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Loop formation in Cu and Al after low-temperature fast-neutron irradiation

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Abstract. Single crystals of Cu and Al were irradiated with 2.4×10^{18} fast neutrons/cm^2 ($E > 0.1$ MeV) at 4.6 K. Asymptotic diffuse scattering of x-rays was measured after irradiation and after several annealing steps up to 300 K. The formation of dislocation loops of interstitial and vacancy type was observed; their size distribution was determined. In Cu after recovery at 60 K most of the interstitials are contained in loops with a mean loop radius of 11 Å. On further annealing, the mean radius increases to 18 Å at 300 K, where 25% of the initially induced defects are retained. At 60 K, between 20% and 40% of the vacancies are contained in loops of a mean radius of about 10 Å. During further recovery the total number of vacancies in loops as well as the mean vacancy loop size remain rather constant. In Al, no evidence for loop formation was found.

1. Introduction

By fast-neutron irradiation of solids, vacancies and interstitials are produced in displacement cascades. The strong correlation of defects within a cascade—a vacancy-rich core is surrounded by a cloud of interstitials—favours the agglomeration of defects. Large and dense agglomerates tend to collapse into dislocation loops. This mechanism has consequences of practical importance: first, the defects forming the dislocation loop remain immobile up to temperatures far above those of the single-defect mobility, and defect annihilation is effectively suppressed. Second, the dislocation loops may act as nuclei for larger agglomerates and owing to their elastic properties may support self-organization of the defect system during continuous irradiation (Bullough and Wood 1986, Abromeit and Wollenberger 1988).

The formation of dislocation loops during irradiation has mainly been studied by transmission electron microscopy (TEM) in ion-irradiated samples. Many experiments after high-temperature irradiation were reported (see, e.g., English and Jenkins 1987), or after low-temperature irradiation and immediate recovery at high temperatures (see, e.g., Bullough *et al* 1987), but only few after low-temperature irradiation and subsequent measurements at low temperatures (Robertson *et al* 1984, Kirk *et al* 1987). TEM examinations after 14.4 MeV neutron irradiation at medium temperatures were conducted by Kiritani *et al* (1984) and Shimomura *et al* (1987).

In recent years the size distribution of dislocation loops was determined by analysing the intensity distribution in the region of asymptotic diffuse scattering of x-rays: after low-temperature electron irradiation (Ehrhart *et al* 1982a), and after reactor neutron irradiation and recovery at room temperature (Larson and Young 1987). We have applied this experimental tool to study the formation of dislocation loops in Cu and Al after low-temperature fast-neutron irradiation and during subsequent thermal recovery. After a brief review of the theory of diffuse scattering in section 2 we present experimental details in section 3. Experimental results are given in section 4 and are discussed in section 5. We focus on our results for Cu, and finally compare then with the experiment on Al.

2. Theoretical background

The defect-induced diffuse scattered intensity $I_D(\boldsymbol{q})$ from randomly distributed point defects is given within the single-defect approximation by incoherently adding the squares of the scattering amplitudes due to the single defects (Larson and Young 1987, Krivoglaz 1983, Trinkaus 1972):

$$I_D(\boldsymbol{q}) = cN_a |f_D(\boldsymbol{K}) + f\sum_n \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_n)[\exp(i\boldsymbol{K}\cdot\boldsymbol{u}_n) - 1]|^2. \qquad (1)$$

The total number of defects which contribute to the diffuse intensity is given by the product of the mean defect concentration c and the number N_a of scattering atoms. f is the atomic scattering factor including the thermal and static Debye–Waller factors, and $\boldsymbol{q} = \boldsymbol{K} - \boldsymbol{G}$ is the deviation of the scattering vector $\boldsymbol{K}$ from the nearest reciprocal lattice vector $\boldsymbol{G}$. $f_D(\boldsymbol{K})$ is the scattering contribution of the defect itself.

The second term in equation (1) describes the scattering from lattice distortions caused by the defect. The displacement of the atom n from its new ideal position $\boldsymbol{r}_n$ in the mean defective lattice is given by $\boldsymbol{u}_n$. Close to the Bragg reflection, for $\boldsymbol{K}\cdot\boldsymbol{u} \ll 1$, the diffuse intensity is dominated by scattering from the long-range displacement field far away from the defect. In this case the diffuse intensity can be approximated by the linear term in the expansion of the phase factor $\exp(i\boldsymbol{K}\cdot\boldsymbol{u})$, and one obtains the Huang diffuse (HD) scattering intensity. Two characteristic properties of the HD intensity are the decrease by $1/q^2$ and the dependence on the square of ΔV_D, the relaxation volume of the defect in units of the atomic volume V_a.

For strongly distorting defects such as defect agglomerates the HD scattering is restricted to a very small region near Bragg reflections where the scattering from the long-range displacement field ($\boldsymbol{K}\cdot\boldsymbol{u} \ll 1$) still dominates. For larger q values the scattering from the highly strained ($\boldsymbol{K}\cdot\boldsymbol{u} > 1$) vicinity of the defect dominates and the HD approximation is no longer valid.

In principle the diffuse intensity can then be calculated from equation (1), if the individual displacements $\boldsymbol{u}_n$ close to the defect are known. A simplified treatment of the problem was given by Trinkaus (1971), who assumes an isotropic decrease in the displacement field near the defect by $1/r^2$. Enhanced intensity—due to coherent superposition of scattered waves—arises from regions $\boldsymbol{r}_s$ in the crystal where the phase φ becomes stationary (i.e. $\varphi = i\boldsymbol{q}\cdot\boldsymbol{r}_s + \boldsymbol{K}\cdot\boldsymbol{u}(\boldsymbol{r}_s) = \text{constant}$), and 'local' Bragg reflection occurs. Intuitively, the intensity distribution reflects the probability distribution of the distances and orientations of the reflecting lattice planes. For a displacement field $u(r) \sim \Delta V_D/r^2$, Trinkaus finds for the asymptotic diffuse (AD) scattering

$$I_{AD} \propto cN_a(f^2/V_a^2)|\Delta V_D|(|\boldsymbol{K}|/q^4). \qquad (2)$$

In contrast with the HD scattering the intensity in the asymptotic region depends only

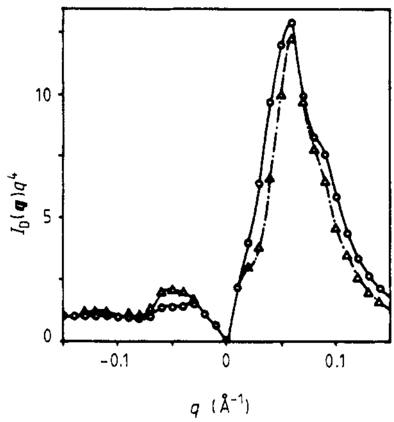

Figure 1. Theoretical distributions of $I_D(\boldsymbol{q})q^4$ for Cu near the (222) reflection in the [111] direction. Loops on (111) planes: ○, perfect loop; △, Frank loop. Calculations by Ehrhart *et al* (1982b).

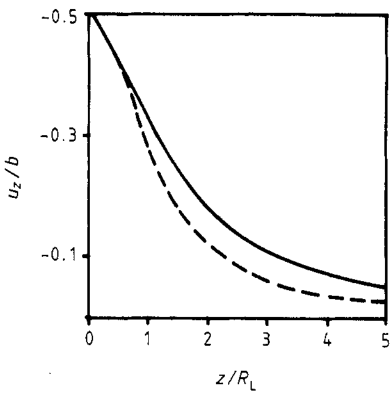

Figure 2. Displacements u_z perpendicular to the plane of a vacancy loop, as a function of the distance z to the loop plane, calculated by Ohr (1974), where R_L is the loop radius and b its Burgers vector: ——, Cu; – – –, isotropic crystal.

linearly on the defect strength ΔV_D, and decreases by $1/q^4$. With the relaxation volume of $\Delta V_L = b\pi R^2$ for a dislocation loop with radius R and Burgers vector $\boldsymbol{b}$ perpendicular to the loop plane (with $|\boldsymbol{b}| := b$) one gets from equation (2)

$$I_{AD} \propto c(|\boldsymbol{K}|b\pi R^2)/q^4. \tag{3}$$

The asymptotic diffuse intensity is proportional to $c\,\Delta V_D$, the total defect volume, and therefore is a measure of the total number of defects in the agglomerates independent of their size distribution.

The assumption of an isotropic decrease in the displacement field by $1/r^2$, which leads to the simple analytical formulae of equations (2) and (3), is strictly not justified for dislocation loops. In the vicinity of the loop, and above all in directions perpendicular to the loop plane, extended regions exist where the lattice strain is rather constant; these regions have approximately a constant altered lattice parameter. They cause an intensity enhancement if the loop plane is perpendicular to $\boldsymbol{K}$ because of the coherent superposition of scattered waves from these planes.

The consequence is an intensity maximum at $q = q_{max}$ which is superimposed on the $1/q^4$ decrease. In directions perpendicular to an interstitial loop the distances between lattice planes are decreased. This causes an intensity maximum at positive q. The dilated regions in the loop plane near the loop's edges have a smaller volume and contribute a weak smeared-out intensity at negative q. The detailed diffuse intensity distribution due to a dislocation loop can only be calculated numerically from equation (1). These calculations were first conducted by Ehrhart *et al* (1982a, b); results from this work for $I_{AD}(q)$ for an interstitial loop are shown in figure 1.

Vacancy loops increase the distances between lattice planes situated parallel to them. Their displacement fields are quite similar to those of interstitial loops but of opposite sign, and the corresponding intensity maximum is found at negative q. By measuring the asymptotic diffuse intensity in directions perpendicular to the loop planes it is possible to distinguish between vacancy and interstitial loops, and to follow their formation and reactions separately.

The displacement field perpendicular to the habit plane of a vacancy loop was calculated by Ohr (1974) and is shown in figure 2. The intensity maximum will occur at positions of q_{max}, which correspond to distances z for which the phase is constant, i.e. $d^2u_z/dz^2 = 0$. The strength of the displacement scales with the loop radius R. Accordingly q_{max} is proportional to $1/R$, and the proportionality factor depends on the material: $q_{max} \approx Kb/5R$ for Cu, and $q_{max} = Kb/3.4R$ for Al (a nearly isotropic solid).

These approximate values are in good agreement with the results from exact calculation (see figure 1) where, for Cu, $q_{max} = Kb/4.4R$.

3. Experimental procedure

We conducted measurements of asymptotic diffuse scattering in Cu and Al single crystals after low-temperature fast-neutron irradiation. The samples were spark cut and their surfaces electrolytically polished to remove surface damage. (111) surfaces were chosen as sample faces since, in an FCC lattice, (111) lattice planes are expected to be the preferred habit planes for dislocation loops, and because the measurements were performed in a symmetrical scattering geometry. The initial purity was 99.999% for Cu and for Al.

The samples were irradiated at 4.6 K in the low-temperature irradiation facility (TTB) at the Research Reactor Munich to a total dose of 2.4×10^{18} fast neutrons/cm^2 ($E > 0.1$ MeV). Without warming the specimens, they were transferred into the measuring cryostat on a two-circle diffractometer where the x-ray measurements were conducted at 10 K.

The radiation from a 6 kW rotating-anode x-ray source with line focus was monochromated by a bent quartz crystal (Johannson type) which selected the Cu Kα line ($\lambda \approx 1.54$ Å). A semifocusing arrangement was used. The scattered intensity was detected point by point in a scintillation counter; a second counter monitored the primary intensity. Several slits limited the divergence of the incoming and scattered beams (resolution volume, about 1×10^{-5} Å^{-3}). The measurements were performed near the (222) reflection in the [111] direction.

The diffuse scattered intensity was measured after irradiation and after thermal anneals at several temperatures. Defect-induced diffuse intensity was obtained as the difference between scattered intensity from the crystal after irradiation, and after complete thermal annealing (at 1000 K for Cu, and at 500 K for Al). This defect-induced intensity was put on an absolute scale by comparison with scattering from polystyrene.

In addition, after each annealing step the lattice parameter change was measured by the Bond method. The results agree with those reported previously (van Guerard and Peisl 1976).

4. Experimental results and discussion

Figure 3 shows the scattered intensity for Cu near the (222) reflection in the [111] direction after irradiation (by crosses) and after complete thermal recovery (by open circles). The diffuse intensity is enhanced after irradiation and shows a significant anisotropy with increased intensity at positive $\Delta(2\theta)$. This anisotropy shows that the displacement field in the crystal is dominated by defects that expand the lattice, i.e. by

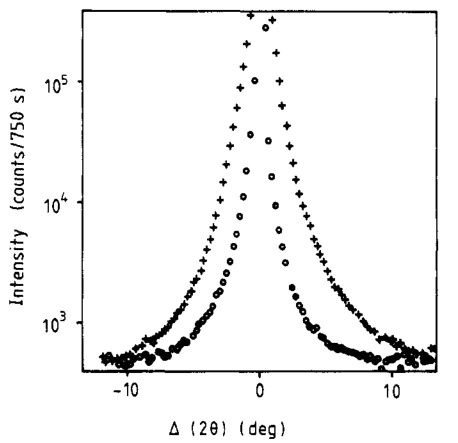

Figure 3. Diffuse intensity in Cu near the (222) reflection in the [111] direction: ×, after irradiation at 4.6 K; ○, after complete thermal recovery at 1000 K. $\Delta(2\theta)$ is the angular displacement of the detector from the Bragg angle.

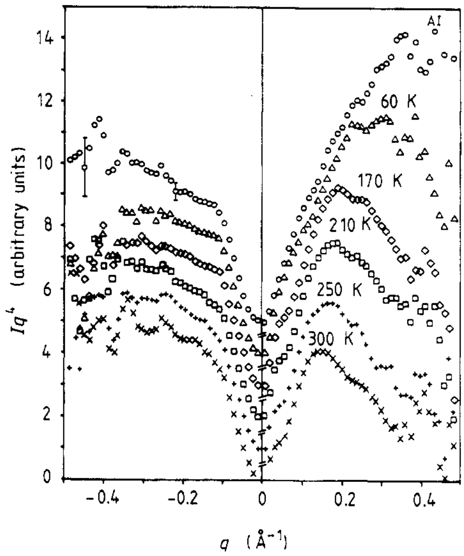

Figure 4. Defect-induced diffuse intensity scaled by q^4 in Cu, after irradiation (curve AI), and after recovery at the different temperatures T_A as indicated.

interstitials. From the lattice parameter change for Cu a total induced defect concentration of 640 ± 60 PPM was calculated using relaxation volumes $\Delta V_i = 1.55V_a$ for the interstitial, and $\Delta V_v = -0.25V_a$ for the vacancy (Ehrhart 1985). In Al a defect concentration of 1000 ± 80 PPM was induced.

The defect-induced diffuse intensity from these samples in the HD scattering regime after irradiation was investigated by the present authors (Rauch *et al* 1989). From a detailed analysis of a correlation contribution superimposed on the HD intensity they conclude that the interstitial distribution within the defect cascade in Al is very dilute with a mean concentration of $\langle c_i \rangle = 360$ PPM. In contrast with that for Cu, very dense cascades with $\langle c_i \rangle \simeq 4000$ PPM are found, and spontaneous formation of three-dimensional interstitial agglomerates with a mean size of about 14 interstitials at the irradiation temperature is observed.

The defect-induced diffuse intensity scaled by q^4, after irradiation and after recovery at temperatures T_A indicated is shown in figure 4. At positive q, where the intensity distribution is dominated by scattering from interstitials, the curvature in the asymptotic scattering region strongly changes with increasing T_A. The intensity distribution at negative q, which is more sensitive to vacancies, remains rather constant. During recovery a peak in the asymptotic diffuse scattering appears at positive q values, which moves to lower q with increasing T_A. This is evidence for the formation of interstitial loops on (111) planes, and for their growth upon thermal recovery.

For further interpretation of the annealing behaviour of Cu above 60 K we assume that all defects which contribute to the observed diffuse intensity have condensed into loops on (111) planes.

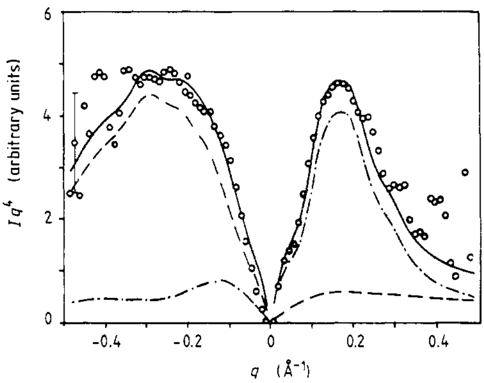

Figure 5. Defect-induced diffuse intensity scaled by q^4 in Cu after recovery at 250 K: ○, experimental data; ——, theoretical result of best fit; —·—, contribution from interstitial loops; – – –, contribution from vacancy loops.

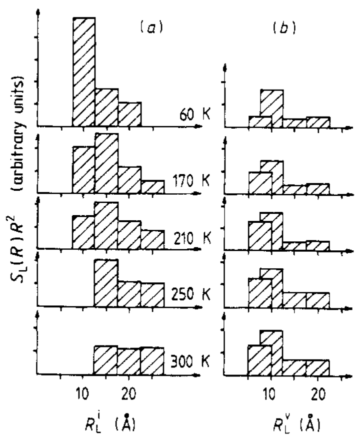

Figure 6. Loop size distribution $S_L(R)$ scaled by R^2 as obtained from the best fit to experimental data: (*a*) interstitial loops; (*b*) vacancy loops.

For interstitials this assumption certainly is justified. Already at the irradiation temperature there is a strong tendency for the spontaneous formation of large agglomerates (Rauch *et al* 1989). After annealing through stage I, von Guerard and Peisl (1976) found a marked change in the defect symmetry in measurements of HD scattering and concluded that a large fraction of interstitials had formed loops on (111) planes. This result is confirmed by computer simulations (Ingle *et al* 1982), which show that interstitial agglomerates containing more than 13 interstitials prefer to form interstitial loops.

For vacancies the above assumption will be justified only to a certain degree. Single vacancies or small three-dimensional vacancy agglomerates may survive up to the temperature at which vacancies become freely mobile. Above that temperature all surviving vacancies will form large agglomerates which tend to collapse into loops. At the irradiation temperature, however, only a small fraction of vacancies is spontaneously bound into loops. After irradiation at 30 K with 30 keV self-ions, Kirk *et al* (1987) found that 10% of the vacancies athermally converted to loops. On annealing to successively higher temperatures this fraction will increase by two effects:

(i) Free vacancies are preferentially absorbed by mobile interstitials.
(ii) Agglomerates can possibly collapse by thermal activation.

Since the contribution to the asymptotic difuse intensity of single vacancies or of vacancies bound in small three-dimensional agglomerates is smaller by a factor of $\Delta V_v/\Delta V_L \simeq 0.25$ than that of vacancies in loops, it may dominate after irradiation and lose its significance only after recovery at the temperature of vacancy mobility. In the same way our assumption will be fully justified only after recovery at that temperature.

In order to determine the size distribution $S_L(R)$ of interstitial and vacancy loops theoretical curves—corresponding to those given in figure 1—were calculated and compared with experimental results by a least-squares fitting method. In the case of interstitials, perfect loops give best agreement with the data, although the difference from faulted loops is not significant. For vacancies, Frank loops were used. Figure 5 shows

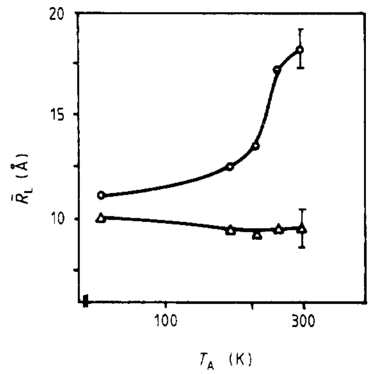

Figure 7. Mean loop radius R_L as a function of annealing temperature T_A calculated from the loop size distribution (see figure 6): ○, interstitial loops; △, vacancy loops.

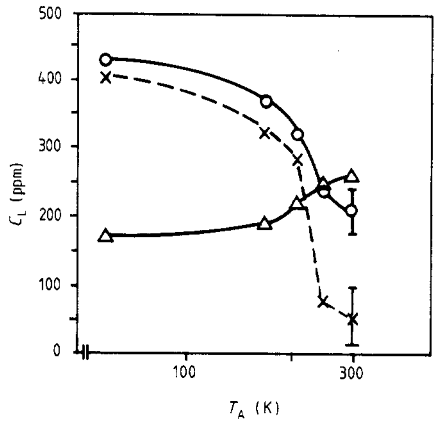

Figure 8. Concentration of defects contained in loops as a function of annealing temperature (○, interstitials; △, vacancies), compared with the recovery of the induced lattice parameter change $\Delta a/a(x)$.

the intensity distribution (scaled by q^4) after annealing at 250 K (open circles) together with the fitted curve. The contributions from interstitial loops (chain curve) and from vacancy loops (broken curve) are shown separately.

The loop size distributions $S_L(R)$—scaled by R^2—obtained through this fitting procedure are given in figure 6 as a function of annealing temperature T_A. $S(R)R^2$ is directly proportional to the contribution of the loops to the asymptotic diffuse scattering and to the number of defects in the loops. It should be noted that only contributions from loops with $R > 8$ Å could be clearly resolved experimentally. With increasing T_A the number of small interstitial loops decreases, while larger loops are formed. This process is accompanied by a loss of interstitials evidenced by the decrease of $\int S_L(R)R^2\,dR$ (the total shaded area in figure 6). Quite differently the size distribution of vacancy loops shows only minor changes during annealing up to 300 K. This behaviour is reflected in the dependence of the mean loop radius R_L defined as $R_L = (\int S(R)R^3\,dR)/(\int S(R)R^2\,dR)$, and the total number N_L of defects bound in loops, on the annealing temperature T_A (figures 7 and 8).

Inspection of figure 8 shows that the numbers of interstitials and vacancies contained in loops are markedly different at low annealing temperatures. Since the total number of vacancies in a perfect volume sample should be equal to that of interstitials, an appreciable fraction of vacancies is not bound in observable loops up to $T_A \simeq 200$ K. If we assume that these vacancies do not significantly contribute to the asymptotic diffuse intensity in the experimentally accessible region—as would be the case if they formed very small loops—the fraction of vacancies in loops could be greater than 40% at 60 K. If on the other hand these vacancies contribute by a factor of 4 less in the asymptotic region—as would be the case if they were single or if they formed small three-dimensional agglomerates—the fraction of vacancies in loops is about 20% at 60 K. These loops will have either formed spontaneously at the irradiation temperature or collapsed by thermal activation at 60 K. On further annealing, $S_L^V(R)$ of vacancies remains unchanged up to 170 K, which may be explained by the preferential annihilation of single vacancies or small vacancy agglomerates by mobile interstitials.

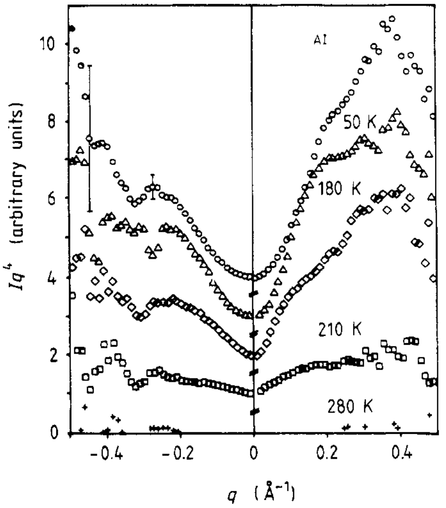

Figure 9. Defect-induced diffuse intensity scaled by q^4 in Al after irradiation (curve AI) and after recovery at different temperatures T_A as indicated. The measurement was made near the (222) reflection in the [111] direction.

During recovery above 170 K the mean number of vacancies in loops slightly increases. This indicates that vacancies become mobile and migrate to already existing loops or form new loops by agglomeration. During the entire range of annealing temperatures the mean vacancy loop size R_L^v is about 10 Å and fairly constant. Since small loops cannot be detected reliably, and because of the broad size distribution (no distinct intensity maximum can be found at negative q), this value should be considered only as an upper bound for R_L^v.

The mean radius of interstitial loops increases from 11 Å at 60 K to 18 Å at 300 K. In parallel the total number of interstitials in loops decreases. This effect is due to the disappearance of small interstitial loops, which become mobile in stage II (50–170 K) and to annihilation by mobile vacancies at $T_A < 200$ K. Mobile vacancies may decrease the size of an interstitial loop by annihilation or owing to induced break-up, causing the mobility of the remaining agglomerates which can thus enhance the mean size of existing loops.

After recovery at 250 K the number of interstitials bound in loops is equal to that of vacancies bound in loops; we conclude that all remaining defects are contained in loops. In this way, about 25% of the initially induced defects can survive recombination at a temperature far above that of single defect mobility. The recovery of the lattice parameter change $\Delta a/a$ above 170 K is considerably more pronounced than that of interstitials and vacancies (crosses in figure 8). This is in accordance with the prediction of theory that—in a first approximation—$\Delta a/a$ tends to zero if identical numbers of interstitals and vacancies are contained in loops (Krivoglaz 1983).

The annealing behaviour of Cu after low-temperature fast-neutron irradiation is characterized by agglomeration and loop formation. The occurrence of these reactions is strongly promoted by the initial separation of interstitials and vacancies during the primary damage event (Protasov and Chudinov 1982), the high defect densities in the very compact cascades in Cu (Rauch *et al* 1989), and by the strong elastic interaction between defects due to the marked elastic anisotropy of the lattice.

The importance of these factors may be illustrated by comparison with the results of the experiment on Al (figure 9). No evidence for the formation of interstitial or vacancy loops was observed in Al during recovery, and consequently there is only insignificant defect retention above stage III. In contrast with Cu, the defect cascades in Al are very dilute (Rauch *et al* 1989), and the lattice is nearly elastically isotropic.

Finally we compare the results of our measurements on Cu with findings from other work; Larson and Young (1987) deduced dislocation loop size distributions after low-temperature reactor neutron irradiation to a dose of 1.3×10^{18} fast neutrons/cm^2 and annealing at room temperature. They found a mean interstitial loop radius R_L^i of 14.5 Å, and a mean vacancy loop radius R_L^v of 11 Å. The fact that R_L^i found in the present work is significantly higher may be explained by the higher initial defect concentration as well as by the different annealing procedure. Ehrhart *et al* (1982a) conducted low-temperature irradiations with 3 MeV electrons and determined loop size distributions during an annealing programme. For irradiation to a defect concentration of about 925 PPM they found $R_L^i = 13.5$ Å at 200 K and $R_L^i = 19$ Å after recovery at 300 K. Although the initial defect configuration is markedly different after fast-neutron irradiation compared with high-dose electron irradiation, the formation of loops seems to proceed in a comparable way.

Acknowledgments

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