anharmonic potential, it is certainly large enough to account for the observed maximum. This interpretation is supported by the fact that maxima of similar shapes have been observed previously in the energy spectra of channeled particles, e.g., in Farmery et al.[3] and Sattler and Dearnaley.[4] Thus one may infer that the population of the peaks in Fig. 1 is determined primarily by the mosaic sturcture and the beam divergence rather than by the interaction potential.

The method proposed to calculate the distribution of amplitudes can be extended to deal with an anharmonic potential. Then further applications arise, because it might soon be possible to determine experimentally the energy loss as a function of the amplitude.[1] The calculated distribution of amplitudes can then be used to obtain the energy and range distributions for channeled ions in terms of experimental parameters, e.g., the angle of incidence, beam divergence, mosaic structure, and crystal thickness.

I am pleased to acknowledge helpful discussions with the authors of Ref. 1.

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TEMPERATURE-DEPENDENT SPIN-SPIN RELAXATION TIMES: APPLICATION TO THE MÖSSBAUER SPECTRA OF FERRIC HEMIN*

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The Mössbauer spectra of ferric hemin are interpreted on the basis of a temperature-dependent electronic spin-spin relaxation time. The relaxation slows down with increasing temperature as a result of a change in population of ionic energy levels. The slowing down of the relaxation time, together with other effects resulting from population changes, produces a quadrupole-split line which becomes asymmetric as the temperature is increased.

Several studies of hemoglobin and related compounds have been made using the Mössbauer effect,[1] and a thorough interpretation of many of the results has been given.[2] The spectrum of ferric hemin is the only one of the compounds studied for which even a qualitative explanation is lacking, and in this Letter one is suggested.

The experimental features for which an interpretation is required can be seen in the results of Shulman and Wertheim, which are shown in Fig. 1. At 4°K, the Fe^{57} spectrum shows a pair of lines which appear to be the usual two-line quadrupolar pattern. As the temperature is raised this pattern becomes asymmetric, with one of the lines broadening considerably more than the other, until, at room temperature, the spectrum consists of a single broad line. This behavior is reminiscent of the asymmetric quadrupole doublets which can be produced by magnetic relaxation effects,[3] and it is reasonable to expect that magnetic relaxation is in some way responsible for the observed temperature dependence. The difficulty here is that the spectrum becomes asymmetric as the relaxation becomes slower, so that a relaxation mechanism must be found which becomes slower as the temperature is raised.

The essential features of the proposed explanation of these phenomena are the following: (a) As the temperature is increased, excited states of the Fe^{3+} ion, which have slower relaxation rates, are populated, so that nuclei whose ions are in these states produce asymmetric spectra, and (b) the spin-spin relaxation time itself, which is the dominant relaxation mechanism, varies with temperature even for the ground state, and indeed becomes somewhat slower as the temperature is raised. The temperature dependence of the spin-spin relaxation time is somewhat surprising at first

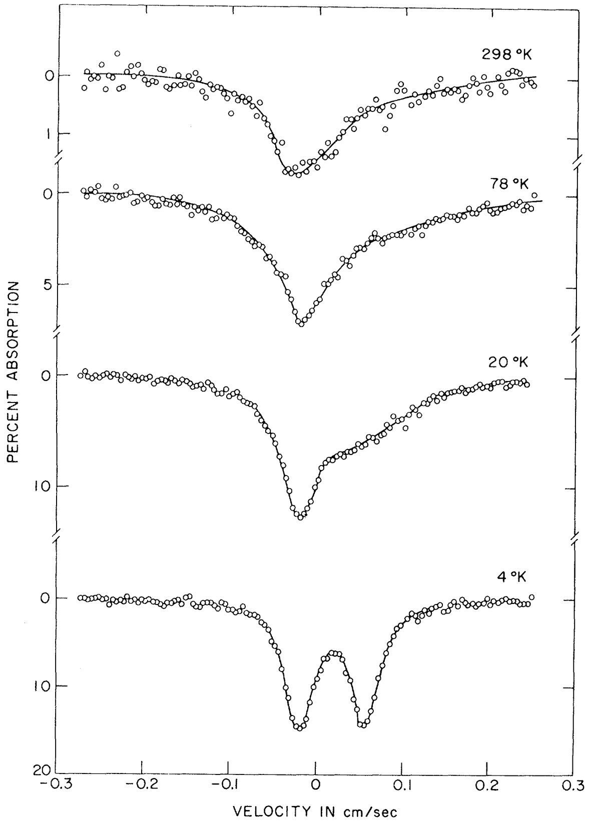

FIG. 1. Experimental results of Shulman and Wertheim for ferric hemin.

sight, but it is simply due to the change in population of the energy levels of the ions.

Let us consider these points in more detail. The energy levels of the Fe^{3+} ion in ferric hemin are as shown in Fig. 2. The $^6S_{5/2}$ ground state of Fe^{3+} has been split by axial crystalline fields into three doublets, as shown. The splitting Δ, which has been determined to be 18°K,[4] is large for an S-state ion, but it is consistent with values found in similar compounds. The hyperfine structure of the $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$ levels can be represented by an effective magnetic field at the nucleus, since $g_\perp = 0$ for these levels, but the structure of the $\pm\frac{1}{2}$ level is more complicated.[5] We can remove this complication by imagining a small magnetic field along the z axis to be present which lifts the degeneracy of the $\pm\frac{1}{2}$ levels, so that the hyperfine structure of these levels can also be represented by an effective magnetic field at the nucleus. This should not change the qualitative picture greatly. The electric field gradient at the nucleus is assumed due to the fixed charges which surround the ion. We expect that the spin-lattice relaxation of the ion is slow compared with the spin-spin relaxation, since the ion is in an S state. The spin-spin relaxation causes the ion to make transitions between the different sublevels, and these transitions will produce a randomly varying time-dependent magnetic field at the nucleus. The Hamiltonian for the nucleus on this picture can then be represented by

$$\mathcal{H}(t) = Q(3I_z^{\,2} - I^2) + g\mu h I_z f(t), \tag{1}$$

where $f(t)$ is a random function of time which can take on the six values $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{5}{2}$, and these values represent the effects of the ion being in the different states. The constant h is the value of the hyperfine field produced by the ion at the nucleus. For hemin, $\frac{5}{2}h = 550$ kOe. In order to specify the function $f(t)$ completely we must construct the matrix of the transition probability per unit time between the various values which the function can take on. We do this on the assumption that the transitions are due to the dipole-dipole interaction between the ion which contains the Mössbauer nucleus and the other ions in the sample. This interaction is proportional to $(r_j^{\,3})^{-1}\{(\vec{S}\cdot\vec{S}_j) - 3(\vec{S}\cdot\hat{r}_j)(\vec{S}_j\cdot\hat{r}_j)\}$, and the transitions will be induced by the terms of the form $(r_j^{\,3})^{-1}(1-3\times\cos^2\theta_j)(S_+S_{j-} + S_-S_{j+})$. Using the golden rule, we find that the transition probabilities are of the form

$$W(m \rightarrow m') = |\langle m'|S_\pm|m\rangle|^4 \times C \times \bar{n}(m'). \tag{2}$$

The fourth power of the matrix element enters because the golden rule involves the square of the matrix element of the interaction, and in order for one ion to make a transition from m to m', another must make a transition from m' to m. For the same reason the factor $\bar{n}(m') = e^{-Em'/kt}/\sum_m e^{-Em/kt}$, the Boltzmann fac-

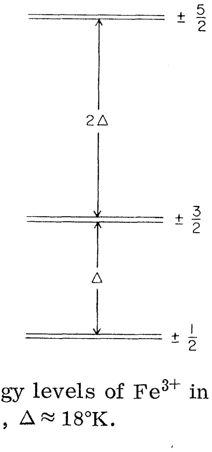

FIG. 2. Energy levels of Fe^{3+} in an axial crystalline field. In hemin, $\Delta \approx 18$°K.

tor for the level m', enters. Finally, the constant C is proportional to $\sum_j (1-3\cos^2\theta_j)^2/r_j^6$ and is dependent on the interionic Fe^{3+}-Fe^{3+} distance. We see from this how the temperature dependence of the spin-spin relaxation arises in the $\pm\frac{1}{2}$ levels. In order for one ion to go from $+\frac{1}{2}$ to $-\frac{1}{2}$, a neighboring ion must make a transition from $-\frac{1}{2}$ to $+\frac{1}{2}$. At low temperatures only the $\pm\frac{1}{2}$ levels are occupied, but at temperatures large compared with Δ the $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{5}{2}$ levels are occupied equally. The transition probability is thus reduced by a factor of 3 on increasing the temperature. Calculation of the matrix elements of S_+ in (2) gives

$$W(\pm\tfrac{1}{2}\rightarrow\mp\tfrac{1}{2}) = 81C\bar{n}(\tfrac{1}{2}),\quad W(\pm\tfrac{1}{2}\rightarrow\mp\tfrac{3}{2}) = 64C\bar{n}(\mp\tfrac{3}{2}),$$
$$W(\pm\tfrac{3}{2}\rightarrow\pm\tfrac{5}{2}) = 25C\bar{n}(\pm\tfrac{5}{2}),$$

etc., and

$$\bar{n}(\pm\tfrac{1}{2}) = 1/Z,\quad \bar{n}(\pm\tfrac{3}{2}) = e^{-\Delta/kT}/Z,$$
$$\bar{n}(\pm\tfrac{5}{2}) = e^{-3\Delta/kT}/Z;$$
$$Z = 2(1+e^{-\Delta/kT}+e^{-3\Delta/kT}).$$

From these expressions we see that the relaxation times in the excited states will be longer than those of the ground states. Hence, as the excited levels are populated, the spectrum should become more asymmetric, since it will consist of a superposition of the spectrum of ions in the ground state with spectra of ions in the more slowly relaxing excited states. To calculate the line shape quantitatively we use the expression[6]

$$I(\omega) = \frac{2}{\Gamma}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t-\frac{1}{2}\Gamma t}(\langle H^{(-)}H^{(+)}(t)\rangle)_{\mathrm{Av}}, \tag{3}$$

where $H^{(+)}$ is the operator for emission of a γ ray by the nucleus, Γ is the natural linewidth, and $(\;)_{\mathrm{Av}}$ indicates an average over the random function $f(t)$. Such averages have been discussed by Anderson[7] and Sack,[8] and they involve the inversion of the matrix of transition probabilities. The calculations have been done numerically, and they yield the spectra shown in Fig. 3. The constant C in (2) has been chosen to give the best fit to experiment. All other parameters are fixed. The relaxation time in the $\pm\frac{1}{2}$ level to which the value of C corresponds is $\approx 10^{-10}$ sec, which is the order of magnitude expected for spin-spin relaxation of Fe^{3+} ions separated by ~7 Å. The agreement with experiment is excellent.

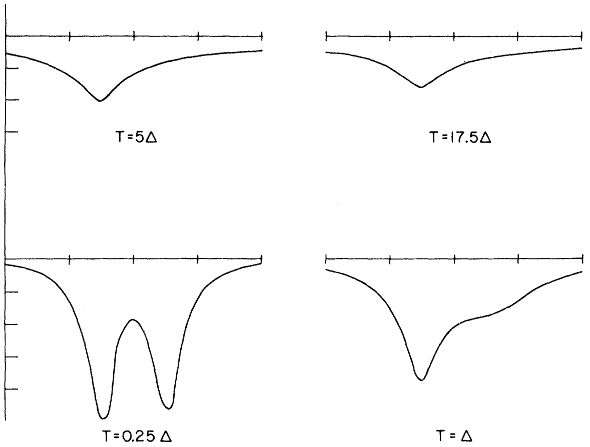

FIG. 3. Theoretical Mossbauer spectra. Temperatures are given in units of the crystalline field splitting Δ.

A number of features have not been considered in the simplified model presented here. Foremost is the nature of the hyperfine interaction in the $\pm\frac{1}{2}$ level. We have assumed that relaxation between these levels produces a field at the nucleus which jumps at random along the z axis between the values ±110 kOe. This is strictly correct only if there is a small external field along the z axis. If an external field is placed along the x axis, the field at the nucleus would jump along that axis between the values ±330 kOe (the larger value occurs because of the anisotropy of the g factor in the $\pm\frac{1}{2}$ levels). The solution of the line shape in the case where the field jumps from one axis to another is also possible, although it is more complicated. No great change in the spectra or in the temperature dependence is expected in that case.

In summary, the Mössbauer spectra of ferric hemin can be explained on the basis of spin-spin relaxation effects. The spin-spin relaxation time is temperature dependent, slowing down somewhat as the temperature is increased.

I would like to thank R. M. Housley for helpful discussions, and R. G. Shulman and G. K. Wertheim for permission to use their unpublished data (Fig. 1).

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EXCHANGE INTEGRAL IN RARE-EARTH METALS

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Calculations of 4*f*-6*s* electron exchange integrals have been made in order to determine the sign of the exchange integral and the dependence of the integral upon interatomic distance. The exchange integral is found to be positive in sign, and insensitive to changes of interatomic distance. By contrast, the magnetic interactions in rare-earth metals are quite sensitive to changes of interatomic distances in the crystal; it is concluded that this sensitivity is not attributable to variations of the exchange integral.

Two questions which are of interest in the theory of magnetic and electronic interactions in the rare-earth metals are as follows: (1) What is the sign of the 4*f*-electron–conduction-electron exchange integral $I(k,k')$? (2) What is the dependence of $I(k,k')$ upon interatomic distance? The first question is discussed in detail by Van de Braak and Caspers[1]; the second is of interest in the interpretation of the effect of pressure upon the Curie temperatures of the rare-earth metals.[2-4]

A problem which arises in a calculation of $I(k,k')$ is that accurate wave functions for the conduction electron are not available. One approximation has recently been made by Van de Braak and Caspers[1] who evaluated $I(k,k')$ for the case when the conduction electron is represented by a plane wave in an *s* state. They found $I(k,k')$ to be positive; their $I(k,k')$ is insensitive to interatomic distance.

Elliott[5] has suggested that "$I(k,k')$ will be similar to the atomic 6*s*-4*f* exchange integrals. It will probably not depend very strongly on *k* and *k'*." Based upon this suggestion we have calculated upon the 7094 computer the exchange integral I for gadolinium, using a 6*s* wave function to represent the conduction electron instead of the plane-wave approximation. It appears quite reasonable to assume that where the 4*f* wave function is large, i.e., in the inner regions of the electronic structure of the ion, the conduction electron is expected to possess some of the characteristics of a bound 6*s* electron.

The general expression for a 6*s*-4*f* exchange integral is

$$I=\iint\psi_{4f}^*(\vec{r}_1)\psi_{6s}^*(\vec{r}_2)\frac{e^2}{r_{12}}\times\psi_{4f}(\vec{r}_2)\psi_{6s}(\vec{r}_1)d\vec{r}_1d\vec{r}_2, \tag{1}$$

where each symbol has its usual meaning.

Substituting

$$\psi_{6s}(\vec{r})=R_{6s}(r)Y_0^{\,0}(\theta,\varphi), \tag{2}$$

$$\psi_{4f}(\vec{r})=R_{4f}(r)Y_{l'}^{\,m'}(\theta,\varphi), \tag{3}$$

and

$$\frac{1}{r_{12}}=\sum_{l,m}\frac{4\pi}{2l+1}\frac{r_<^{\,l}}{r_>^{\,l+1}}Y_l^{\,m}(\theta_1,\varphi_1)Y_l^{\,m*}(\theta_2,\varphi_2) \tag{4}$$

into Eq. (1), with $l'=3$ for a 4*f* electron, one finds that

$$I=\frac{e^2}{2l'+1}\int_0^\infty dr_2\,r_2^{\,2}R_{6s}(r_2)R_{4f}(r_2)\times\int_0^\infty dr_1\,r_1^{\,2}R_{6s}(r_1)R_{4f}(r_1)\frac{r_<^{\,3}}{r_>^{\,4}}. \tag{5}$$

Equation (5) was evaluated upon the computer. The radial wave functions used were those given by Freeman and Watson[6] based upon their Hartree-Fock calculations for a free ion. The 4*f* function for Gd^{+3} was given in the form

$$rR_{4f}(r)=\sum_{i=1}^{4}C_i r^4\exp(-Z_i r).$$