

## Effect of diffusion by the vacancy mechanism on Mössbauer line broadening\*

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The effect of the self-diffusion of a Mössbauer active atom, by the vacancy mechanism, on the resonance line shape is studied in several approximations and by direct computer calculation of the motions of the active atom and a vacancy. The results for self-diffusion in simple and body-centered-cubic lattices show that the empty-lattice solution can be used as a first approximation if the jump time is scaled by the Bardeen-Herring correlation coefficient for bulk diffusion. This approximation is correct within about (5 to 10)%.

### I. INTRODUCTION

In 1960 Singwi and Sjölander<sup>1</sup> predicted that the Mössbauer effect could be used to study diffusion in solids and liquids. With some simplifying assumptions, they showed that the resonant line should broaden by an amount proportional to the diffusion coefficient of the Mössbauer probe. It can thus be expected that such an effect will be observed if the lifetime of the excited state is of the order of the inverse of the jump frequency.

For the case of uncorrelated jumps in random directions in space, the predictions of Singwi and Sjölander could be shown to give a broadening

$$\Delta\Gamma \cong 2\hbar/\tau_a. \quad (1)$$

From this and the uncertainty relation we can immediately see that when  $\tau_a \cong \tau_m$  the broadening is of the same order of magnitude as the natural line width, where  $\tau_a$  is the inverse of the atomic jump frequency, and  $\tau_m$  is the lifetime of the Mössbauer excited state.

The first direct measurements of diffusion broadening of the Mössbauer peaks in solids, carried out by Knauer and Mullen,<sup>2,3</sup> did show the general behavior predicted by Eq. (1). The peak shapes were Lorentzian, as predicted by the theory, but the actual broadening measured differed by about a factor of 2 from the predicted one. Later measurements on Fe-3-wt%-Si by Lewis and Flinn,<sup>4</sup> however, gave results close to the predicted ones.

Several other measurements of diffusion coefficients of solids and liquids have been done using this method.<sup>5-9</sup> Two of these are on solids. Anand and Mullen report a broadening about 0.6 of the one predicted by equation. Measurements by Sørensen and Trumpy do not contribute to the existing controversy as the authors doubt the reliability of the bulk diffusion measurements used for comparison.

The Singwi and Sjölander assumptions differ from the physical situation for diffusion in polycrystal-

line metals in two ways. Diffusion in metals occurs in crystallographically determined directions rather than in random directions and since it occurs by the vacancy mechanism, successive jumps of a given atom are correlated. The effects of the crystallographic restriction of jump directions has been discussed in a previous paper.<sup>10</sup> In this paper we will discuss the correction to equation one due to the correlation effect.

Previous attempts to obtain a theoretical expression for broadening in the case of diffusion by the vacancy mechanism have used several approximations and adjustable parameters.<sup>11-13</sup> It seemed worthwhile, then, to carry out a direct calculation.

We follow the movements of the active atom and a vacancy in detail, showing that the principal correction to the uncorrelated solution for single crystals (as obtained by Chudley and Elliott<sup>14</sup>) for the simple cubic and bcc cases is simply the well-known Bardeen-Herring correlation factor for bulk diffusion and there is no reason to expect that the fcc will be significantly different. The method used can easily be generalized to cases where the marked atom jump frequency is different from the host's.

When the single-crystal solution is averaged over all directions, the result is substantially different from the solution to the liquidlike model generally used to analyze experimental data. Application of this correction, together with the bulk diffusion correlation factor, largely eliminates the discrepancy between theory and experiment.

### II. GENERAL FORMULATION

It is well known<sup>15</sup> that the intermediate scattering function  $\mathcal{F}_s(\vec{k}, t)$  is the space Fourier transform of the Van Hove function  $G(\vec{R}, t)$ , which in the classical limit is the probability that the particle be at  $\vec{R}$  at the time  $t$  if it was at  $\vec{R}=0$  at  $t=0$ . The cross section of resonant absorption  $\sigma$  may be obtained from the intermediate scattering function as

$$\sigma(E) \propto \int_{-\infty}^{+\infty} dt e^{i t(E-E_0)/\hbar - \Gamma |t|/2\hbar} \mathcal{F}_s(\vec{k}, t), \quad (2)$$

where  $E_0$  is the resonant energy and  $\Gamma$  the natural width.

The motions of an atom in a lattice include both oscillations and jumps to neighboring sites (diffusion). We assume that these two types of motion are uncorrelated, since even at very high temperatures, the frequency of diffusive jumps is much smaller than the frequency of oscillation ( $\nu_{\text{diff}} \sim 10^8$  jumps per sec;  $\nu_{\text{vibr}} \sim 10^{13}$  vibrations per sec). Then we may write

$$G_{\text{tot}} = G_{\text{diff}} G_{\text{vibr}}.$$

$G_{\text{vibr}}$  has been thoroughly studied<sup>1, 14</sup> for harmonic solids and is known to give an absorption cross section with a central peak of Lorentzian shape and natural width (Mössbauer effect). We will concentrate on the effect of diffusion which can then be convoluted with this Lorentzian.

### III. DIFFUSION IN AN EMPTY LATTICE

The simplest case, that of diffusion in an empty lattice, was studied by Chudley and Elliott.<sup>14</sup> The probability  $G(\vec{r}, t)$ , of finding an atom at a position  $\vec{r}$  at a time  $t$ , satisfies the following differential equation:

$$\begin{aligned} \frac{\partial}{\partial t} G(\vec{r}, t) &= \frac{1}{n\tau_a} \sum_{\vec{I}} [G(\vec{r} + \vec{I}, t) - G(\vec{r}, t)] \\ &= \frac{1}{n\tau_a} \left( \sum_{\vec{I}} \hat{g}(\vec{I}) - n \right) G(\vec{r}, t), \end{aligned} \quad (3)$$

where  $\hat{g}(\vec{I})$  is the displacement operator,<sup>16</sup> defined such that

$$\hat{g}(\vec{I})f(\vec{r}) = f(\vec{r} + \vec{I}),$$

and we sum over the set  $\{\vec{I}\}$ , the positions of the  $n$  nearest neighbors relative to the atom.  $\tau_a$  is the inverse of the jump frequency of the atom, which we will also call the jump time. The time actually spent in the jump itself is of the order of one vibration period and can be neglected. The solution may be obtained by using the time Fourier transform

$$G(\vec{r}, t) = \frac{1}{(2\pi)^3} \int d\vec{k} e^{-i\vec{k} \cdot \vec{r} - [1 - D(\vec{k})]t/\tau_a}, \quad (4)$$

and thus the broadening can be shown to be of Lorentzian shape and of width

$$\Delta\Gamma = (2\hbar/\tau_a)[1 - D(\vec{k})], \quad (5)$$

where for sc

$$D(\vec{k}) = \frac{1}{3} [\cos(k_x a) + \cos(k_y a) + \cos(k_z a)],$$

for bcc

$$D(\vec{k}) = \cos(\frac{1}{2}k_x a) \cos(\frac{1}{2}k_y a) \cos(\frac{1}{2}k_z a), \quad (6)$$

for fcc

$$D(\vec{k}) = \frac{1}{3} [\cos(\frac{1}{2}k_x a) \cos(\frac{1}{2}k_y a) + \cos(\frac{1}{2}k_x a) \cos(\frac{1}{2}k_z a) + \cos(\frac{1}{2}k_y a) \cos(\frac{1}{2}k_z a)].$$

$k_x, k_y, k_z$  are the components of the momentum of the  $\gamma$  ray, referred to the crystal axes, and  $a$  is the lattice parameter.

### IV. DIFFUSION BY THE VACANCY MECHANISM

When diffusion occurs by means of vacancies, the atomic jumps are correlated. When an atom has just interchanged places with a vacancy, it is more probable that it will jump back to its original position than that the vacancy will jump around, by interchanging with other atoms, so that the atom we are considering can jump forward.

We will see, however, that if we do not resolve the jumping process for times of the order of the atomic jump time, we will still be able to write an equation similar to Eq. (3) for diffusion by the vacancy mechanism.

We will study systems with a low concentration of vacancies, such that our equations will not describe the case of two vacancies meeting. This also implies that once a vacancy is near a marked atom, during the time that the atom has a significant probability of interchanging with the vacancy, there is near zero probability that another vacancy will approach. This approximation leads to a useful concept, that of "encounter." An encounter designates all interchanges<sup>17</sup> between one given vacancy and the marked atom. We can define the encounter time  $\tau_e$  as the time elapsed from the moment the vacancy first approaches the atom to the moment when it leaves its neighborhood, after possibly more than one jump of the marked atom. Our approximation can then be stated as

$$\tau_e \ll \tau/C \cong \tau_a,$$

where  $C$  is the vacancy concentration,  $\tau$  is the jump time of the vacancy (the time it takes for any atom, not just the marked one, to jump into the empty space), and  $\tau/C$  gives a typical time between arrivals of vacancies to a fixed point, i.e., the site of the marked atom.

Let us suppose we can consider  $dt$ , the time differential, such that

$$\tau_e \ll dt \ll \tau/C,$$

which means, essentially, that we do not resolve (i.e., "look into") the jumping process for times of the order of the atomic jump time, but take the

results of one encounter as a whole, that is, as one process with more complex results.

With this assumption, we can now write an equation for diffusion by the vacancy mechanism similar to Eq. (3) but including additional terms corresponding to the probability that an atom may move more than one nearest-neighbor distance during one encounter:

$$\frac{\partial}{\partial t} G(\vec{r}, t) = \left( w_1 \sum_{\vec{r}'} [\hat{g}(\vec{r}') - 1] + w_2 \sum_{\vec{r}''} [\hat{g}(\vec{r}'') - 1] + \dots \right) G(\vec{r}, t), \quad (7)$$

where  $w_1$  is the probability that the atom will jump from the original site to a nearest neighbor position,  $w_2$  to the second, etc. This equation has been obtained by Krivoglaz.<sup>11</sup> The solution to this equation is similar to Chudley and Elliott's, with the same time dependence of the space Fourier transform, which thus also leads to a Lorentzian peak shape.

We will study Eq. (7) in more detail because it gives the limiting behavior (for large  $t/\tau_a$ ) of the exact solution which will be discussed later.

The probability that the atom will go to a second-nearest-neighbor position in an encounter is very small: 0.2% in the bcc case, so we can neglect, on a first approximation, the second term in Eq. (7). But the probability of the tracer atom jumping to the first nearest neighbor is no longer  $1/\tau_a$ , as it is modified by the probability that it will return to its original position. There is  $1/z$  probability that it will return there with the next jump of the vacancy plus a slowly convergent series of probabilities that it will return after the  $n$ th jump of the vacancy, plus the probability that the tracer atom will go back to the origin but after more than one of its jumps.

If, in addition to the condition on  $dt$ , we add that  $dr \gg a$  (i.e., our process cannot resolve distances of the order of interatomic distances, as is the case in bulk diffusion measurements) we can show that, using the crystal symmetries, the sums become the second derivatives of a Laplacian.

For sc Eq. (7) becomes, up to the second nearest neighbors,

$$\frac{\partial}{\partial t} G(\vec{r}, t) = a^2(w_1 + 4w_2)\Delta G(\vec{r}, t); \quad (8)$$

for bcc

$$\frac{\partial}{\partial t} G(\vec{r}, t) = a^2(w_1 + w_2)\Delta G(\vec{r}, t). \quad (9)$$

Thus we have obtained, for both cases, equations similar to the one used for bulk diffusion<sup>18</sup>:

$$\frac{\partial}{\partial t} G(\vec{r}, t) = D\Delta G(\vec{r}, t),$$

where for the case of diffusion by the vacancy mechanism,  $D$  the diffusion coefficient, is

$$D = a^2 f / n\tau_a,$$

and  $f$  is the Bardeen-Herring correlation coefficient, defined as the limit, when the number of jumps goes to infinity, of the ratio of the mean square displacement of the tracer atom after  $n_0$  jumps and that of a vacancy for the same number of jumps.

Compaan and Haven<sup>19</sup> have shown that the infinite series for  $f$  may be summed as

$$f = (1 + \cos\theta_1)/(1 - \cos\theta_1), \quad (10)$$

where  $\cos\theta_1$  is the mean value of the cosine of the angle between the last tracer jump and the next.  $\cos\theta_1$  may be calculated as

$$\cos\theta_1 = \sum_{k=1}^z p_k \cos\theta_k, \quad (11)$$

where  $p_k$  is the probability that the tracer will make its next jump to the  $k$ th nearest neighbor.  $p_k$  is thus calculated by summing all the probabilities of the various vacancy trajectories which will move the tracer to  $k$  on the tracer's first jump. This calculation of  $p_k$  converges very slowly with increasing number of vacancy jumps considered, but very accurate values of  $f$  have been obtained by Compaan and Haven.

We have obtained from Eqs. (8) and (9) the following expansion of  $f$  in terms of  $w_1$ ,  $w_2$ , etc.: for sc

$$f = n\tau_a(w_1 + 4w_2 + \dots); \quad (12)$$

for bcc

$$f = n\tau_a(w_1 + w_2 + \dots). \quad (13)$$

This expansion can be used to estimate  $w_1$  and  $w_2$  from  $f$ . For example, for bcc, if we use as a rough estimate for  $w_2 \cong \frac{1}{170}w_1$ , we can obtain

$$w_1 \cong f/n\tau_a \left(1 + \frac{1}{170}\right) \quad (14)$$

to use in the estimation of the peak width with the "encounter" approximation using terms up to  $w_2$ .

## V. NUMERICAL SOLUTION OF THE EXACT EQUATION

We will now construct an equation analogous to Eq. (3) which does not involve the approximations of Eq. (7). This we will do by constructing equations for the probabilities of configurations with one marked atom and one vacancy in a finite crystal, in a form suitable for numerical calculation.

tions. Periodic boundary conditions are used at the edges of this finite "crystal." Thus one vacancy can travel through the crystal simulating different vacancies or "encounters." As the marked atom travels "via" vacancies, its movement is much slower, and, throughout our study, there is a negligible probability of the atom getting near the boundaries. This avoids the problem of in-

cluding in our description, through the boundary conditions, what would be the equivalent of other incoming marked atoms.

We will start with the one dimensional case, for simplicity. There are two conditions our equations must describe:

(i) When the marked atom and the vacancy are not nearest neighbors

$$\frac{\partial}{\partial t} P(r_a, r_v, t) = \frac{1}{2\tau} [P(r_a, r_v + l, t) + P(r_a, r_v - l, t) - 2P(r_a, r_v, t)]. \quad (15)$$

(ii) When they are nearest neighbors

$$\frac{\partial}{\partial t} P(r_a = r, r_v = r + l, t) = \frac{1}{2\tau} [P(r_a = r + l, r_v = r, t) + P(r_a = r, r_v = r + 2l, t) - 2P(r_a = r, r_v = r + l, t)], \quad (16)$$

and similarly for  $r_v = r - 1$ .

We can describe both cases in one formula by using the Kröenecker  $\delta$  functions and the displacement operator. We may then write Eqs. (15) and (16) as a single equation

$$\begin{aligned} \frac{\partial P}{\partial t}(r_a, r_v, t) = \frac{1}{\tau} \{ [1 - \delta(r_a - r_v) - \delta(r_a - r_v + l) - \delta(r_a - r_v - l)] [\frac{1}{2}\hat{g}_v(l) + \frac{1}{2}\hat{g}_v(-l) - 1] \\ + [\delta(r_v - r_a + l)] [\frac{1}{2}\hat{g}_a(-l)\hat{g}_v(l) + \frac{1}{2}\hat{g}_v(-l) - 1] + [\delta(r_v - r_a - l)] [\frac{1}{2}\hat{g}_a(l)\hat{g}_v(-l) + \frac{1}{2}\hat{g}_v(l) - 1] \} P(r_a, r_v, t), \end{aligned} \quad (17)$$

and this may be written in the form

$$\frac{\partial}{\partial t} P(r_a, r_v, t) = \frac{1}{\tau} \hat{\Theta} P(r_a, r_v, t), \quad (18)$$

where the operator  $\hat{\Theta}$  is defined as

$$\begin{aligned} \hat{\Theta} = [1 - \delta(r_a - r_v) - \delta(r_a - r_v + l) - \delta(r_a - r_v - l)] [\frac{1}{2}\hat{g}_v(l) + \frac{1}{2}\hat{g}_v(-l) - 1] \\ + \delta(r_v - r_a + l) [\frac{1}{2}\hat{g}_a(-l)\hat{g}_v(l) + \frac{1}{2}\hat{g}_v(l) - 1] + \delta(r_v - r_a - l) [\frac{1}{2}\hat{g}_a(l)\hat{g}_v(-l) + \frac{1}{2}\hat{g}_v(l) - 1]. \end{aligned} \quad (19)$$

Equation (18) may be solved symbolically as

$$P(r_a, r_v, t) = e^{(t/\tau)\hat{\Theta}} | P(r_a, r_v, 0) \rangle, \quad (20)$$

where  $P(r_a, r_v, 0)$  is the initial condition, which in this case may be written

$$P(r_a, r_v, 0) = \delta(r_a) [1 - \delta(r_v)] / (N_l - 1)$$

for the atom at the origin and the vacancy with equal probability of being anywhere in the lattice except at the origin.  $N_l$  is the number of lattice points in the finite crystal.

The exponential with an operator as an exponent means, as is customary

$$e^{(t/\tau)\hat{\Theta}} = \left[ 1 + \frac{t}{\tau}\hat{\Theta} + \left(\frac{t}{\tau}\right)^2 \frac{\hat{\Theta}^2}{2} + \dots \right], \quad (21)$$

and  $\hat{\Theta}^2$  means the operator is to be applied twice on the initial condition,  $\hat{\Theta}^3$  three times, etc. Each term of the expansion may be obtained from the former one by applying  $t\hat{\Theta}/\tau N$ , where  $N$  is the order of the expansion being calculated. It is to be noticed that the displacement operator and the deltas do not commute.

We may write for the general three-dimensional case the equation corresponding to (15) and (16):

$$\frac{\partial P}{\partial t}(\vec{r}_a, \vec{r}_v, t) = \frac{1}{n\tau} \left( \sum_l P(\vec{r}_a, \vec{r}_v + \vec{l}, t) - nP(\vec{r}_a, \vec{r}_v, t) \right), \quad (22)$$

$$\frac{\partial P}{\partial t}(\vec{r}_a = \vec{r}, \vec{r}_v = \vec{r} + \vec{l}, t) = \frac{1}{n\tau} \left( P(\vec{r}_a = \vec{r} + \vec{l}, \vec{r}_v = \vec{r}, t) - \sum_{l'} P(\vec{r}_a = \vec{r}, \vec{r}_v = \vec{r} + \vec{l} + \vec{l}', t) - nP(\vec{r}_a = \vec{r}, \vec{r}_v = \vec{r} + \vec{l}, t) \right). \quad (23)$$

These can be written in the form of Eq. (17) with the solution given by Eq. (20), but now the operator  $\hat{\Theta}$  takes into account displacements in a three-dimensional lattice. It may be written

$$\hat{\Theta} = \left( 1 - \delta(\vec{r}_a, \vec{r}_v) - \sum_{\vec{I}} \delta(\vec{r}_v - \vec{r}_a + \vec{I}) \right) \left( \sum_{\vec{I}} \frac{\hat{g}_v(\vec{I})}{n} - 1 \right) + \left( \sum_{\vec{I}} \delta(\vec{r}_v - \vec{r}_a + \vec{I}) \right) \left( \frac{\hat{g}_v(-\vec{I})\hat{g}_a(\vec{I})}{n} + \sum_{\vec{I}'} \frac{\hat{g}_v(\vec{I}')}{n} - 1 \right), \quad (24)$$

where the sum' is over all nearest neighbors except  $\vec{I} = -\vec{I}'$ . The term with  $\vec{I} = -\vec{I}'$  accounts for the exchange of the marked atom and the vacancy and is written out separately.

Let us study this operator  $\hat{\Theta}$  in more detail. Since the nearest-neighbor and the non-nearest-neighbor cases are selected by deltas, we can see that the operators, when applied to a function  $F(\vec{r}_a, \vec{r}_v, t)$ , simply tells us to take  $F(\vec{r}_a, \vec{r}_v, t)$ , multiplied by  $-1$ , and add to this the same function evaluated for lattice sites adjacent to the previous ones, multiplied by  $1/n$ .

The series expansion (21) converges very slowly for large increments (large  $t/\tau$ ) and leads to large roundoff errors. We can, however, carry out an iterative calculation. As, of course,  $\hat{\Theta}$  commutes with itself, we can use the fact that, if  $t_1 + t_0 = t$

$$\begin{aligned} G(\vec{r}_a, \vec{r}_v, t = t_1 + t_0) &= e^{(t_1 + t_0)\hat{\Theta}} |G(\vec{r}_a, \vec{r}_v, t = 0)\rangle \\ &= e^{t_1\hat{\Theta}} [e^{t_0\hat{\Theta}} |G(\vec{r}_a, \vec{r}_v, t = 0)\rangle] \\ &= e^{t_1\hat{\Theta}} |G(\vec{r}_a, \vec{r}_v, t = t_0)\rangle. \end{aligned} \quad (25)$$

We calculate the probabilities at given time intervals, each probability at  $t$  being calculated by propagating the solution at  $t - \Delta t$ . We also store these solutions at convenient time intervals as we need them to carry out the time Fourier trans-

form, Eq. (2).

For each selected value of the time  $t$  and each point of the vacancy-atom configuration, the terms of the expansion (20) and (21) are evaluated until the last term calculated constituted a correction less than 1 part in  $10^7$ , the maximum precision practical on the 360/67 computer used. Time intervals from 0.1 to 1 give satisfactory convergence with from two to seven terms in the expansion. The detailed programs are given elsewhere.<sup>20</sup>

In the calculation, the work of the deltas of selecting the cases is done as follows: first all possible configurations in the lattice are calculated as if they were non-nearest-neighbors (these are, indeed, the majority of cases); then we recalculate explicitly for the nearest-neighbor configurations.

To obtain the  $m$ th term of the series for a given  $r_a$  and  $r_v$ , we take the previous term for that point, multiply it by  $-t/\tau$  and add the previous terms for configurations with vacancies in adjacent sites, multiplied by  $t/mn$ .

As an example, formulas (26) and (27) show one term of the calculation  $Q_{m+1}$  being obtained from the former  $Q_m$  for a non-nearest-neighbor case and one particular nearest neighbor in a simple cubic lattice.

$$\begin{aligned} Q_{m+1}(I_v, J_v, K_v, I_a, J_a, K_a) &= (t/6\tau) [-6Q_m(I_v, J_v, K_v, I_a, J_a, K_a) + Q_m(I_v + 1, J_v, K_v, I_a, J_a, K_a) \\ &\quad + Q_m(I_v - 1, J_v, K_v, I_a, J_a, K_a) + Q_m(I_v, J_v + 1, K_v, I_a, J_a, K_a) + Q_m(I_v, J_v - 1, K_v, I_a, J_a, K_a) \\ &\quad + Q_m(I_v, J_v, K_v + 1, I_a, J_a, K_a) + Q_m(I_v, J_v, K_v - 1, I_a, J_a, K_a)] \end{aligned} \quad (26)$$

and

$$\begin{aligned} Q_{m+1}(1, 1, 2, 1, 1, 1) &= (t/6\tau) [-6Q_m(1, 1, 2, 1, 1, 1) + Q_m(1, 1, 1, 1, 1, 2) + Q_m(1, 1, 3, 1, 1, 1) \\ &\quad + Q_m(2, 1, 2, 1, 1, 1) + Q_m(0, 1, 2, 1, 1, 1) + Q_m(1, 2, 2, 1, 1, 1) + Q_m(1, 0, 2, 1, 1, 1)]. \end{aligned} \quad (27)$$

The cubic symmetry of the crystal made it sufficient to carry out calculations for atomic positions for only  $\frac{1}{28}$  of the crystal. If other positions were needed in the calculation, appropriate logi-

cal statements converted them to the symmetrical-equivalent sites.

Finally, we obtained the desired probability for the marked atom by summing over all possible

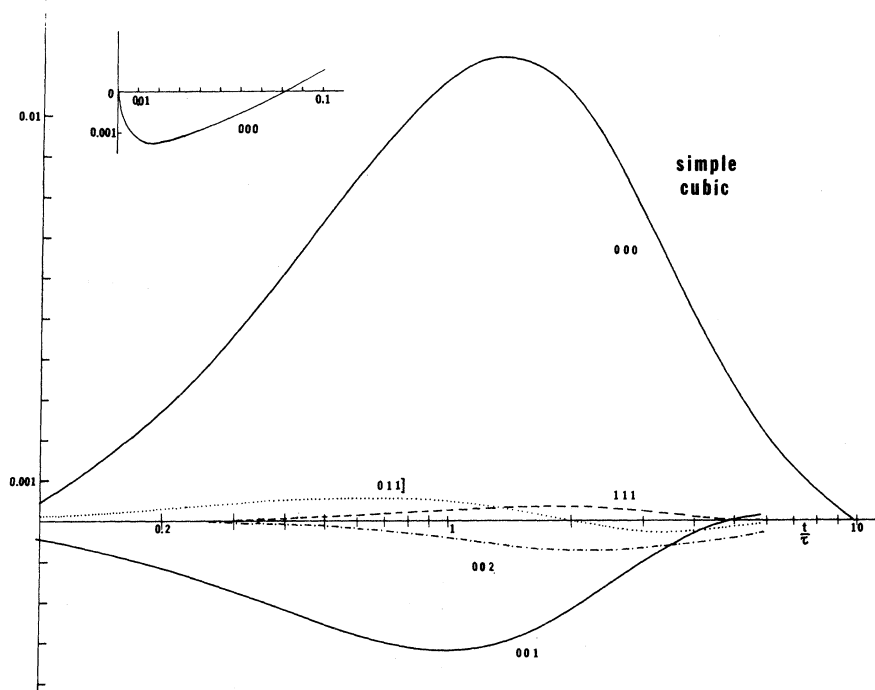


FIG. 1. Corrections to the probabilities calculated from the empty lattice solution (with  $\tau$  scaled by the correlation factor). The corrections obtained by our method are shown for several lattice sites of the simple cubic case. For all plots, the corrections obtained by our method have the times scaled by the concentration of vacancies, as described in the text. The inset shows the rapid change in this function for the atom at 000 for very small times (a linear scale was used).

positions of the vacancy:

$$G(\vec{r}_a, t) = \frac{1}{N_i} \sum_{\vec{r}_v} P(\vec{r}_a, \vec{r}_v, t),$$

where  $N_i$  is the number of lattice points.

We used the fact that the probability must be normalized, that is

$$G(\vec{r}_a, t) = 1$$

for the sum over all the lattice, to check the roundoff errors. This condition was satisfied to a precision of 0.08%.

Once the crystal is sufficiently large, changing the crystal size only scales the times at which encounters follow each other. This was verified

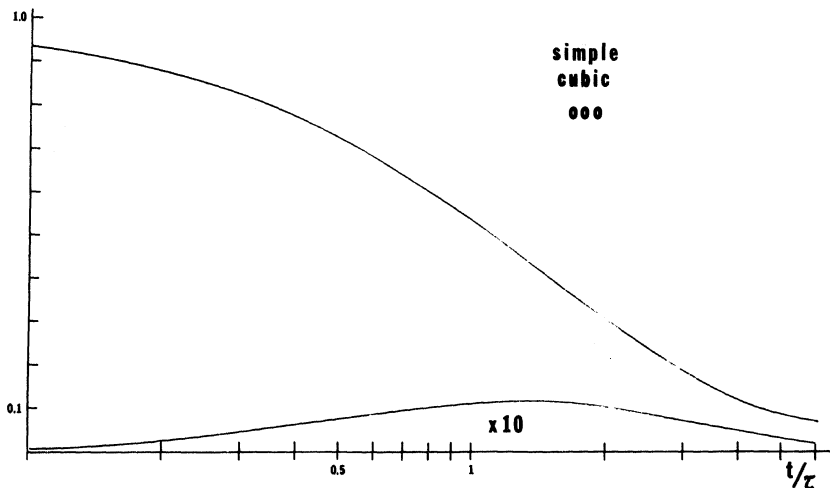


FIG. 2. Correction for the atom at the origin, compared to the empty-lattice solution (with  $\tau$  scaled by  $f$ ).

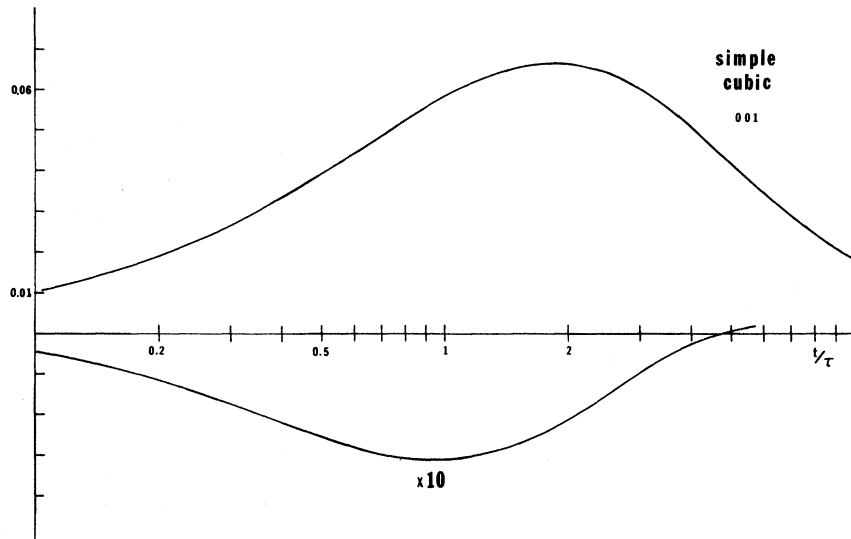


FIG. 3. Correction for the atom at 001, compared to the empty-lattice solution (with  $\tau$  scaled by  $f$ ).

for our runs; for both bcc and simple cubic, the solutions for the crystal with  $9^3$  lattice sites scale to the  $7^3$  case, while the  $5^3$  does not (and we observed that for this smaller one the probabilities for finding the tagged atom at the boundaries could no longer be neglected).

#### VI. LIMITING BEHAVIOR AT LONG TIMES

Let us now discuss the limiting behavior expected. We know that for long times we expect to re-

cover the solution obtained by solving the problem in coarser steps of  $dt$ . We have already shown that, to a very good approximation, this solution has the form of the empty lattice solution, but with the jump time scaled by the correlation factor. This provides a test for the convergence of our calculations. Figures 1-6 show the corrections to this limiting solution, as obtained by our method. The limiting behavior is reached, to a good approximation, when  $t/\tau$  is of the order of 7.

Another independent check of the calculation was

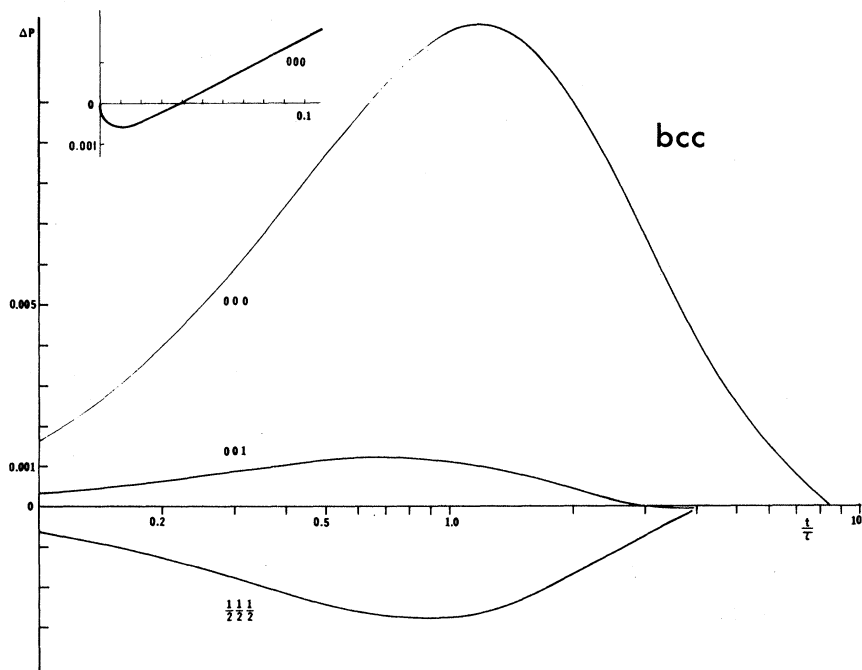


FIG. 4. Corrections for several bcc lattice positions.

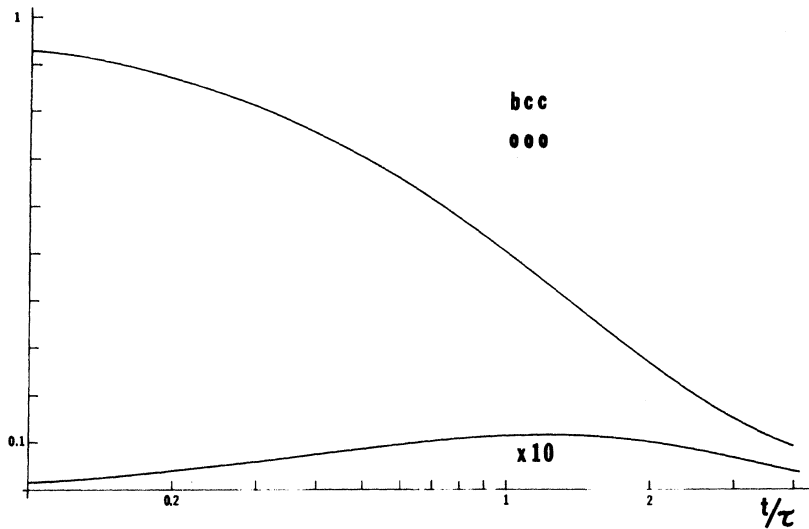


FIG. 5. Correction for the atom at the origin, in a bcc lattice, compared to the empty-lattice solution (with  $\tau$  scaled by  $f$ ).

obtained by computing the Bardeen-Herring correlation coefficient from our results for long times. We can calculate the mean-square displacement of the tracer atom and the vacancy:

$$\langle r_a^2(t) \rangle = \sum_{r_a} \sum_{r_v} r_a^2 P(\vec{r}_a, \vec{r}_v, t)$$

and

$$\langle r_v^2(t) \rangle = \sum_{r_a} \sum_{r_v} r_v^2 P(\vec{r}_a, \vec{r}_v, t).$$

We now obtain  $f(t)$

$$f(t) = \langle r_a^2(t) \rangle / \langle r_v^2(t) \rangle,$$

and, in the limit of long times,  $f(t)$  becomes the Bardeen-Herring coefficient  $f$ . For a simple cubic lattice, at  $t/\tau=2$ , we obtained  $f=0.6557$  as compared to Compaan and Haven's value of  $f=0.6555$ .

For the body centered case, at  $t/\tau=2$ , our value was  $f=0.7218$  compared to  $f=0.7215$ .

#### VII. CALCULATION OF THE MÖSSBAUER PEAK SHAPE

In accordance with Eq. (2), to obtain the effect of diffusion on the peak shape, one must perform Fourier transformation in space and time. To minimize the roundoff errors, we carried out the transformation for the difference between our results and the limiting solution, the result of Chudley and Elliott<sup>14</sup> scaled by the Bardeen-Herring factor  $f$ .

The results obtained are dependent on the angle of the gamma ray with respect to the crystal axes. In no direction are the corrections bigger than 10%. Results for several directions in space are shown in Figs. 7 and 8.

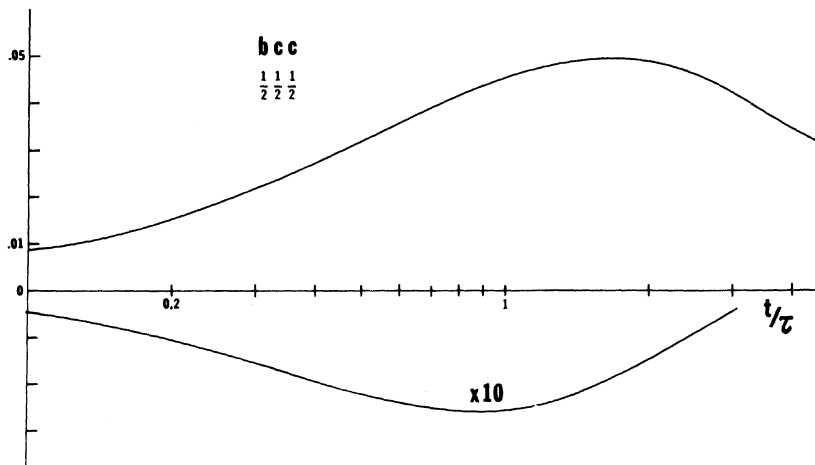


FIG. 6. Correction to the probability at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ , compared to the empty-lattice solution (with  $\tau$  scaled by  $f$ ).



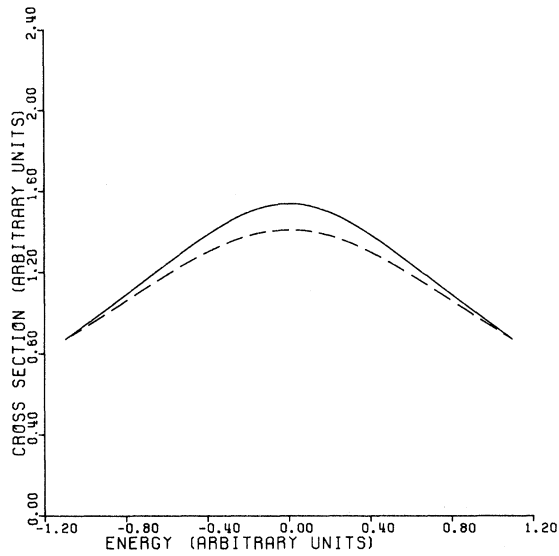


FIG. 7. Line shape from diffusion by the vacancy mechanism in the  $[710]$  direction for the bcc case. The dashed line shows the approximation obtained from the empty-lattice case (with  $\tau$  scaled by  $f$ ). The solid line shows the complete solution. This is one of the directions where the correction is greatest ( $\approx 10\%$ ).  $ka = 21.1$ , as appropriate for Fe-3-wt.%-Si and similar alloys.

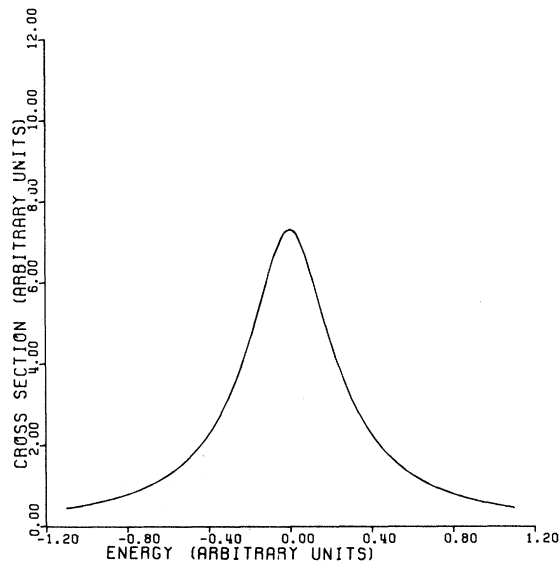


FIG. 8. Line shape for diffusion by the vacancy mechanism in the  $[031]$  direction for the bcc case. Here the correction is negligible, but the empty-lattice solution in this direction is near the direction of smallest width (smallest diffusion broadening). The experimental solid angle was estimated to be about  $5^\circ$ , and the results were averaged over this angle.  $ka = 21.1$ .

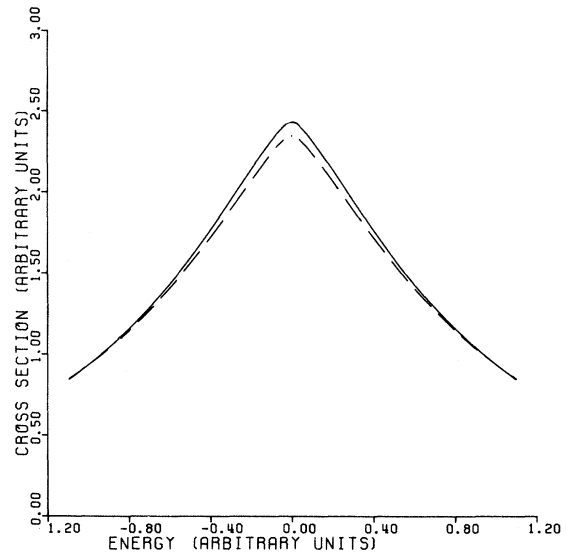


FIG. 9. Line shape for a bcc polycrystalline sample. The dashed line shows the empty-lattice approximation (with  $\tau$  scaled by  $f$ ). The solid line shows the complete solution. The correction to the width is about 5%.  $ka = 21.1$ .

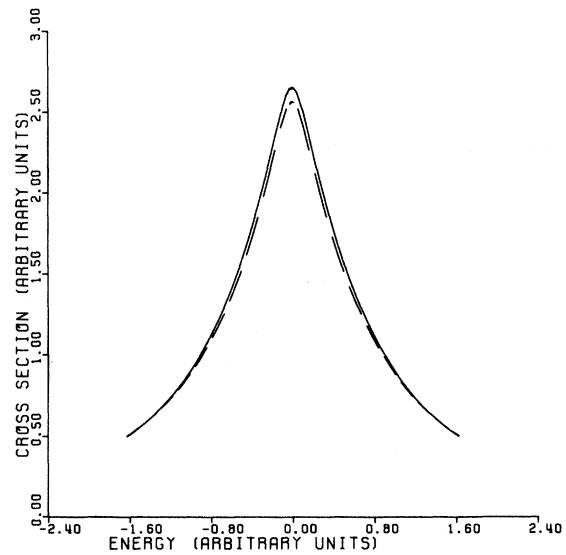


FIG. 10. Line shape for a simple cubic polycrystalline sample. The dashed line shows the empty-lattice approximation (with  $\tau$  scaled by  $f$ ). The solid line shows the complete solution. The correction to the width is about 4%.  $ka = 10$ .

For single-crystal experiments the result should only be averaged over the solid angle of measurement. For powdered samples it should be averaged over the complete solid angle.<sup>10</sup> Figures 9 and 10 show the complete solution from our calculation compared with the approximate solution obtained by scaling Chudley and Elliott's result

by the bulk diffusion correlation factor. These show that our correction, once averaged over solid angle is about 5% narrower for both the simple cubic and the bcc case.

The actual peak shape is obtained by adding the correction to the Lorentzian obtained from the scaled Chudley and Elliott result.

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