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EFFECT OF RESTRICTED DIFFUSION OF TRAPPED INTERSTITIALS ON THE CENTRAL SHIFT OF MÖSSBAUER IMPURITIES (*)

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Abstract. — The central shift of $^{57}$Fe atoms with trapped interstitials (mixed dumbbells) in aluminium increases steeply at temperatures between 10 and 20 K. Influences of restricted diffusion of the Mössbauer atom in a cage on the isomer shift and second order Doppler shift are discussed.

1. Introduction. — Mössbauer spectroscopy can be used to study structural lattice defects in solids in a microscopic way. A particularly useful method is to trap the defects at impurity atoms suitable for Mössbauer spectroscopy. These atoms then are probes for the defects [1].

In previous work irradiation induced interstitials in aluminium and silver have been studied by trapping them at $^{57}$Co impurity atoms and performing Mössbauer studies at the daughter nuclei $^{57}$Fe [2, 3]. The trapped interstitials gave rise to an additional line in the Mössbauer spectrum (defect line). Besides information on defect kinetics these experiments yielded information on the special dynamical behaviour of interstitials. A particularly surprising phenomenon was found after low dose electron irradiation of $^{57}$Co samples at a temperature of about 100 K [4]. Whereas the intensity of the Mössbauer line of $^{57}$Co atoms on substitutional sites (the original line) showed a normal behaviour in agreement with a Debye temperature of about $\theta_D = 290$ K, the apparent Debye-Waller factor of the defect line dropped in a narrow temperature range (10 to 20 K) from about 0.89 to 0.3. This was a reversible temperature dependence and not due to the annealing of the interstitials.

The interpretation of this effect is the following [4]: The $^{57}$Co impurity atom forms a mixed dumbbell with the trapped aluminium interstitial. The mixed dumbbell has an extraordinary dynamical behaviour: between 10 and 20 K it performs low frequency vibrations, the amplitudes of which are so large that the $^{57}$Co partner of the mixed dumbbell is able to leave its aluminium partner at least once during the lifetime of the Mössbauer level ($10^{-7}$ s). Then it forms a new mixed dumbbell with another one of six octahedrally arranged aluminium atoms which constitute a cage (Fig. 1). To allow the $^{57}$Co atom to leave the cage a much higher temperature (higher than 200 K) is necessary since the binding between the $^{57}$Co impurity atom and the interstitial has to be broken [5]. The radical drop of the intensity of the Mössbauer line in a narrow temperature interval is thus attributed to vibrations of the mixed dumbbell with large amplitudes, which enable the $^{57}$Co atom to diffuse in a restricted region (the cage) without being able to leave this region.

This paper now will report the temperature dependence of the central shift of the Mössbauer line of $^{57}$Co atoms having trapped interstitials during low-dose electron irradiation of aluminium.

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(1) Trapping of defects occurs at the mother isotope $^{57}$Co whereas Mössbauer measurements strictly speaking are performed on the daughter isotope $^{57}$Fe. For the sake of simplicity the impurity is called $^{57}$Co in the following.
2. Experiments and results. — Polycrystalline aluminium samples containing about 20 ppm cobalt (part of which was $^{57}$Co) were irradiated with 2.8 MeV electrons at a temperature above defect annealing stage I (about 100 K). Under these conditions irradiation induced interstitials are highly mobile and can escape annihilation only if they are trapped at the cobalt impurity atoms. After irradiation the samples were transferred to the measuring cryostat without warming up. Mössbauer measurements were performed with the samples as sources at varying temperatures beginning from 4.2 K. The absorber was a natural iron foil thermally coupled to liquid nitrogen.

Figure 2 shows the Mössbauer spectra obtained after irradiation with three different doses at a measuring temperature of 4.2 K and 30 K. From the spectra at 4.2 K (2) the percentage of cobalt atoms having trapped interstitials was derived as 17%, 36% and 67%, respectively. Combining these values with the irradiation induced electrical resistivity in the samples we determined, that about 90% (sample 1), 70% (sample 2) and 30% (sample 3) of these cobalt atoms have then trapped only a single interstitial.

The observed temperature dependences of the central shifts for the three samples are shown in figure 3. A striking difference in the central shifts of the original line ($^{57}$Co on substitutional lattice sites) and defect line is evident. The first one shows a temperature dependence in reasonable agreement with values for $^{57}$Fe in aluminium measured by Nasu and Murakami [6] and Janot and Gibert [7], which can be explained in a Debye model as second order Doppler shift with $\theta_D = 220$ K: the shift starts with zero slope at 0 K and tends to become linear in temperature at higher temperatures.

The central shifts of the defect line, however, increase rapidly in a narrow temperature interval from around 10 K to about 20 K. For sample No. 1 above 20 K and for sample No. 2 above 30 K the shift becomes rather indefinite since the fit of the defect line is ambiguous because of the strong decrease in its intensity. For the highest irradiation dose such problems did not occur: The temperature dependence above 20 K approached that of a normal second order Doppler shift as observed after fast neutron irradiation [8].

3. Discussion. — The strong change in the central shift of the defect line occurs between about 10 and 20 K as visible in figure 3. As already mentioned, in the same temperature range the intensity of the defect line shows a strong decrease explained by jumps of the $^{57}$Co impurity atom inside an octahedral cage (see Fig. 1). Therefore, it is most probable, that the temperature shift of the defect line has to do with the unusual dynamical behaviour of the jumping Mössbauer atom.

In ref. [4] it was mentioned, that the reduction of intensity of the defect line is strongly anisotropic. Since the broad defect line can be explained by an unresolved quadrupole splitting a possible Goldanski-Karyagin effect should be taken into account. Since the defect line was fitted with a symmetric line doublet, the neglect of the Goldanski-Karyagin effect could produce a line shift. An estimation showed that this cannot be large enough to explain the observed change in central shift.

The central shift is a sum of the isomer shift $\delta_R$ and the second order Doppler shift $\delta_{Dop}$. First we discuss the isomer shift. It is a measure for the electron density at the nucleus of the Mössbauer atom. To estimate the change in isomer shift on jumping we make the following considerations. As has been shown in ref. [9] the major part of the central shift difference between original line and defect line can be attributed to a reduction of the atomic volume causing an increase in electron density of a Mössbauer atom on a mixed dumbbell site with respect to a substitutional lattice site. From the central shift difference of 0.42 mm s$^{-1}$ at 4.2 K we can infer an atomic volume reduction of about 40%. Computer simulations for self-interstitial dumbbells in a fcc metal [10] yield volume reductions of 30 to 40% taking into account the relaxation of the neighbours around the dumbbell. If relaxation would not occur the volume reduction would be of the order of 50%. This would yield an isomer shift of the order of $\Delta\delta_R = 0.10$ mm s$^{-1}$ higher than in the relaxed case. When the Mössbauer atom undergoes large displacements as e. g. jumps in the cage the neighbours cannot relax immediately.

(2) The Debye-Waller factor of the defect line and the original line at 4.2 K are equal [4,8].
The observed change in isomer shift due to jumps \( \Delta \delta_{IS} \) should be, therefore, of the order of

\[
\Delta \delta_{IS} = \Delta \delta_{IS}^0 \cdot \tau_{v} (\tau + \tau_v)^{-1}
\]

where \( \tau_v \) is the mean relaxation time of the lattice and \( \tau \) is the mean jump time of the Mössbauer atom. Since lattice relaxation times are of the order of \( 10^{-10} \) s to \( 10^{-12} \) s only in the case of very fast jumps an appreciable contribution of the isomer shift to the observed central shift with increasing temperature has to be expected. It would be worthwhile to look for a mechanism, which would allow \(^{57}\)Co atoms in a mixed dumbbell configuration to increase their mean jump frequency from practically zero at 10 K to \( 10^{10} \) s\(^{-1}\) to \( 10^{12} \) s\(^{-1}\) at about 20 K. Such a mechanism, however, is outside our present understanding of the dynamics of interstitials.

In the following, we will discuss the observed temperature shift of the defect line in terms of the second order Doppler shift. According to Josephson [11] the thermal shift is proportional to the expectation value of the kinetic energy of the Mössbauer atom \( < E_k > \)

\[
\delta_{SOD} = \frac{< E_k >}{mc} = \frac{< v^2 >}{2c}
\]

where \( m \) is the mass of the Mössbauer atom and \( < v^2 > \) is its mean squared thermal velocity. The observed change in the central shift then implies that the mean kinetic energy of \(^{57}\)Co atoms having trapped interstitials is increasing very rapidly between 10 K and 20 K.

In a phenomenological way such an increase in energy can be attributed to an increase in the Debye temperature of the vibrating Mössbauer atom due to strong lattice anharmonicity [12]. An increase of the Debye temperature is an indication of a hardening of the lattice modes. We think, that the onset of jumps of
a $^{57}$Co atom as a partner of a mixed dumbbell at a temperature of about 10 K would rather be an indication of lattice softening than of hardening. Speaking of hardening might, therefore, give a misleading physical picture of what happens microscopically when the $^{57}$Co atoms start jumping.

To explain an increase in mean kinetic energy by lattice softening we make the following considerations: In our discussions of the dynamical properties of mixed dumbbells till now we have not taken into account the difference in atomic sizes of the dumbbell partners. There are indications from recent computer simulations on the stable configuration of a mixed dumbbell (3), that for sufficiently small impurity atoms the dumbbell axis can be distorted from the $<100>$ direction to the saddle point in $<110>$ direction. We suggest, that in such a configuration the low frequency resonance libration modes as characteristics for $<100>$ dumbbells [5] might not exist at low temperatures (4.2 K), since they would make this configuration unstable. The dumbbell atoms then should only perform high frequency vibrations also known for interstitial atoms. This would imply that the $^{57}$Co dumbbell partner would vibrate in a narrow potential well. Such a behaviour would fit the high value of the Debye-Waller factor of the defect line found at 4.2 K [4, 8].

We further suggest, that above 10 K by anharmonic coupling with low frequency lattice vibrations the $^{57}$Co atom can leave its narrow potential well. The $^{57}$Co atom now moves in a broader potential having relatively large thermal displacements. Approximating this broad potential by a square well one can conclude, that now most of the energy inherent in the $^{57}$Co atom in this excited level is kinetic energy, since a particle in a square well has only kinetic energy. Assuming equipartition of energy between the lower more localized level and the excited less localized one at a temperature of about 20 K in this model the gain in kinetic energy of the $^{57}$Co atom would be 30%.

Taking for the localized vibration at 4.2 K a value of $\omega = 6 \times 10^{13}$ s$^{-1}$ [8] one gets a gain in kinetic energy of about 15 meV which corresponds to an increase in $\delta_{OD}$ of about 0.08 mm/s. This would be just the order of the observed change in the central shift between 10 and 20 K in the case of sample 1 in figure 3.

One could imagine that such a strong increase in kinetic energy triggers the jumps of the $^{57}$Co atom in the octahedral cage [4]. One could also consider, that the excitation of the upper energy level does not only trigger the cage jumps but corresponds to the jumps themselves. This, however, would imply a rapid increase in the jump rate of the $^{57}$Co atoms from practically zero at 10 K to nearly free jumping in the cage at about 20 K.

Finally, a comment regarding the dose-dependence. The absolute increase in the central shift is the smaller the higher the irradiation dose, e.g. it becomes less pronounced when clustering of interstitials at $^{57}$Co atoms begins (Fig. 3). In terms of the models for the central shift as presented here, this is in agreement with the weaker temperature dependence of the Mössbauer line intensity for Mössbauer atoms with interstitial clusters [4]: Clustering prohibits the jumps in the cage. A significantly smaller increase of the central shift between 10 and 20 K is found when $^{57}$Co atoms have trapped larger interstitial clusters after neutron irradiation followed by annealing to 160 K [8]: The temperature dependence of the central shift is rather smooth and can be explained in normal way by characteristic interstitial vibrations. The dose dependence as observed in this work can thus be well understood as the transition from trapped single interstitials to trapped clusters.

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