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Direct Observation of Solid-State Diffusion Using the Mössbauer Effect*

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Iron diffusion in copper has been measured using the Mössbauer effect. The temperature dependence of the Mössbauer line broadening is proportional to the temperature dependence of the diffusivity as determined by the tracer-sectioning technique. The magnitude of the broadening is about $\hbar/\tau$ (where τ is the mean time an atom spends at a given site), instead of $2\hbar/\tau$ as predicted by the jump model of diffusion. No evidence for sidebands is observed in the broadened Mössbauer spectra, which have approximately Lorentzian line shape. The temperature dependence of the recoil-free fraction appears to be anomalously large in the region where diffusion broadening of the Mössbauer line was observed.

SHORTLY after the discovery of the Mössbauer effect, theoretical arguments[1] were given to show how the effect might be used as a microscopic probe for studying diffusion in solids. Although earlier experimenters[2,3] reported the observation of diffusion associated with the Mössbauer effect, these data were handicapped by the indirect way in which the linewidth was measured, they failed to show the expected temperature dependence[1] for the broadened line, and they were not convincingly correlated to macroscopic diffusion experiments. By contrast, other observers have sought direct observations of diffusion broadening but they did not observe the expected effect.[4] We wish to report the *direct* observation of diffusion broadening of the Mössbauer line of Fe^{57} in copper. We have observed the temperature dependence of this broadening, and, within present experimental errors, the increase in linewidth does follow the exponential temperature dependence observed in the usual type of diffusion measurement, which is in accord with theory, although the magnitude of the broadening appears to be only about half of the amount predicted by the simple diffusive jump model originally considered in relation to the Mössbauer effect by Singwi and Sjölander.[1] In harmony with their analysis, we find no evidence of side peaks in the wings of the resonance as has been observed in time filtering experiments.[5,6]

The data were taken with a crank velocity spectrometer system.[7] As a check on possible systematic errors, a source experiment using Co^{57} in Cu versus a $Na_4Fe(CN)_6 \cdot 10H_2O$ absorber was used for one set of measurements, while an Fe^{57}-doped copper absorber scanned with a Co^{57}-in-Pd source was used for the other set of experiments. The furnace design[8] used a hydrogen atmosphere in the chamber where the Mössbauer source or absorber was contained, with special precautions taken to prevent thermocouple damage due to possible reactions with the hydrogen atmosphere. Both the source and the absorber experiments indicate a broadening of the Mössbauer line in a 100°K temperature interval slightly below the melting temperature of copper. The Mössbauer spectra are shown in Fig. 1, and the broadening of the line as a function of temperature is shown in Fig. 2. In Table I, we give the temperature, total linewidth, and area under the absorption curve S for each spectrum shown in Fig. 1. The values shown in Fig. 2 were obtained by subtracting the unbroadened linewidth Γ_M from the measured linewidths. Because of finite thickness corrections, temperature-dependent solubility questions, etc., Γ_M could not be determined with great confidence. For the Co^{57}:Cu source experiment, we estimate $\Gamma_M = 0.35$ mm/sec and for the Fe^{57}:Cu absorber experiment $\Gamma_M = 0.44$ mm/sec. Although large variations in Γ_M were considered, the qualitative features of the data were not changed. The values chosen for Γ_M were indicated from data taken at

TABLE I. Relevant Mössbauer parameters obtained from the data in Fig. 1.

Fig.	T (°C)	Γ (mm/sec)	S (area under absorption curve)
	Co^{57}-in-Cu source		
1a	1061	0.96	0.015
1b	1036	0.70	0.018
1c	1020	0.68	0.020
1d	1001	0.55	0.020
1e	951	0.47	0.026
1f	23	0.34	0.145
	Fe^{57}-in-Cu absorber		
1g	1060	1.15	0.021
1h	1041	0.88	0.021
1i	1026	0.76	0.023
1j	1002	0.62	0.023
1k	953	0.54	0.036
1l	875	0.45	0.040

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[1] K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

[2] A. J. F. Boyle, D. St.P. Bunbury, C. Edwards, and H. E. Hall, Proc. Phys. Soc. (London) **77**, 129 (1961).

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[4] W. A. Steyert and R. D. Taylor, Phys. Rev. **134**, A716 (1964).

[5] F. J. Lynch, R. E. Holland, and M. Hamermesh, Phys. Rev. **120**, 513 (1960).

[6] C. S. Wu, Y. K. Lee, N. Benczer-Koller, and P. Simms, Phys. Rev. Letters **5**, 432 (1960).

[7] J. G. Mullen, Phys. Rev. **131**, 1410 (1963).

[8] A description of the furnace used in these experiments will appear in a later publication.

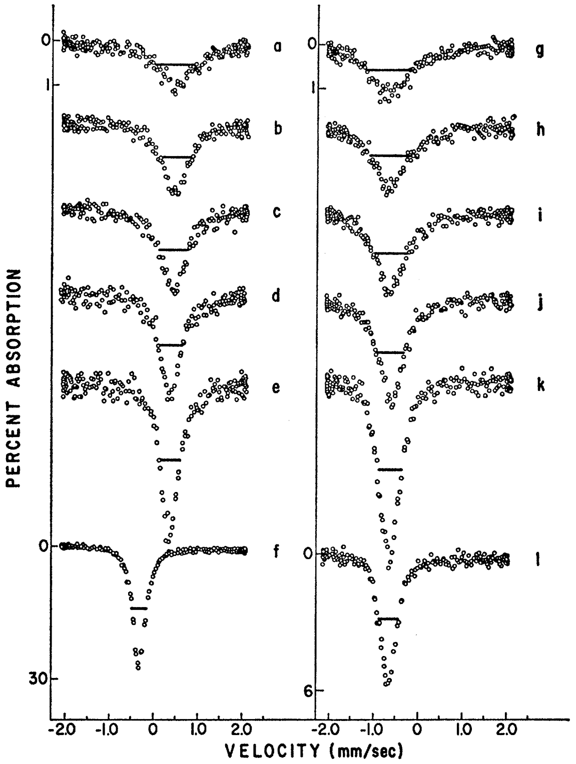

FIG. 1. Mössbauer spectra displayed in order of decreasing temperature. The data on the left are for the Co^{57}-in-Cu-source experiment and those on the right are for the Fe^{57}-in-Cu-absorber experiment. The vertical scale is the same for all spectra except for those in (f and l). The linewidths obtained from a least-squares fit of the data to Lorentzian line shapes are represented by horizontal lines on each spectrum. Approximately one million counts per channel were taken for the high-temperature runs in order to obtain the small statistical counting errors shown.

temperatures where diffusion is unimportant and gave a slope consistent with the macroscopically measured diffusivity. These data are shown in Fig. 1(f and l). When the Mössbauer spectrum of the Co^{57}:Cu source was run against a thin absorber, it yielded the natural linewidth (0.2 mm/sec), which shows that the broadening in the spectrum shown in Fig. 1(f) was only caused by the finite thickness of the absorber used. Also, it should be noted that low-temperature broadening of Γ_M in the Fe^{57}:Cu absorber experiment was not caused by any solubility problem, since the concentration of iron in this absorber was only of order 1%, well below the 4% solubility limit for iron in copper in the temperature interval where diffusion broadening was observed. As an added check on the systematic errors, the lowest-temperature resonances [Fig. 1(f and l)] were run before and after the high-temperature runs, and they reproduced with respect to linewidth and area. The temperature sequence of the two experiments was carried out in the opposite order, i.e., as shown on Fig. 1(a–e) and Fig. 1(k–g).

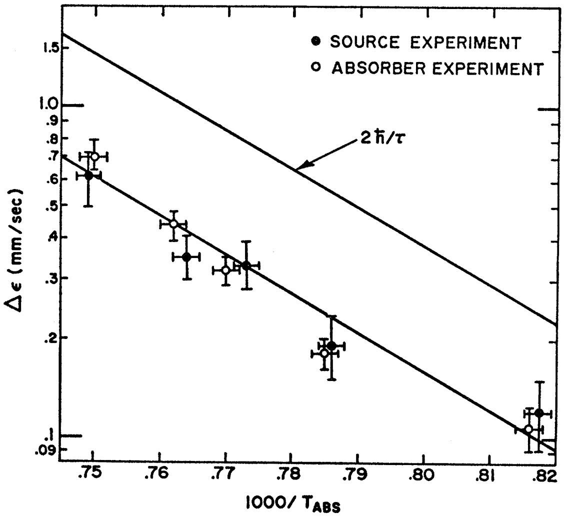

FIG. 2. Line broadening as a function of temperature. The errors in Δε reflect the dispersion found from a least-squares fit of the data to Lorentzian line shapes. The horizontal error bars indicate a possible ±3°K temperature error.

Singwi and Sjölander[1] have shown that the Mössbauer line broadening Δε is given by

$$\Delta\epsilon=(2\hbar/\tau)(1-\alpha)\,,$$

where

$$\alpha=\int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}h(\mathbf{r})\,.$$

τ is the mean lifetime of an atom in a given atomic site and $h(\mathbf{r})$ is the probability that an atom has moved to a position $\mathbf{r}$ relative to the origin after one jump. In cases such as the one under consideration, where $kr_0\gg1$ (r_0 being the distance of one jump), it would appear that the effect of α on Δε would be quite small, although an exact calculation for a polycrystalline material has not been carried out. Assuming, however, approximately that $h(r)=\delta(r-r_0)/4\pi r_0^2$, we find $\alpha=(\sin kr_0)/kr_0$, which is always small for $kr_0\gg1$. The mean life of the atom in a specified lattice position can be inferred from the macroscopic diffusivity D. The result for cubic materials is

$$\tau=r_0^2 f/6D\,,$$

where f is the Bardeen-Herring correlation factor.[9] The isotope-effect measurements[10] show that f is between $\frac{2}{3}$ and unity for iron diffusing in copper. If one takes the self-diffusion value of 0.8 as a reasonable estimate, the predicted line broadening $2\hbar/\tau$, shown in Fig. 2, is seen to be about twice the measured value.

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[9] The theory of Singwi and Sjölander does not include effects due to correlation. Therefore it is inconsistent to include correlation in the calculation of τ. However, the use of $f=0.8$ is an approximation which we believe to be better than neglecting correlation entirely.

[10] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

Although the discrepancy is not understood at present, the theoretical models used so far to estimate diffusion broadening are highly idealized. Both the jump model and the continuum-diffusion model indicate a greater broadening than was actually observed (the first by a factor of 2 and the second by more than an order of magnitude). The jump model, which might be considered as a rough approximation to solid-state diffusion, accounts only qualitatively for the observed broadening. It has the added limitation that it indicates a temperature dependence to the recoil-free fraction of e^{-2W}, while we find a more rapid decrease in $f(T)$ in the temperature interval where diffusion occurs. Over the temperature range from 950–1060°C, the calculated decrease in f (derived from data of Steyert and Taylor[4] with a first-order anharmonic correction) is 23%, whereas our measurements indicate a decrease of 42%, in the source experiment with fixed absorber, over the same temperature interval.

The success of reaction-rate theory in explaining diffusion in solids, which requires that the activated state be sufficiently long-lived to make the specification of thermodynamic parameters such as temperature meaningful, may indicate that the sudden-jump approximation is not valid. Thus a more precise model might very well account for the reduced broadening of the Mössbauer line which was observed, and also might be hoped to account for the anomalous behavior of $f(T)$ observed in the temperature range where diffusive effects are important. It is easy to give qualitative arguments to show that these two effects might be expected to correlate. If this view is correct, it should be a general property of diffusion-broadened Mössbauer lines that the observed broadening is less than $2\hbar/\tau$. This might explain why the extensive studies of $f(T)$ by Steyert and Taylor[4] did not reveal any significant diffusion broadening for iron diffusion in gold in the temperature region studied. Their highest temperatures studied, however, were sufficiently low (about 300°C below the melting temperature of gold) that the expected broadening for their case would have been very small in any event.

Another possible explanation for the discrepancy between the simple diffusion-jump model and our experimental results may be connected with the assumption that an Fe^{57} ion will relax out of a lattice site with an exponential time dependence. Because the diffusion of Fe^{57} in Cu is known to occur via the vacancy mechanism,[10] diffusion is related to two processes: the probability that a vacancy is next to an Fe^{57} ion and the vacancy-impurity exchange probability. If this two-step process resulted in a relaxation-probability dependence on time approaching a step function, then a linewidth of order $\hbar/\tau$ might be accounted for an analogy with time-filtering experiments.

Considerable effort was made to show that the discrepancies between the jump model and our experimental results were not due to systematic errors. One possible systematic error which has not yet been eliminated is that caused by the difference in environment of the macroscopic diffusion measurements compared with the present Mössbauer experiment. The experiments on tracer diffusion of iron in copper[10,11] were done in vacuum with vacuum-grown Cu crystals, while the present Mössbauer experiments were carried out in a hydrogen atmosphere. Because the solubility of hydrogen in most metals at elevated temperatures is not generally negligible, the iron diffusivity may have been altered due to the presence of dispersed atomic hydrogen. This effect is not thought to be important, although experiments are planned to investigate this possibility further.

We plan to extend these experiments to the case of Fe diffusion in gold, where comparable broadening should be observed, but where differences due to model-dependent effects may be manifest.

[*Note added in proof.* Since this manuscript was submitted we have carried out the study of iron diffusion in gold as suggested above. The results are to be published in the Journal of Applied Physics Letters.]

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[11] C. A. Mackliet, Phys. Rev. **109**, 1964 (1958).