

alloying with an element which either donates extra electrons into the  $d$  band or causes a lattice expansion narrowing the  $d$  band. At the surface, we expect the  $5d$ -band structure to be perturbed by virtue of the change in local symmetry and the reduction of the coordination number,  $z$ . It is not clear without detailed calculations which of these mechanisms is dominant. It is easy to see, however, that a narrowing of the  $d$  band by virtue of the reduced coordination number (bandwidth is assumed proportional to  $\sqrt{z}$ ) would raise the Fermi energy and begin to populate the  $4f^6$  state. This in turn would cause an expansion of the lattice, resulting in further band narrowing. In this way a relatively small perturbation could result in an instability leading to the intermediate-valence state which is experimentally observed. More detailed theoretical treatment is clearly needed to provide an understanding of this surface-valence transition.

It is natural to inquire whether this phenomenon is likely to occur in other elements. Among the rare-earth metals only thulium has a similar low-lying empty  $4f$  state,<sup>8,9</sup> but the excitation energy is  $\sim 1$  eV, making it less likely to have a sponta-

neous surface-valence transition. Other examples may be found among the intermetallic compounds of trivalent samarium and ytterbium.

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## Frequency Dependence of the Spin-Spin Relaxation Rate from Mössbauer Spectroscopy

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The frequency dependence of the relaxation parameter which determines the line shape of the Mössbauer spectrum in spin-spin relaxation is derived directly from the experimental spectrum for the case of the 84-keV resonance of  $^{170}\text{Yb}$  in  $\text{Cs}_2\text{NaYbCl}_6$ . The scale of the frequency variation of its relaxation parameter is in agreement with a theoretical estimate.

Theoretical treatment of Mössbauer hyperfine spectra in the presence of electronic relaxation characterizes, by a correlation time  $\tau_c$ , the fluctuation of the electromagnetic field acting on the Mössbauer atom. These fluctuations then cause relaxation processes in the atoms electronic shell which are described by the relaxation time

$\tau_r$ . Most present theories<sup>1-4</sup> deal with the limiting case where  $\tau_c$  is much shorter than either  $\tau_r$  or the "precession time"  $\tau_L$  of the nuclear spin in the hyperfine field ( $\tau_L = \hbar/A$ , with  $A$  = hyperfine coupling constant). Both conditions, are safely fulfilled in spin-lattice processes<sup>1</sup> where, for example,  $\tau_L \approx \hbar/k_B \Theta$  ( $\Theta$  = Debye temperature) and

for relaxation mechanisms involving conduction electrons,<sup>3,4</sup> e.g., Korringa relaxation, where  $\tau_c \approx \hbar/k_B T$ . The relaxation spectra can then be expressed in terms of a set of relaxation parameters which are independent of frequency within the range of the hyperfine splitting (white-noise approximation, WNA).

In spin-spin relaxation,  $\tau_c$  and  $\tau_r$  are both given by the same interaction  $J$  which could either be a dipole-dipole or an exchange coupling. If, in addition,  $J \sim A$  (which is not uncommon in actual situations), the theoretical treatment must be modified by introducing frequency-dependent relaxation functions. A first calculation<sup>5</sup> of Mössbauer line shapes under these conditions used a phenomenologically introduced  $\omega$  dependence of the relaxation operator. There, as in all treatments of relaxation spectra performed to date, one used an approximate theoretical function for the relaxation operator which reproduces the experimental spectrum as accurate as possible.

In contrast, we are concerned in this work with the possibility of extracting information on the specific form of the frequency dependence of the relaxation function directly from the measured spectrum without using any explicit form of a theoretical approximation of the relaxation operator. Little is known from first principles on the actual form of its  $\omega$  dependence. A considerable amount of theoretical work has been done with the aim to derive analytical expressions<sup>6</sup> for the spin-spin correlation function or to calculate it numerically<sup>7</sup> for various physical processes. The problem of spin-spin correlations is in particular a long-standing one with respect to EPR and NMR line shapes. Such calculations of line shapes again require some type of approximation. To circumvent this problem the method of moments<sup>8</sup> is commonly used. However, the theoretical calculation of higher-order moments becomes difficult and their experimental determination unreliable.

The derivation of the formalism used in this work to extract the relaxation function from the Mössbauer resonance pattern will be given in detail elsewhere.<sup>9</sup> The main emphasis of this Letter is to demonstrate that this task can indeed be achieved but requires the availability of experimental data of high accuracy. Such data have been obtained by measuring in transmission geometry the Mössbauer spectrum of <sup>170</sup>Yb in the cubic compound Cs<sub>2</sub>NaYbCl<sub>6</sub>, where the relaxation process is known to be due to spin-spin interactions and where the breakdown of the WNA has

been shown<sup>5</sup> to be significant. A specially developed fast counting system<sup>10</sup> was used which made possible to obtain the required statistical accuracy of the data. The geometrical variations of the "off-resonance baseline" were kept small by measuring with a sinusoidal velocity sweep at high frequency (65 Hz) and by a careful alignment of source and absorber. The source consisted of 15 wt% Tm in Al with 8 Ci of <sup>170</sup>Tm activity. The isotopically enriched absorber had a thickness of 20 mg/cm<sup>2</sup> of <sup>170</sup>Yb. Both the source and absorber were kept at 4.2 K.

The general expression for the Mössbauer line shape in the presence of electronic relaxation is given by<sup>5,11-13</sup>

$$\rho(\omega) = -\text{Im} \sum_{\alpha} \langle \vec{\eta}_{\alpha} * \vec{j}(\kappa) [\mathbf{u}]^{-1} \vec{\eta}_{\alpha} \vec{j}^{\dagger}(\kappa) \rangle, \quad (1)$$

$$\mathbf{u} = \omega - \hat{L}_A - \hat{M}(\omega) + i\Gamma/2.$$

This expression is exact<sup>13</sup> as long as very low temperatures are excluded (i.e.,  $A \ll k_B T$ ) which is fulfilled in most experiments. The Liouville operator  $\hat{L}_A$  describes the various transitions caused by the hyperfine interaction. The current operators  $\vec{j}(\kappa)$  contain the transition probabilities and  $\vec{\eta}_{\alpha}$  is the  $\gamma$ -ray polarization vector. The formal expression for the relaxation superoperator  $\hat{M}(\omega)$  can be found, for example, in Ref. 13. In general, the inapplicability of the WNA causes the number of independent matrix elements of  $\hat{M}(\omega)$  to increase sharply besides the already-mentioned fact that they are now functions of the frequency (energy) of the incident resonant photon. Their number depends on the nuclear spin in the ground ( $I_g$ ) and the excited ( $I_e$ ) state, on the effective spin  $S$  of the electronic ground state and on the environmental symmetry of the resonant atom. Here one has  $I_g = 0$ ,  $I_e = 2$ ,  $S = \frac{1}{2}$ , and cubic symmetry, which represents the simplest situation available in Mössbauer spectroscopy. The electronic ground state is an isolated  $\Gamma_6$  doublet which has isotropic hyperfine coupling. This allows the application of well-known group-theoretical principles<sup>14</sup> which finally reduce the number of independent relaxation functions to only two. They shall be denoted  $\gamma_1(\omega)$  and  $\gamma_2(\omega)$ . These complex functions can be expressed in terms of the real functions  $\bar{\gamma}_{1,2}(\omega)$  with the help of the transformation

$$\gamma_{1,2} = \pi^{-1} \int \bar{\gamma}_{1,2}(\omega') d\omega' [\omega - \omega' + i\Gamma/2]^{-1}. \quad (2)$$

In subsequently calculating the moments,

$$M_{1,2}^{(n)} = \int \omega^n \bar{\gamma}_{1,2}(\omega) d\omega, \quad (3)$$

it is found that any difference between  $\bar{\gamma}_1$  and  $\bar{\gamma}_2$  reveals itself only in the fourth and higher moments. We therefore may make use of the approximation

$$\gamma_1(\omega) \approx \gamma_2(\omega) = \gamma(\omega) \quad (4)$$

which now allows us to describe the relaxation process with only one frequency-dependent function  $\gamma(\omega)$ .

The experimental spectrum can be expressed in the form [see also Eq.(1)]

$$\rho(\omega) = -\text{Im}\tilde{F}(\omega) = -\text{Im}F(\omega)e^{i2\xi} = \tilde{F}''(\omega). \quad (5)$$

The factor  $e^{i2\xi}$  which transforms  $F(\omega)$  into  $\tilde{F}(\omega)$  arises from the dispersion term in the line shape of the 84-keV resonance in  $^{170}\text{Yb}$  because of an interference between photoelectrons and conversion electrons.<sup>15</sup> The value of the dispersion amplitude  $\xi = -0.02$  is known from independent experiments.<sup>16</sup> Normalization of the experimental spectrum to  $\int \rho(\omega) d\omega = \pi$  directly gives  $\tilde{F}''(\omega)$  (see Fig. 1). The real part of  $\tilde{F}(\omega)$  can be obtained by a numerical calculation using the Kramers-Kronig relation

$$\begin{aligned} \tilde{F}'(\omega) &= \text{Re}\tilde{F}(\omega) \\ &= -\pi^{-1} \int \tilde{F}''(\omega') d\omega' [\omega - \omega']^{-1}. \end{aligned} \quad (6)$$

It is shown in Fig. 2.

The connection between the modified experimental spectrum  $F(\omega)$  and the relaxation function  $\gamma(\omega)$  is given by<sup>9</sup>

$$\gamma(\omega) = \bar{\omega} + A/2 - 1.5A^2 F(\omega) [\bar{\omega} F(\omega) - 1]^{-1}, \quad (7)$$

where  $\bar{\omega} = \omega + i\Gamma/2$ . Note that Eq. (7) contains  $F(\omega)$  and not  $\tilde{F}(\omega)$ . This simple analytical relation can easily be evaluated and from  $F(\omega) = F'(\omega) - iF''(\omega)$  the relaxation function  $\gamma(\omega) = \gamma'(\omega)$

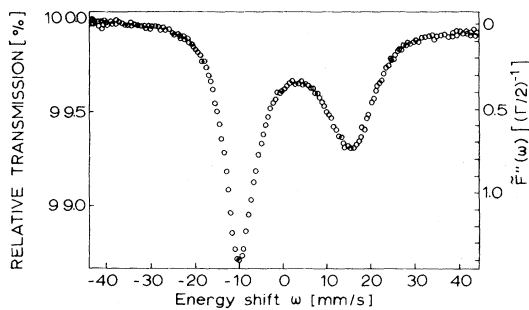


FIG. 1. Mössbauer spectrum of  $\text{Cs}_2\text{NaYbCl}_6$  at 4.2 K. The total number of counts per velocity point is  $2 \times 10^8$ . The right-hand scale give  $\tilde{F}''(\omega)$  as obtained by the normalization procedure described.

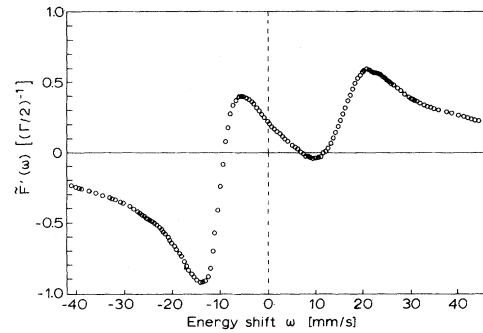


FIG. 2.  $\tilde{F}'(\omega)$  as obtained from the data of Fig. 1 using Eq. (6).

$-i\gamma''(\omega)$  was determined using<sup>17</sup>  $A = 10.2$  mm/s. The result is shown in Fig. 3. The procedures of normalization and integration which are necessary to obtain  $F''(\omega)$  and  $F'(\omega)$  require high statistical accuracy and exactly straight baseline if usable results for  $\gamma''(\omega)$  and  $\gamma'(\omega)$  are to be gained. The error bars in Fig. 3 are solely based on the statistical error of each datum point. The additional term which arises from the uncertainty of the exact location of the baseline is difficult to estimate but believed to be smaller. It has been omitted. The relaxation functions of Fig. 3 show a noticeable frequency dependence suggesting, for example, two weak maxima in  $\gamma''(\omega)$ . Within the present limits of error which rapidly increase towards larger energy shifts, we cannot exactly locate the positions of the maxima. They appear to be related to the hyperfine-interaction

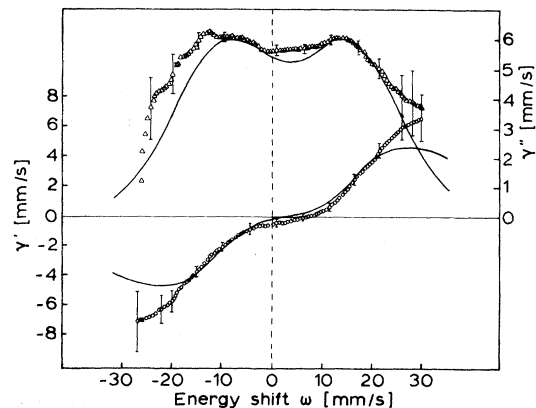


FIG. 3. Frequency dependence of the imaginary part (triangles, upper curve, right-hand scale) and the real part (circles, lower curve, left-hand scale) of the relaxation function as derived from the data of Figs. 1 and 2. The full lines are calculated functions as explained in the text.

frequencies. An interpretation in terms of the underlying physical processes has to await even better data. The frequency dependence of  $\gamma(\omega)$  as derived from the present experiment reflects the dipole-dipole interaction as seen through the nuclear hyperfine coupling. It is thus not possible to obtain in this manner the total frequency spectrum of the pure dipole bath.

We have simply approximated the experimental functional dependence of  $\gamma''(\omega)$  by a sum over two identical Gaussians centered at the frequencies  $\omega_1 = -\frac{3}{2}A$  and  $\omega_2 = A$  of the static hyperfine interaction

$$\gamma''(\omega) = K(\omega - \omega_1) + K(\omega - \omega_2). \quad (8)$$

Here  $K(\omega) = (\sqrt{\pi}/4)\Delta\omega \exp[-\omega^2/(\Delta\omega)^2]$  and  $\Delta\omega$  is the width of the Gaussians which is connected<sup>9</sup> to the moment  $M^{(2)}$  as defined in Eq. (2). Its value was calculated to be  $\Delta\omega = 17$  mm/s in a similar manner as that for the dipolar field in Ref. 5. This curve (solid lines in Fig. 3) roughly reproduces the experimental result. It mainly shows that the variations of  $\gamma(\omega)$  lies within the range of hyperfine frequencies which is to be expected if the white-noise approximation is not valid. Finally we wish to point out, that the approximation (4) is not basic to this type of analysis. It can be avoided if a single-crystal absorber is used. It is then always possible to select the direction of the  $\gamma$ -ray beam such that  $F(\omega)$  is completely determined by either  $\gamma_1(\omega)$  or  $\gamma_2(\omega)$  alone.<sup>9</sup>

In summary, we have shown that the functional dependence of the relaxation parameter can be derived from the Mössbauer spectra. This is of importance since details of the physical processes which govern spin-spin relaxation are not understood at present. In order to keep the errors in such limits that definite conclusions on the underlying physical processes can be drawn, further improvements designed to reduce the remaining experimental uncertainties (e.g., baseline location) are necessary. Such work is presently in progress.

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