the phase θ given by

$$\theta = \tfrac{1}{2}q\ln(p^2+q^2)$$

TABLE I. Comparison of the linewidths obtained from our expression with those obtained from the Singwi-Sjölander expression for different values of α. Results are for a particle of size $a = 0.5$ μ and viscosity $\eta = 1.0$ P. $\hbar\beta = 11.8\times10^{-8}$ eV.

				Ratios	Singwi-Sjölander	Ours			
				$\Delta_{119_{Sn}}/\Delta_{57_{Fe}}$ =	2.754	2.509			
				$\Delta_{127_I}/\Delta_{57_{Fe}}$ =	16.00	10.94			
Different nuclei	α	E (eV)	γ (sec)	Γ (eV)	$\hbar\alpha\beta$ (eV)	$2\hbar\alpha\beta$ (eV)	$\Gamma + 2\hbar\alpha\beta$ (eV)	Our expression (eV)	Our broadening (eV)
^{57}Fe	0.08	14.4×10^3	9.77×10^{-8}	4.670×10^{-9}	9.441×10^{-9}	18.88×10^{-9}	23.55×10^{-9}	23.25×10^{-9}	18.580×10^{-9}
^{119}Sn	0.22	23.9×10^3	1.84×10^{-8}	2.485×10^{-8}	2.600×10^{-8}	5.200×10^{-8}	7.685×10^{-8}	7.148×10^{-8}	4.663×10^{-8}
^{127}I	1.28	57.6×10^3	1.86×10^{-9}	2.453×10^{-7}	1.510×10^{-7}	3.02×10^{-7}	5.473×10^{-7}	4.486×10^{-7}	2.033×10^{-7}

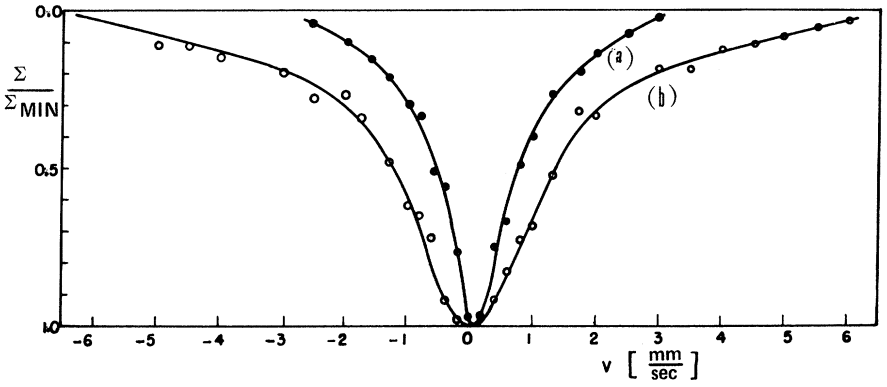

FIG. 1. Resonance-absorption line for ^{119}Sn in (a) solid ^{119}Sn ^{57}Fe O_3 obtained after precipitating the suspension used for case (b) and (b) in suspended particles of ^{119}Sn ^{57}Fe O_3 in machine oil.

$$+(p-\tfrac{1}{2})\tan^{-1}\left(\frac{q}{p}\right)-q\left(1+\frac{1}{12(p^2+q^2)}\cdots\right)$$

$$\simeq q\ln p\,;$$

thus

$$\sigma_a(\omega)=\sigma_0\frac{\Gamma}{2\beta}A\exp(\alpha)2\pi^{1/2}\times\exp\left[-p\left(1-\ln\frac{\Gamma+2\alpha\beta}{2\alpha\beta}\right)\right]\cdot\exp\left(-\frac{q^2}{2p}\right)\times\cos\left(\frac{\omega}{\beta}\ln\frac{\Gamma+2\alpha\beta}{2\alpha\beta}\right)$$

$$=\sigma_0\frac{\Gamma}{2\beta}A(2\pi)^{1/2}\cdot\exp\left(-\frac{q^2}{2p}\right),$$

since $2\alpha\beta>\Gamma$; and $1+(q^2/p^2)\simeq\exp(q^2/p^2)$. This is a Gaussian of full width Δ given by

$$\Delta=2[\beta(\Gamma+2\alpha\beta)\ln 2]^{1/2}\,. \tag{15}$$

IV. DISCUSSION

It is seen that when $\alpha>1$, the width of the resonance line is dependent on the lifetime of the nucleus in the excited state, and for the same particle would be different if different Mössbauer nuclei were investigated. Secondly, the width of the resonance line varies as $(T/\eta)^{1/2}$, rather than T/η as predicted by Singwi and Sjölander.

For $\alpha>1$, the linewidth is always less than $\Gamma+2\alpha\beta$. Since the expression for the linewidth was derived using asymptotic expansion, we felt

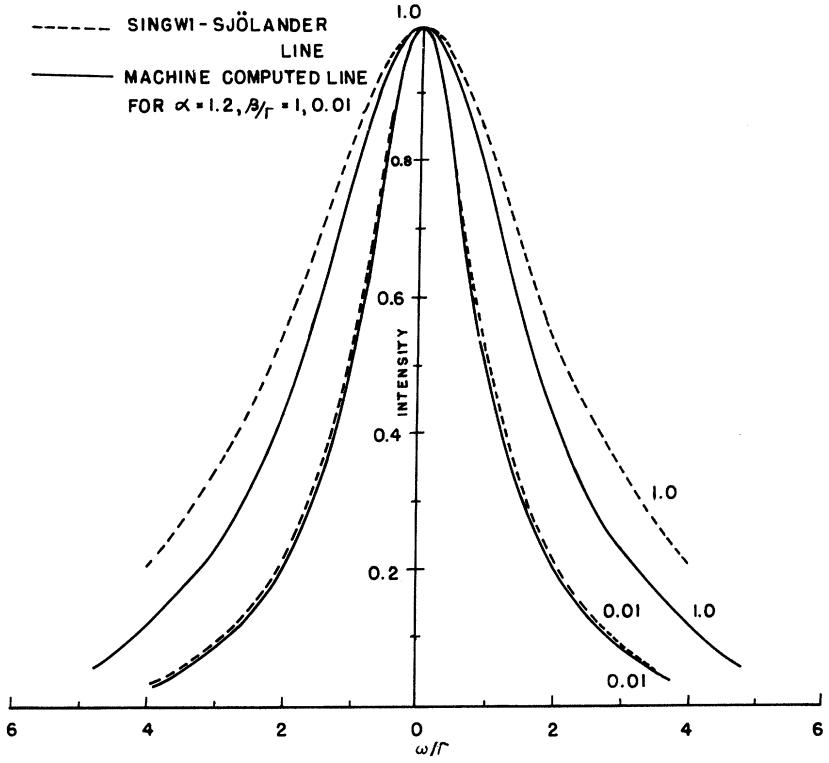

FIG. 2. Comparison of the machine-computed line with the Singwi-Sjölander Lorentzian for $\alpha=1.2$ and $\beta/\Gamma=1$ and 0.01 (2Γ is taken as the natural width).

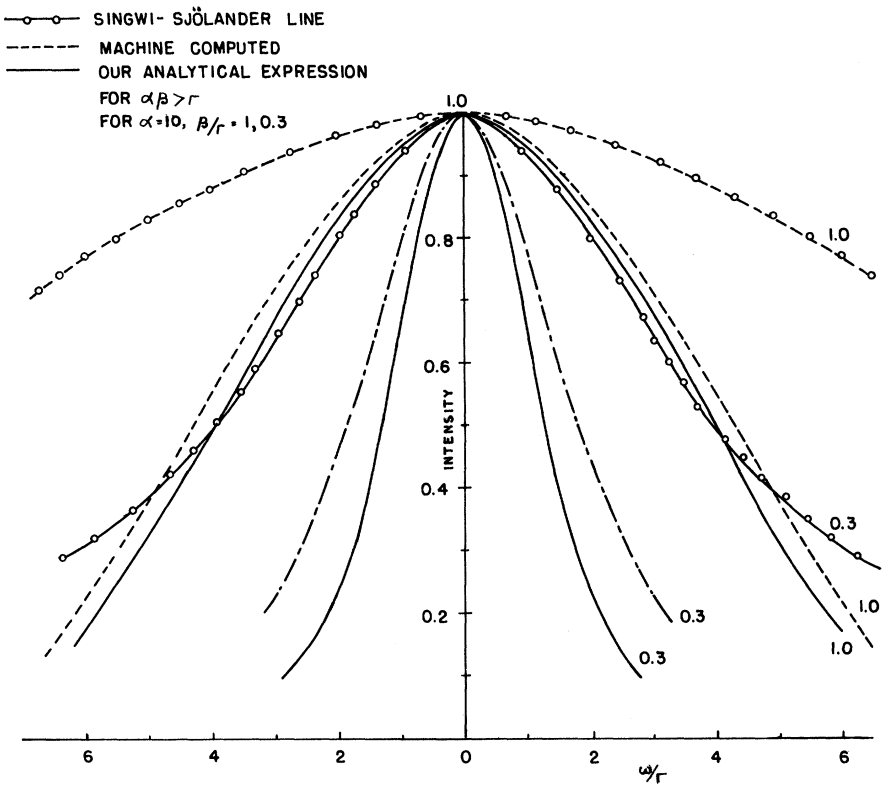

FIG. 3. Comparison of the machine-computed line with the Singwi-Sjölander Lorentzian and the line obtained from our expression for $\alpha\beta > \Gamma$ for $\alpha = 10$, and $\beta/\Gamma = 1$ and 0.3 (2Γ is taken as the natural width).

the need to evaluate the integral in Eq. (4) by machine computation. Figures 2 and 3 give a comparison of the machine-computed widths with those predicted by Singwi and Sjölander and by us. The narrowing predicted by our expression, as well as the shape of the line, are amply demonstrated by machine computation.

The narrowing is indeed expected from the nature of the expression

$$2\exp(\alpha)\int_0^\infty \exp(i\omega t)\cdot\exp[-(\tfrac{1}{2}\Gamma+\alpha\beta)t] \times\exp[-\alpha\exp(-\beta t)]\,dt\,.$$

The term $\exp[-\alpha\exp(-\beta t)]$ modulates the intensity I and alters the width of the resonance line. In the absence of this term, we get a linewidth $(\Gamma+2\alpha\beta)$ equal to that given by Singwi and Sjölander. When $\alpha > 1$, the term $\exp[-\alpha\exp(-\beta t)]$ cannot be neglected; in such a case it modulates the line and reduces the width of the line to a value less than $\Gamma+2\alpha\beta$. This situation is similar to the one encountered in nuclear magnetic resonance, where, under fast modulation, one obtains motional narrowing. Indeed, the line becomes increasingly narrow as α is increased.

There are several other situations in which such a narrowing can occur. In this context, it may be useful to refer to the work of Dash and Nussbaum[10] who pointed out the possibility of relaxational narrowing of the Mössbauer line. They considered a system in which emission of the resonance γ ray was preceded by a relatively energetic nuclear event such that the local environment is initially disturbed from equilibrium which subsequently relaxes. They assumed that the mean square displacement $\langle x^2\rangle$ of the impurity averaged over a period of localized mode relaxes with a single relaxation time β^{-1} (in our notation) according to

$$x^2-\langle x^2\rangle = (x_0^2-\langle x^2\rangle)\exp(-\gamma t) = 2\alpha\lambda^2\exp(-\beta t)\,,$$

where x_0^2 and x^2 are the initial and thermally relaxed values. They obtained the expressions for $E(t)$ and $E(\omega)$ as under

$$E(t) = \langle f\rangle^{1/2} e^{i\omega_0 t}e^{-(\Gamma/2)t}\exp(-\alpha e^{-\beta t})\,,$$

$$E(\omega) = \langle f\rangle^{1/2}\int_0^\infty e^{i\omega_0 t}e^{-(\Gamma/2)t}\exp(-\alpha e^{-\beta t})dt\,.$$

These expressions are similar to Eq. (4). Computer analysis showed that under certain circumstances, one could get a line narrower than the Mössbauer line. Although they did not explicitly specify the conditions, by implication they had chosen the condition $\alpha > 1$ and $1/\beta$ comparable with the nuclear lifetime. Indeed, if $1/\beta$ is very small of the order 10^{-12}–10^{-20} sec, much smaller than nuclear lifetime, the width of the line would

be the natural linewidth.

An upper limit on narrowing due to diffusion broadening can be inferred from our general expression

$$\sigma_a(\omega)=\frac{\sigma_0\Gamma}{2\beta S}A\left(1+\frac{\alpha}{s+1}+\frac{\alpha^2}{(s+1)(s+2)}+\cdots\right).$$

When $\alpha\to\infty$, $\beta\to 0$, the above goes over to

$$\sigma_a(\omega)=\frac{\sigma_0\Gamma A}{2\beta S}\left(1+\frac{\alpha}{s}+\frac{\alpha^2}{s^2}+\cdots\right)$$

$$=\frac{\sigma_0\Gamma A}{2}\frac{1}{\Gamma+i\omega},$$

giving a Lorentzian with natural linewidth. This is the adiabatic approximation. In the present model which we have considered, namely, the Langevin model of diffusion, the satisfaction of the space-resolution condition does not yield any additional information regarding the time aspects of the motion; but if we can consider the atomic motion in a liquid where such a condition is satisfied, then γ-ray scattering can yield information regarding the dynamics of motion in the liquid.

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Mössbauer Determination of Fe^{57} Nuclear Quadrupole Coupling Parameters in Ferric Oxychloride

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The nuclear quadrupole coupling parameters have been determined at the nonaxially symmetric Fe^{3+} site in ferric oxychloride by Mössbauer spectroscopic measurements. This compound should be suitable for checking theoretical models used to calculate electric field components and their derivatives in ionic solids. The quadrupole splitting (peak separation) is found to be 0.916 ± 0.001 mm/sec. The x, y, and z principal axes of the electric field gradient (EFG) are parallel to the c, b, and a crystallographic axes, respectively ($c<a<b$). The EFG asymmetry parameter is $\eta=0.32\pm0.03$ and $V_{zz}<0$. A lattice-sum calculation of the EFG based on the self-consistent monopole-point dipole model can be made to fit the data by suitable adjustment of the anion polarizabilities; however, the necessary polarizabilities and the Fe^{57} quadrupole moment which is obtained do not seem entirely satisfactory.

I. INTRODUCTION

In recent years, the calculation of electric potentials and potential derivatives at sites in ionic crystals has usually employed some version of the self-consistent monopole-point dipole model.[1-5] Briefly, the model involves the evaluation of monopole contributions by a lattice-sum technique and the inclusion of dipole contributions by a self-consistent calculation of ionic dipole moments. The dipole-moment calculation requires independent knowledge of ionic polarizabilities.

There have been few experimental tests of this model. The most rigorous of these was a compari-