PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 3, NO. 3 — 1 FEBRUARY 1971

Effect of Vacancy Diffusion on Mössbauer Line Broadening*

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(Received 6 July 1970)

Recent Mössbauer-effect experiments on iron in copper and iron in gold indicate that the line broadening due to diffusion is about a factor of 2 smaller than the value predicted by the independent-jump model of Singwi and Sjölander. A model for vacancy diffusion is advanced which results in Mössbauer spectra that are Lorentzian in shape with a broadening $\Delta\epsilon$ that is proportional to the average diffusive jump rate τ_D^{-1}, as is also the case for the independent-jump model. The slope of $\Delta\epsilon$ vs τ_D^{-1} is related to the probability for a vacancy to dissociate completely from a Mössbauer atom and can be inferred from the correlation factor. The model indicates that the broadening can range from 0 in the highly correlated limit to a value less than $2\hbar\tau_D^{-1}$ in the uncorrelated limit.

I. INTRODUCTION

The effect of atomic motion on the resonant absorption of nuclear γ radiation can be succinctly described by the self-correlation function formalism[1] of Singwi and Sjölander. According to these authors the cross section for absorption of a γ ray having momentum $\hbar\vec{k}$ and energy $\hbar\omega_{\vec{k}}$ is given by

$$\sigma(\vec{k},\omega)=(\sigma_0\Gamma_\gamma/4\hbar)\int d\vec{r}\,dt\,e^{i(\vec{k}\cdot\vec{r}-\omega t)}\times e^{-(1/2)\Gamma_\gamma|t|}G_s(\vec{r},t)\ ,\qquad(1)$$

where σ_0 is the on-resonance ($\omega_{\vec{k}}=\omega_0$) cross section, $\hbar\Gamma_\gamma$ is the natural width of the excited nuclear state, and ω is $\omega_{\vec{k}}-\omega_0$. In general $G_s(\vec{r},t)$, the self-correlation function, is a complex quantity due to quantum effects. However, if the region of interest in (1) is such that $\hbar\omega \ll k_BT$, where T is the absolute temperature of the sample, then to a very good degree of approximation $G_s(\vec{r},t)$ is a real function describing how often on the average an atom is at position $\vec{r}$ at time t, having begun its motion from $\vec{r}=0$ at $t=0$.

In the last two decades there has been increased interest in the problem of understanding the fundamental mechanisms responsible for mass transport in solids.[2] The widely used tracer-sectioning technique provides sufficient experimental accuracy to measure thermodynamic parameters, such as the activation energy, so that meaningful correlation with theory is possible. However, the results of these experiments reflect long-term averages over the detailed motions constituting the diffusion process. By contrast, the Mössbauer effect can provide resolving times (of order Γ_γ^{-1}) that are in principle sufficiently short to enable determining the behavior of the system on a time scale of order τ_D, the mean time between jumps of a given atom.

In order to illustrate the connection between Mössbauer absorption and diffusion in solids, Singwi and Sjölander proposed a model[1,3] in which an atom was seen to make sudden jumps between identical vibrational states centered at different positions in the lattice. Employing the stochastic assumption that the relaxation of an atom from a given vibrational state can be described as e^{-t/τ_D}, they predicted that the Mössbauer absorption cross section would have Lorentzian shape with line broadening given by (in energy units)

$$\Delta\epsilon=2\hbar\tau_D^{-1}\,[1-\alpha(\vec{k})]\ ,$$

where $\alpha(\vec{k})$ is the Fourier transform of the one-jump distribution function $h(\vec{r})$, and is essentially 0 for most cases of interest.

Recent experiments on iron diffusion in copper[4] and in gold[5] indicate that although the Mössbauer spectra are Lorentzian within experimental errors, the broadening is more nearly given by

$$\Delta\epsilon\cong\hbar\tau_D^{-1}\ .$$

It was suggested[4-6] that this reduced broadening might be a manifestation of the short-term effects of the vacancy-diffusion mechanism. Since diffusion in this case represents a process in which atomic jumps are not statistically independent of one another on a time scale of order τ_D, the stochastic assumption employed in the independent-jump model[3] may not be an accurate representation. In fact, the characterization of the atomic motion by a single parameter τ_D has meaning only if τ_D^{-1} represents the average jump rate

$$\tau_D^{-1} = \lim\,[N(t)/t] \quad \text{as } t \to \infty \ ,$$

where $N(t)$ is the average number of jumps of a given atom that occur in a time interval of length t. In order to understand the results of diffusion-broadening experiments on systems in which the vacancy mechanism is dominant, it is necessary to specify other parameters which reflect the dynamics of the vacancy-atom system on a time scale of order τ_D.

In contrast to the cases above, recent experiments[7] have been done on the iron-silicon system in which the investigators report that the broadening is more nearly $2\hbar\tau_D^{-1}$, as expected from the independent-jump model. This may be a consequence of the fact that in bcc structures the dominant diffusion mechanism may be one in which atoms jump independently of one another, such as the interstitial or the ring mechanism.

It is the purpose of this paper to show that for the vacancy mechanism the time constant measured by diffusive line-broadening experiments is not in general the same as inferred from macroscopic diffusion experiments. A model is advanced to illustrate the effect of correlated diffusion on the line broadening for the fcc lattice. The results of the calculation show that the broadening ranges from 0 in the highly correlated limit to a value less than $2\hbar\tau_D^{-1}$ in the uncorrelated case, and points out the usefulness of the Mössbauer effect in identifying the mechanism of diffusion.

II. GENERAL FORMULATION

Assuming that the motion of an atom undergoing diffusion in a solid can be represented as a succession of vibrational states centered about different lattice sites, the self-correlation function can be written as[8]

$$G_s(\vec{r}, t) = \int d\vec{r}\,'\, g_V(\vec{r} - \vec{r}\,', t) F(\vec{r}\,', t) \ , \tag{2}$$

in which $g_V(\vec{r}, t)$ is the self-correlation function for the vibrational motion and $F(\vec{r}\,', t)$ is the average (fractional) number of times that an atom is at a position $\vec{r}\,'$ at time t given that $\vec{r}\,'(0) = 0$. In Eq. (2) it is assumed that there is no correlation between the vibrational motion and the diffusive motion. Using the convolution theorem for Fourier transforms, the cross section for resonant absorption, Eq. (1), becomes

$$\sigma(\vec{k}, \omega) = (\sigma_0 \Gamma_\gamma / 4\hbar) \int dt\, e^{-i\omega t} e^{-(1/2)\Gamma_\gamma |t|} \times \left[\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} g_V(\vec{r}, t) \right]\left[\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} F(\vec{r}, t) \right] . \tag{3}$$

Owing to the oscillatory behavior of $g_V(\vec{r}, t)$ with time, the cross section (3) will exhibit peaks in frequency, with the zero-phonon or Mössbauer peak centered at $\omega = 0$. Therefore it is necessary only to consider the long-time behavior of $g_V(\vec{r}, t)$ to obtain that region of the frequency spectrum of interest for the Mössbauer effect:

$$\sigma_M(\vec{k}, \omega) = (\sigma_0 \Gamma_\gamma / 4\hbar)\, e^{-2W} \int dt e^{-i\omega t} e^{-(1/2)\Gamma_\gamma |t|} \times \left[\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} F(\vec{r}, t) \right] , \tag{4}$$

where $2W$ is the Debye-Waller factor found from

$$e^{-2W} = \lim \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} g_V(\vec{r}, t) \quad \text{as } t \to \infty \ .$$

In the sudden-jump approximation, $F(\vec{r}, t)$ can be obtained from the theory of random flights.[9] The probability that an atom is at a position $\vec{r}$ after n jumps is given by

$$P_n(\vec{r}) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} [\alpha(\vec{k})]^n \ , \tag{5}$$

where

$$\alpha(k) = \int dr\, e^{i\vec{k}\cdot\vec{r}} P_1(\vec{r}) \ .$$

The quantity $\alpha(\vec{k})$ also appears in the formulation of Singwi and Sjölander[1] in which $P_1(\vec{r})$ is the probability distribution for one jump, $h(\vec{r})$. The time dependence is introduced with $W_n(t)$, the average fractional number of times that an atom will make n jumps in a time interval of length t. $F(\vec{r}, t)$ is then given by

$$F(\vec{r}, t) = \sum_{n=0}^{\infty} P_n(\vec{r}) W_n(t) \ . \tag{6}$$

The cross section for Mössbauer absorption is computed using Eqs. (4)–(6):

$$\sigma_M(\vec{k}, \omega) = \frac{\sigma_0 \Gamma_\gamma}{4\hbar} e^{-2W} \int dt\, e^{-i\omega t}\, e^{-(1/2)\Gamma_\gamma |t|} \times \sum_{n=0}^{\infty} W_n(t) [\alpha(\vec{k})]^n \ . \tag{7}$$

This is the general expression for the cross section in terms of $\alpha(\vec{k})$ and $W_n(t)$. If the wavelength of the γ ray is much smaller than the distance of one atomic jump, then for polycrystalline samples[10] $\alpha(\vec{k}) = 0$ and Eq. (7) reduces to

$$\sigma_M(\vec{k}, \omega) = (\sigma_0 \Gamma_\gamma / 4\hbar) e^{-2W} \int dt e^{-i\omega t} e^{-(1/2)\Gamma_\gamma |t|} P(t) \ , \tag{8}$$

where $P(t) \equiv W_0(t)$. According to Eq. (8), the Mössbauer cross section is found from the time Fourier transform of $P(t)$, the relaxation function which describes how often on the average an atom remains at a given lattice site for a time interval of length t. Since diffusion processes are stationary in time, $P(t)$ can be calculated from a consideration of the average number of atoms in an ensemble which do not jump for any time interval $0 \rightarrow t$.

The effect of diffusive motions is to broaden the frequency spectrum through the relaxation $P(t)$. This can be seen from a different point of view by considering an alternate expression for the cross section,[1]

$$\sigma(\vec{k}, \omega) = (\sigma_0 \Gamma_\gamma / 4\hbar) e^{-2W} \int dt \, e^{-i\omega t} e^{-(1/2)\Gamma_\gamma |t|} K(t) \quad ,$$

where

$$K(t) = \langle e^{-i\vec{k}\cdot\vec{r}(0)} e^{i\vec{k}\cdot\vec{r}(t)} \rangle \quad .$$

The angle brackets indicate that both quantum-mechanical and statistical averages are to be taken. In the absence of diffusive motions $K(t)$ approaches the value e^{-2W} for $t \gtrsim 10^{-12}$ sec. If diffusion is present and the vibrational motion at a new site is uncorrelated with the motion at the original site, then on the average $K(t)$ will be reduced to

$$K(t) = e^{-2W} P(t) \quad , \quad t \gtrsim 10^{-12} \text{ sec} \quad .$$

Thus $P(t)$ represents how often on the average the function $e^{i\vec{k}\cdot\vec{r}}$ remains correlated during the interval $0 \rightarrow t$.

Since in the sudden-jump approximation an atom is always in a vibrational state of motion, the recoil-free fraction will be the same as if no jump motion occurs. This can be seen by calculating the area under $\sigma_M(\vec{k}, \omega)$ using Eq. (8):

$$S \equiv \int d\omega \, \sigma_M(\vec{k}, \omega)$$

$$= (\sigma_0 \Gamma_\gamma / 4\hbar) e^{-2W} \int d\omega \int dt \, e^{-i\omega t} e^{-(1/2)\Gamma_\gamma |t|} P(t) \quad .$$

Since $P(t) \rightarrow 0$ as $|t| \rightarrow \infty$, the order of integration can be interchanged with the result

$$S = \frac{\sigma_0 \Gamma_\gamma}{4\hbar} e^{-2W} 2\pi \int dt \, e^{(1/2)\Gamma_\gamma |t|} \delta(t) P(t)$$

$$= \frac{\sigma_0 \Gamma_\gamma}{4\hbar} e^{-2W} 2\pi P(0) \quad .$$

Because $P(0) \equiv 1$, independent of the parameters specifying the diffusion process, the area will be proportional to the recoil-free fraction for vibrational motion alone, e^{-2W}.

III. EFFECT OF DIFFUSION MECHANISM ON $P(t)$

For the $\alpha(\vec{k}) = 0$, the cross section in the independent-jump model of Singwi and Sjölander[1,3] takes the same form as Eq. (8), except that $P(t)$ is replaced by the *a priori* probability e^{-t/τ_D} inferred from the long-term-average behavior of the system. The time constant τ_D, which represents the mean time between jumps of a given atom, is obtained from macroscopic diffusion measurements through the relation (for cubic crystals)

$$D = r_0^2 f_C / 6\tau_D \quad ,$$

where D is the diffusion constant, r_0 is the nearest-neighbor distance, and f_C is the Bardeen-Herring correlation factor.[9] If all atoms in the sample can participate in the diffusion process on a time scale of order τ_D, the relaxation $P(t)$ is given by the probability e^{-t/τ_D}, and the results of Singwi and Sjölander are obtained.

The vacancy mechanism, however, represents a diffusion process in which only a limited number of atoms can engage in jump motion on a time scale of order τ_D. In general, the relaxation will be slower than e^{-t/τ_D}, since not all atoms in the lattice will have had an opportunity to contribute to mass transport. For example, if the motion of an atom is highly correlated, as is the case when a vacancy is tightly bound to an impurity, only a small fraction of the N_M Mössbauer atoms will jump in time τ_D ($\sim N_V/N_M$, where N_V is the number of vacancies present), giving $P(\tau_D) \cong 1$. Similar results obtain even if the motion is not highly correlated. Thus the Mössbauer effect provides a sensitive technique for the determination of the extent to which the diffusive motion of atoms is correlated when combined with the results of macroscopic experiments.

It might be argued that although a large fraction of the Mössbauer atoms do not diffuse during a time interval of length $\tau_D \cong \Gamma_\gamma^{-1}$, the spectrum is nevertheless broadened by an amount $2\hbar\tau_D^{-1}$, since those atoms that do diffuse do so at a rate greater than Γ_γ. According to Eq. (8), however, the spectrum is given by the transform of $P(t)$, the function which describes how many atoms do not jump during the time interval $0 \rightarrow t$. Thus, within the context of the self-correlation-function formulation, repeated jumps of one group of atoms cannot be considered to compensate directly for lack of diffusive motion of the other atoms in the lattice. In the extreme limit of highly correlated diffusion, in which only N_V ($\ll N_M$) Mössbauer atoms jump during the lifetime of the excited nuclear state, the broadening will be essentially nonexistant,[11] even if the average diffusive jump rate is of order Γ_γ.

IV. $P(t)$ FOR VACANCY DIFFUSION

An exact calculation of $P(t)$ could require following the detailed motions of vacancies through the lattice in a manner similar to the computation of the correlation factor and will not be attempted here. Instead we present a model for the relaxation based on a consideration of the average behavior of the vacancy system and its effect on the jump motion of Mössbauer atoms.

Consider a lattice containing N_M Mössbauer atoms.

At time t the number of such atoms that still remain at their initial lattice sites is $N(t)$. In time $t \rightarrow t+dt$, $N(t)$ will change to the value $N(t+dt)$ according to the equation

$$N(t+dt) = N(t)(1-\beta\, dt) \ , \qquad (9)$$

where β is the jump probability for those atoms which have survived the interval $0 \rightarrow t$. If the jump probability for atoms which survive is the same as for atoms which have previously jumped, β takes the value τ_D^{-1}. The solution of Eq. (9) in this case is

$$N(t) = N_M e^{-t/\tau_D} \text{ or } P(t) = e^{-t/\tau_D} \ .$$

It can be seen that the relaxation function for the independent-jump model is obtained if for any time interval each Mössbauer atom has an equal *a priori* probability to jump, whether or not a previous jump has occurred.

The situation, however, is different for vacancy diffusion. For an atom to jump during the interval $t \rightarrow t+dt$ two events must occur in sequence: (a) A vacancy must occupy one of the nearest-neighbor (nn) sites of the atom and (b) the atom must exchange positions with the vacancy in time dt. If p_V is the probability that any one of the 12 nn sites of an atom is vacant (for a fcc lattice) and $w\, dt$ is the probability that the atom will jump into the vacant site, then the average diffusive jump rate can be written as

$$\tau_D^{-1}\, dt = 12 p_V w\, dt \ .$$

Consider two distinct Mössbauer atoms in the lattice, labeled A and B. Atom A has just exchanged with a vacancy which is presently located at a nn site of A, whereas atom B has not yet jumped during the time interval $0 \rightarrow t$. In the next increment of time $t \rightarrow t+dt$, the probability that atom B jumps, $\beta\, dt$, will depend on whether the vacancy at A diffuses away or remains in the nn shell of A. If the vacancy diffuses away and does not immediately return, the probability that it will occupy a nn site of B is $12p_V$. By contrast, if the vacancy is known to remain in the immediate region of A after an initial exchange, the probability for it to be next to B is zero. Thus β will reflect the fraction of vacancies which dissociate completely from one atom thereby contributing to the jump probability for atoms that have not jumped during $0 \rightarrow t$. For example, if the vacancy is bound to a given Mössbauer atom, $\beta \ll \tau_D^{-1}$, whereas if the vacancy is repelled, $\beta \cong \tau_D^{-1}$. Within this approximation, the relaxation time constant can be written as

$$\beta \cong 12 k p_V w = k\tau_D^{-1} \ ,$$

where k is the fraction of vacancies which diffuse away from an initial Mössbauer atom. This represents only the first term in a sequence which describes how those vacancies which do not immediately diffuse away affect the relaxation at a later time. It might be expected that the actual time constant be larger than $k\tau_D^{-1}$. The relaxation function obtained from Eq. (9) is

$$P(t) = e^{-kt/\tau_D} \ ,$$

which gives for the cross section Eq. (8)

$$\sigma_M(\vec{k}, \omega) = \frac{\sigma_0 \Gamma_\gamma}{4\hbar} e^{-2W} \frac{\Gamma_\gamma + 2k\tau_D^{-1}}{\omega^2 + \frac{1}{4}(\Gamma_\gamma + 2k\tau_D^{-1})^2} \ ,$$

a Lorentzian line shape with broadening (in energy units)

$$\Delta\epsilon = 2\hbar k \tau_D^{-1} \ .$$

$\Delta\epsilon$ is linear in τ_D^{-1} as is observed experimentally, with a slope proportional to the fraction of vacancies which completely dissociate from their respective Mössbauer atoms.

A vacancy can remain in the region of one atom either by direct binding, in which case it will be confined to the nn shell of that atom, or by executing a random walk, the path of which is localized around the atom. In either event the probability that other atoms in the lattice jump will be reduced from the value obtained by assuming that a vacancy is located at any one of the nn sites of an impurity with equal probability p_V, independent of the past history of the vacancy motion. By counting only those vacancies known to dissociate completely, an estimate is made of the jump probability for other atoms in the lattice.

The probability that a vacancy will leave the nn shell on the first jump can be found from a consideration of the jump frequencies[12] w_1, w_2, and k_1. w_2 is the frequency for reexchange with the impurity (Mössbauer atom), w_1 is for exchange with one of the atoms that is a nn of both the Mössbauer atom and the vacancy (of which there are four for a fcc lattice), and k_1 is for exchange with one of the atoms that is not a nn of the Mössbauer atom (of which there are seven). The fraction of vacancy jumps to non-nearest-neighbor positions is

$$7k_1/(w_2 + 4w_1 + 7k_1) \ .$$

Of these a fraction R will return to a nn site of the impurity in the next few jumps, giving for k

$$k = 7k_1(1-R)/(w_2 + 4w_1 + 7k_1)$$

or

$$\Delta\epsilon \cong 2\hbar \frac{7(1-R)k_1\tau_D^{-1}}{w_2 + 4w_1 + 7k_1} \ . \qquad (10)$$

The fraction R can be easily computed under the assumption of only nn vacancy-impurity attraction or repulsion. For the fcc lattice, $R \cong 0.26$ is found by summing up to three vacancy jumps; that is, if a vacancy requires more than three jumps to return to a nn site, it is considered to be dissociated.

The effect of correlation can be taken into account by considering the general case in which $w_1 \neq w_2 \neq k_1$. The correlation factor is given by[9]

$$f_C = (2w_1 + 7Fk_1)/(2w_2 + 2w_1 + 7Fk_1) \quad ,$$

where F is the fraction of dissociating vacancies which effectively return to the original nn site. For $k_1 \ll w_1 \ll w_2$, the correlation factor approaches zero. In this limit the broadening $\Delta\epsilon$ [Eq. (10)] also approaches zero in agreement with the considerations of Sec. III. If, in the other limit, the vacancy is strongly repelled by the impurity, $k_1 \gg w_1$ and w_2, and f_C approaches unity. According to Eq. (10) the broadening is $2\hbar(1-R)\tau_D^{-1} \sim 1.5\hbar\tau_D^{-1}$ (for the fcc lattice). Even in the limit of strong impurity-vacancy repulsion there is a larger than random chance that a vacancy will reoccupy a nn site of an impurity. The broadening will be reduced from the purely random value of $2\hbar\tau_D^{-1}$ to $(2\hbar\tau_D^{-1})(1-R)$ for this case.

If all vacancy jump frequencies are equal, k takes the value

$$k = (0.74)\tfrac{7}{12} = 0.43 \quad , \quad w_1 = w_2 = k_1$$

or

$$\Delta\epsilon \cong 0.86\hbar\tau_D^{-1} \quad ,$$

in reasonable agreement with the values measured for iron in copper[4] and iron in gold[5] systems for which it is expected that the host-vacancy and tracer-vacancy exchange rates are nearly the same. However, until more detailed calculations are advanced, such agreement must not be considered to be quantitatively exact. Nevertheless, the results of the model indicate that the broadening should be less than $2\hbar\tau_D^{-1}$, in agreement with experiment, and offers an understanding of the mechanism responsible for the reduced broadening observed for materials known to diffuse by the vacancy mechanism.

The above considerations indicate that the broadening for the vacancy mechanism ranges from 0 in the highly correlated limit to a value less than $2\hbar\tau_D^{-1}$ in the uncorrelated limit. As a consequence the Mössbauer effect can be useful for determining the diffusion mechanism, especially in bcc structures for which similar results can be expected as for the fcc lattice if the vacancy mechanism is dominant. Combined with macroscopic diffusion experiments, Mössbauer line broadening can also provide additional information concerning host-vacancy and impurity-vacancy exchange rates, useful in understanding correlation effects.

ACKNOWLEDGMENTS

I wish to thank Professor J. G. Mullen for interesting discussions concerning the topic of diffusion broadening. I would also like to express appreciation to David Brice, Milton Clauser, David Emin, and Albert Narath for helpful comments on this paper.

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*Work supported by the U.S. Atomic Energy Commission.

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[11] The opposite effect is expected if $N_V \gg N_M$, since during the lifetime Γ_γ^{-1} essentially all Mössbauer atoms have jumped. It might then be expected that the broadening would be of order $2\hbar\nu_i$, where ν_i is the impurity-vacancy exchange rate. This point is discussed in more detail in Ref. 6.

[12] See, for example, the discussions in Refs. 2 and 9.