consistent theory of classical liquids in that both equilibrium and nonequilibrium properties can now be calculated within the same framework. At present, the theory, however, describes the dynamical properties reasonably only for large $q$ and $\omega$. Improvements are needed for the theory to describe the dynamics for all $q$ and $\omega$.

We are particularly thankful to Professor A. Sjölander for getting us interested in the STLS theory and for providing us access not only to his own but also Dr. R. Pynn's unpublished work as well. Dr. A. Rahman has been kind enough to send us his molecular-dynamics data on liquid rubidium as well as a listing of the rubidium potential. We would also like to thank Dr. R. Evans and Dr. R. Kumaradivel for repeating their WCA calculations for the Shyu *et al.* potential for liquid sodium at our request and sending us their results prior to publication.

*Supported in part by the Deutsche Forschungsgemeinschaft.

†Present address: Abteilung Theoretische Physik, Universität Bielefeld, 48 Bielefeld, W. Germany.

[1]J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. 54, 5237 (1971); H. C. Andersen, J. D. Weeks, and D. Chandler, Phys. Rev. A 4, 1597 (1971).

[2]H. C. Andersen, J. D. Weeks, and D. Chandler, J. Chem. Phys. 56, 3812 (1972).

[3a]M. Hasegawa and M. Watabe, J. Phys. Soc. Jpn. 36, 1510 (1974); J. H. Wehling, W.-M. Shyu, and G. D. Gaspari, Phys. Lett. 39A, 59 (1972).

[3b]R. Evans and R. Kumaradivel, to be published; R. Kumaradivel, Ph.D. thesis, University of Bristol, 1975 (unpublished).

[4]R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Interscience, New York, 1961), Vol. 3.

[5]H. Mori, Prog. Theor. Phys. 33, 423 (1965).

[6]L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963).

[7]K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. A 176, 589 (1968).

[8]K. N. Pathak and K. S. Singwi, Phys. Rev. A 2, 2427 (1970); R. Bansal and K. N. Pathak, Phys. Rev. A 11, 1450 (1975).

[9]A. Sjölander, private communication.

[10]R. Pynn, unpublished.

[11]See in particular Eqs. (25) and (20) of Ref. 2 and also H. C. Andersen and D. Chandler, J. Chem. Phys. 53, 547 (1970), and 55, 1497 (1971). The exact relationship between the functional $\mathcal{J}(\psi)$ and Eq. (6) when $\varphi$ is replaced by $\psi$ is given by $\mathcal{J}(\psi) = -(2\mathcal{A}/\beta\rho^2) - \int g(\mathbf{r})\psi(\mathbf{r})\, d^3\mathbf{r}$.

[12]This smoothing procedure due to L. Verlet is discussed by J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, Phys. Rev. A 7, 2130 (1973).

[13]A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A 4, 1607 (1971).

[14]A. Rahman, Phys. Rev. A 9, 1667 (1974).

[15]D. L. Price, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 2, 2983 (1970); D. L. Price, Phys. Rev. A 4, 358 (1971).

[16]W.-M. Shyu, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 3, 237 (1971).

[17]P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972).

# Unusual Dynamical Properties of Self-Interstitials Trapped at Co Impurities in Al†

G. Vogl and W. Mansel
*Physik-Department der Technischen Universität München, 8046 Garching, Germany*

and

P. H. Dederichs
*Institut für Festkörperforschung der Kernforschungsanlage Jülich, 517 Jülich, Germany*

(Received 2 February 1976)

Mössbauer spectroscopy was used to study the dynamics of Al self-interstitials trapped at $^{57}$Co impurities. When a single interstitial atom is trapped at the $^{57}$Co atom, the Debye-Waller factor decreases rapidly by more than a factor 4 in the temperature interval between 13 and 20 K. We try to explain this anomaly by the following model: The $^{57}$Co atom jumps between six different positions, thereby forming mixed Co-Al dumbbells with changing Al partners.

In recent years the study of interstitials in metals and especially of their dynamical properties has received increasing interest. Experimental studies indicated a remarkable lattice softening[1-4] due to interstitials in fcc metals. Mössbauer measurements on dilute *Al*Co alloys[5-7] gave a direct indication[6,7] of low-frequency vibrations of self-interstitials trapped at Co atoms together

forming mixed dumbbells (compare with work of Swanson, Maury, and Quenneville[8]): The Debye-Waller factor (DWF) $f$ of an additional Mössbauer line due to interstitial atom trapping ("defect line"), when measured after fast-neutron irradiation at 4.6 K followed by an annealing to 160 K, showed a significant decrease at elevated temperatures. According to

$$f = \exp[-\langle(\vec{k}\cdot\vec{x})^2\rangle], \quad (1)$$

in the harmonic approximation, this corresponds to large thermal displacements $\langle x^2\rangle$ of the Mössbauer atom ($k$ is the wave number of the Mössbauer $\gamma$ quantum). These could be understood by assuming low-frequency vibrations of the interstitials with a frequency similar to that yielded by theoretical calculations.[9] Since, after neutron irradiation and annealing, multiple trapping of interstitials has to be expected, the observed behavior of the DWF may reflect the dynamics of interstitial clusters rather than of isolated trapped interstitials. The aim of the present investigation was therefore to reduce clustering as much as possible in order to study isolated trapped interstitials.

High-purity polycrystalline aluminum samples containing of the order of 20-ppm cobalt (part of which was the radioactive $^{57}$Co Mössbauer isotope) were irradiated with 2.8-MeV electrons at a temperature above annealing state I. Under these conditions irradiation-induced interstitials are highly mobile and can escape annihilation only if they are trapped at the cobalt impurity atoms. For irradiation doses corresponding to resistivity changes of $\Delta\rho_0 = 2$ and 2.7 n$\Omega$ cm we determined from the Mössbauer measurements that 17% and 36% of the cobalt atoms had trapped interstitials during irradiation; about 90% and 70%, respectively of these trapped only a single interstitial. Figure 1 shows the Mössbauer spectra; the fitting procedure is described in Ref. 7. The temperature dependence of the apparent DWF for the lower irradiation dose is shown in Fig. 2.

A very striking effect is evident. The *apparent DWF decreases rapidly by more than a factor of 4 in a narrow temperature interval from about 13 to about 20 K.* This is very different from the DWF data reported in Refs. 6 and 7, where, in the corresponding temperature range, the decrease of the DWF was observed to be about 5 times weaker. This proves that the dynamics of isolated trapped interstitials is drastically different from the dynamics of trapped interstitial clusters. The extreme behavior of the apparent DWF was only observed at sufficiently low defect concentrations, i.e., for isolated trapped interstitials. Systematic studies have shown that with increasing defect concentration, i.e., with increasing average number of trapped interstitials per $^{57}$Co atom, the temperature dependence of the apparent DWF becomes less pronounced and approaches finally the values observed after neutron

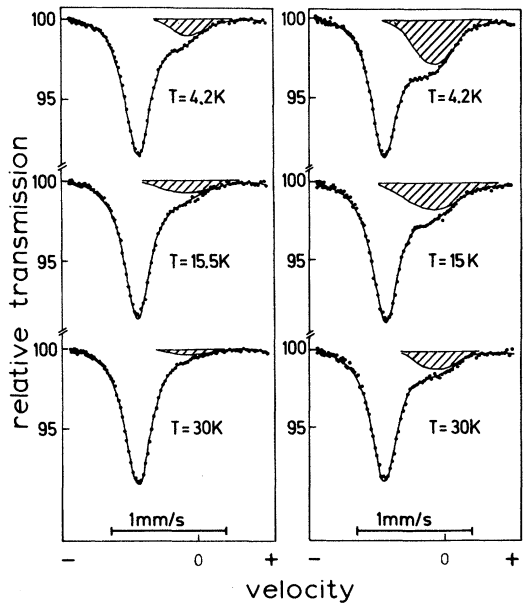


FIG. 1. Mössbauer spectra of *Al* $^{57}$Co with the sample at various temperatures after two electron irradiation runs at about 100 K. Natural iron absorber at 77 K. Hatched: "defect line" corresponding to 17% (left side) and 36% (right side) of $^{57}$Co atoms with trapped interstitials.

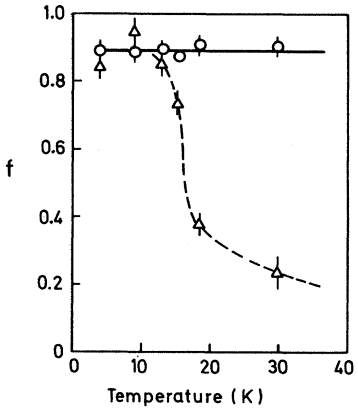


FIG. 2. Temperature dependence of the apparent Debye-Waller factor $f$ of $^{57}$Co in Al. Upper curve circles, $^{57}$Co on substitutional site; lower curve triangles, $^{57}$Co with trapped single interstitial.

irradiation and heating to 160 K.[6,7] Details on the concentration dependence will be published elsewhere. The decrease of the DWF is a reversible process and not due to defect annihilation. Annihilation of the trapped interstitials occurs in stage III, e.g., by heating for 10 min at temperatures higher than 200 K.

Whereas the DWF decrease of $^{57}$Co with trapped interstitial clusters could be explained in a harmonic model as due to low-frequency vibrations of the $^{57}$Co atom,[6,7] such an interpretation is impossible for the most rapid decrease reported here: Such low-frequency vibrations would lead to large zero-point displacements corresponding to an appreciably lower DWF at 4.2 K than observed experimentally. In addition the value of $\langle x^2\rangle^{1/2}$ calculated according to (1) from the DWF at 30 K is about 50% of the distance to the saddle point for an "ideal" dumbbell. Together with the sudden decrease of the apparent DWF this suggests that within the lifetime of the Mössbauer state ($\tau_M = 1.4\times10^{-7}$ sec) the Co atom has an appreciable probability to leave its lattice site via a thermally activated process, e.g., to jump to a neighboring dumbbell position. Since the Mössbauer experiments have shown that the interstitial-impurity complexes are stable up to stage III (200 K), such *jumps cannot lead to long-range diffusion. The Co atom must be confined to a "cage."*

The formation of interstitial-impurity complexes has been studied theoretically.[10] It was found that the formation of a mixed [100] dumbbell is energetically favored only if the impurity atom is smaller[11] than the host atom. For a jump of the impurity-dumbbell atom leading to a mixed dumbbell on a neighboring site, the activation energy can be appreciably lower than the self-interstitial migration energy, if the impurity is sufficiently small.[10] This process does not lead to long-range diffusion since the impurity can only occupy six different mixed-dumbbell configurations centered around an octahedral position, as shown in Fig. 3.

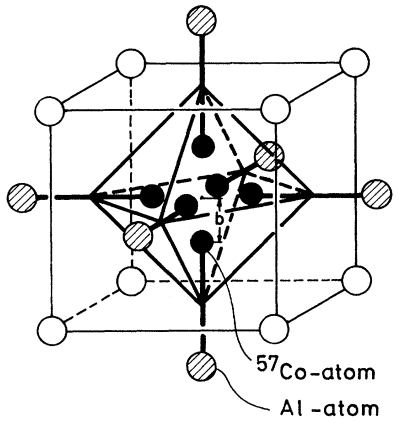


FIG. 3. Equivalent configurations for a mixed dumbbell, which can be formed by jumps of the $^{57}$Co-impurity atom in the octahedral "cage" in a fcc lattice.

In analogy to Singwi and Sjölander,[12] the probability $w_e(\omega,\vec{k})$ for the emission of a $\gamma$ quantum with an energy $E_0+\hbar\omega$ (with $E_0$ the energy difference between the excited and ground states of the nucleus) and a momentum $\hbar\vec{k}$ (with $\vec{k}=E_0/\hbar c$) for a discrete-jump model is given by

$$w_e(\omega,\vec{k}) = (1/2\pi\hbar)\int_{-\infty}^{+\infty} dt \sum_\nu \exp[i\omega t - (\Gamma|t|/2\hbar) + i\vec{k}\cdot\vec{r}_\nu]\, G_s(\vec{r}_\nu,t). \quad (2)$$

Here $\Gamma$ is the natural width of the excited nuclear state. In the classical limit the self-correlation function $G_s(\vec{r}_\nu,t)$ can be written as

$$G_s(\vec{r}_\nu,t) = \sum_n P(\vec{R}_n+\vec{r}_\nu,\vec{R}_n;t)P_0(\vec{R}_n), \quad (3)$$

where $P(\vec{R}_n+\vec{r}_\nu,\vec{R}_n;t) = P(\vec{R}_m,\vec{R}_n;t)$ is the probability of finding the Mössbauer atom at time $t$ at the position $\vec{R}_m = \vec{R}_n+\vec{r}_\nu$ if it was at $t=0$ at the position $\vec{R}_n$. $P_0(\vec{R}_n)$ is the probability of finding the atom at $\vec{R}_n$ at $t=0$. For the cage model, $\vec{R}_n$ refers to the six positions of the $^{57}$Co atom in the cage ($n=1,\ldots,6$) and the $\vec{r}_\nu$'s are the difference vectors between the positions. $P_0(\vec{R}_n)=\frac{1}{6}$ because of the six sites.

We consider the case that the Mössbauer atom performs many jumps [jump time $\tau=\tau_0\exp(U/k_BT)$] during the lifetime of the excited Mössbauer state. The Mössbauer atom is then equally distributed on all six possible cage sites, i.e., $P(\vec{R}_m,\vec{R}_n;\tau_M\gg\tau)=P_0(\vec{R}_m)=\frac{1}{6}$. From Eq. (2) one obtains with Eq. (3) an unbroadened Mössbauer line (of width $\Gamma/\hbar$), the intensity of which is reduced by the factor

$$\begin{aligned} f_J &= \exp(-2M_J) = \sum_\nu \exp(i\vec{k}\cdot\vec{r}_\nu)\sum_n P_0(\vec{R}_n+\vec{r}_\nu)P_0(\vec{R}_n) \\ &= \sum_m\sum_n \exp[i\vec{k}\cdot(\vec{R}_m-\vec{R}_n)]P_0(\vec{R}_m)P_0(\vec{R}_n) = |\sum_n \exp(-i\vec{k}\cdot\vec{R}_n)P_0(\vec{R}_n)|^2 \\ &= |\tfrac{1}{6}\sum_n \exp(-i\vec{k}\cdot\vec{R}_n)|^2 = [\tfrac{1}{3}(\cos k_x b+\cos k_y b+\cos k_z b)]^2. \end{aligned} \quad (4)$$

We call $f_J$ a jump DWF.[13] Here $b$ is the distance of the impurity atom from the cage center (Fig. 3). Equation (4) simply expresses the fact that the $\gamma$ ray is coherently emitted from all six positions in the cage and that the intensities have to be added with the correct phases.

Since in the case of the 14.4-keV Mössbauer transition the wavelength of the $\gamma$ ray, $\lambda = 2\pi/k = 0.861$ Å, nearly equals the distance $b = 0.79$ Å, the jump DWF $f_J$ is very sensitive to the direction of $\vec{k}$ with respect to the crystal orientation [see Eq. (4)]. For polycrystals as in our case one has to average over all $\vec{k}$ directions. In the discussed case of fast jumps the line is unbroadened (width $\Gamma$, independent of the direction of $\vec{k}$) and therefore only the intensity $f_J(\vec{k})$ of this line has to be averaged, yielding a value of $f_J = 0.23$. This is in good agreement with the experimentally observed decrease of the apparent DWF in the range between 13 and 20 K (Fig. 2). From the temperature at which the decrease in $f$ reaches its maximum slope (16 K) with $\tau_0 = 10^{-12}$ sec[7] we obtain the activation energy for jumps in the cage: $U = 0.017 \pm 0.005$ eV.

For a general solution of the problem one has to solve the rate equation for the conditional probability $P(\vec{R}_m, \vec{R}_n; t)$ [with $P(\vec{R}_m, \vec{R}_n; 0) = \delta_{mn}$]:

$$\frac{\partial P(\vec{R}_m, \vec{R}_n; t)}{\partial t} = \frac{1}{\tau} \sum_l [P(\vec{R}_l, \vec{R}_n; t) - P(\vec{R}_m, \vec{R}_n; t)], \quad (5)$$

where one has to sum over the four positions $l$ in the cage which can be reached by one jump from a position $m$. In addition to the unbroadened line one now obtains two broadened Lorentzian lines, of widths $\Gamma + 8\hbar/\tau$ and $\Gamma + 12\hbar/\tau$, containing together the residual intensity $1 - f_J$. Because of $\tau = \tau_0 \exp(U/k_B T)$, the widths of these lines should rapidly exceed the natural linewidth. Therefore their peak intensities should decrease also very rapidly so that it might be rather difficult to detect these lines particularly since they are overlapped by the unbroadened line. An experimental indication for the existence of the broadened lines is the fact that the computer fits with a free linewidth of the Mössbauer spectra measured at 15 K actually gave a 40% broadening compared to the linewidths at 4.2 or 30 K. A definite finding of the two broadened lines might be necessary to prove the model which for the present is meant as a conjecture.

Finally we try to explain the much smaller decrease of the DWF after fast-neutron irradiation at 4.6 K followed by annealing at 160 K.[6,7] If more than one interstitial is trapped at the Co atom, the reorientation effect will disappear: Because of additional interstitials the six cage configurations for the mixed dumbbell are in general no longer equivalent. For instance, a di-interstitial consisting of two aligned [100] dumbbells energetically favors one of the six configurations, so that a reorientation is no longer possible. Then only the low-frequency interstitial vibrations remain leading to a DWF decrease as found in Refs. 6 and 7.

The rapid decrease of the apparent DWF can be explained by the reorientation of a mixed dumbbell within the cage of Fig. 3. However, these results cannot confirm the exact structure of the mixed dumbbell. This, however, can be achieved by the same method if for single crystals the orientation dependence of $f_J(\vec{k})$ is measured and if the broadened Lorentzian lines can be detected. Such experiments are in preparation.

It is a pleasure to thank W. Schilling for drawing the possible existence of the "cage" to our attention. We are grateful to J. Hemmerich for supporting the irradiation experiments.

---

†This work was supported by the German Bundesministerium für Forschung und Technologie.

[1]J. Holder, A. V. Granato, and L. E. Rehn, Phys. Rev. Lett. 32, 1054 (1974).

[2]K. H. Robrock and W. Schilling, to be published.

[3]R. M. Nicklow, R. R. Coltman, F. W. Young, Jr., and R. F. Wood, Phys. Rev. Lett. 35, 1444 (1975).

[4]K. Böning, G. Bauer, H. J. Fenzl, R. Scherm, and W. Kaiser, to be published.

[5]W. Mansel, G. Vogl, and W. Koch, Phys. Rev. Lett. 31, 359 (1973).

[6]G. Vogl and W. Mansel, in *Proceedings of the Fifth International Conference on Mössbauer Spectroscopy, Bratislava, Czechoslovakia, 1973,* edited by M. Hucl and T. Zemcik (The Czechoslovak AEC, Prague, Czechoslovakia, 1975), p. 453.

[7]G. Vogl, W. Mansel, and W. Vogl, J. Phys. F 4, 2321 (1974).

[8]M. L. Swanson, F. Maury, and A. F. Quenneville, Phys. Rev. Lett. 31, 1057 (1973).

[9]P. H. Dederichs, C. Lehmann, and A. Scholz, Phys. Rev. Lett. 31, 1130 (1973).

[10]P. H. Dederichs, C. Lehmann, and A. Scholz, to be published.

[11]As a measure of the atomic size the volume change $\Delta V$ of the impurity in the corresponding matrix can be taken.

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

[13]In addition to the jump DWF we have as a multiplicative factor the DWF due to the thermal vibrations.