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Lattice deformation in TaT_x systems due to ^3He production

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Lattice deformation in TaT_x caused by transmutation-produced helium is investigated by neutron-scattering techniques. The evolution of the position and width of Debye-Scherrer lines is followed in two polycrystalline samples over a period of more than two years. The observed relative lattice parameter expansion with helium concentration $d(\Delta a/a)/dc_{He}=0.10$ yields $d(\Delta a/a)/dc_{He}=0.15$ if corrected for tritium decay. Broadening of Debye-Scherrer lines indicates the presence of an evolving dislocation network. In addition, some long-wavelength phonons are investigated in a $TaT_{0.05}$ single crystal. Comparison with a single crystal of pure Ta taken as reference shows that the phonon intensities in the tritium-charged sample are considerably reduced, however, without any noticeable change in energy and linewidth. Technologically significant, macroscopic fracture of both polycrystalline samples occurs already at helium concentrations below 1 at. %.

I. INTRODUCTION

Lattice damage due to helium atoms implanted with high energies or produced by radioactive tritium decay is an important problem for the design of structural materials to be used in future fusion power reactors. Schematically, at lower temperatures, the evolution of the metal-helium system may be described by the following stages:[1-3] First, the helium atoms being insoluble in the metal have the tendency to aggregate and form clusters. These clusters consisting of a few helium atoms grow by accumulation of additional helium atoms and the consequent creation of Frenkel-pair defects thus rapidly leading to the formation of helium gas bubbles enclosed in the metal matrix. Further growth of the bubbles occurs by dislocation loop punching[4] resulting in a dislocation network gradually degrading the crystal lattice. In some systems a periodic arrangement of gas bubbles has been observed[5] for higher helium concentrations. In order to get deeper insight into the properties of metal-helium systems, an investigation of the atomic distortions connected with bubble formation is of interest. The generation of helium by tritium decay avoids initial radiation damage connected with the implantation of particles at high energies and furthermore allows the investigation of bulk properties in large samples (order of size $\sim 1\ cm^3$).

In the present paper we present a neutron-scattering investigation of the evolution of the metal lattice in TaT_x systems. In the first part we report on the evolution of two polycrystalline TaT_x samples ($x=0.04$ and $x=0.115$, respectively), as manifesting itself in lattice parameter change and broadening of Debye-Scherrer lines. In addition, we present first results concerning the influence of helium formation on lattice dynamical properties derived from the measurement of some low-energy acoustic phonons in a $TaT_{0.05}$ single crystal.

II. EXPERIMENT

Two polycrystalline Ta samples (platelets $1\times10\times50\ mm^3$) were investigated. Tritium charging from the gas phase was performed by Nukem G.m.b.H. (Hanau, Federal Republic of Germany) with tritium concentrations $x=0.04$ and $x=0.115$, respectively. At these concentrations the TaT_x system remains in the α phase. A cylindrical Ta single crystal (volume approximately 1 cm^3) was loaded with $x=0.05$ tritium. Each TaT_x sample was mounted under helium atmosphere into a high vacuum-sealed cylindrical aluminum container (wall thickness 1 mm).

The neutron-scattering measurements extending over a period of more than two years were done mostly on the triple axis spectrometer VALSE located at a cold neutron guide position at the Orphée reactor in Saclay. The neutron energy for all experiments was set near 14 meV and a pyrolytic graphite filter was applied in the incoming beam. For the investigation of the Debye-Scherrer lines, collimations of ten minutes before and after the sample were used. The polycrystalline platelets were rotated on the sample table throughout the experiment in order to avoid texture effects. Polycrystalline platelets of pure Ta and $TaD_{0.12}$ were measured in order to serve as references and to assure constant spectrometer conditions over the entire time period. The inelastic measurements on the $TaT_{0.05}$ single crystal (orientation $[1\bar{1}0]$) were compared to the corresponding phonons obtained with a pure Ta crystal. The phonons were investigated using constant-q scans and relaxed overall collimations of 30 minutes.

III. RESULTS

A. Debye-Scherrer lines

The positions and widths of the Debye-Scherrer lines of the (110), (002), and (211) reflections were determined with Gaussian fits to the data and the lattice parameter change was evaluated relative to that of pure Ta. The resulting $\Delta a/a$ values are shown in Fig. 1 as a function of helium concentration. Most of the measurements were done with the $TaT_{0.04}$ platelet. A linear fit to these data yields a small increase of

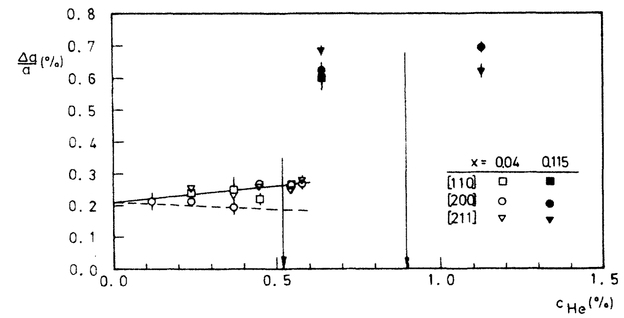

FIG. 1. Relative change of the lattice parameter a in the two polycrystalline TaT_x samples as a function of helium concentration. Data for three reflections are presented. Error bars are drawn only where they exceed the size of the symbols. The full line is a linear least-squares fit to the data obtained from the $TaT_{0.04}$ platelet yielding $d(\Delta a/a)/dc_{He}=0.102\pm0.040$. The dashed line corresponds to the change of the lattice parameter due to the continuously decreasing tritium content: $d(\Delta a/a)/dc_T=0.048$. (This value taken from Ref. 10 was actually determined for deuterium. However, in the present context the difference in lattice expansion between deuterium and tritium can be regarded negligible.) The arrows mark the fracture of the two platelets.

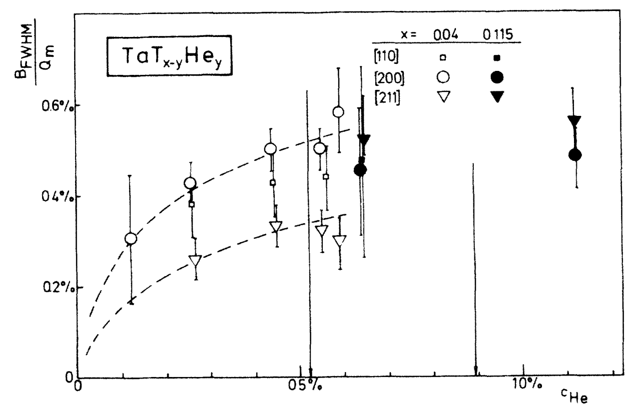

FIG. 2. Broadening of Debye-Scherrer lines as a function of helium concentration. The increase in width due to helium-induced lattice defects is given as percentage fraction of the reciprocal lattice vectors corresponding to the maximum intensity of the respective Debye-Scherrer lines. The dashed lines point to the difference between the (200) and the (211) reflection indicating an anisotropic strain of the Ta lattice. The arrows mark the respective helium concentrations at which fracture of the two platelets occurred.

$$d(\Delta a/a)/dc_{He}=0.102$$

with helium concentration in contrast to the expected decrease of the lattice parameter in view of the continuously falling T content. Within the experimental error a similar behavior is found for the $TaT_{0.115}$ specimen.

A drastic change of the macroscopic state of the platelets occurred when the TaT_x platelets broke into a few parts. This event was confirmed by neutron radiographic methods without opening the sample containers for safety reasons. In Fig. 1 the approximate helium concentration at fracture is marked with arrows for both specimens, respectively. There is no indication that this event induced any microscopic changes in the samples. Since no influence of the macroscopic breakup of the platelets on the results of Fig. 1 is found it can be concluded that no noticeable tritium release followed the fracture.

Widths of Debye-Scherrer lines were determined both for the TaT_x systems and the pure Ta and $TaD_{0.10}$ platelets taken as reference. As expected, a comparison between the pure Ta and $TaD_{0.12}$ platelets showed no difference in their respective linewidths. The widths of the TaT_x samples were compared to that of the pure Ta platelet which was taken as a measure of the resolution of the experimental setup. The intrinsic line broadening of the TaT_x samples due to helium formation was calculated by deconvolution with the resolution function upon the assumption of Gaussian intensity distributions which yield an excellent fit to the shape of the measured Debye-Scherrer lines. The line broadening determined in this way is shown in Fig. 2 versus helium concentration. For the $TaT_{0.04}$ platelet the data exhibit a steep increase below 0.1 at. % He followed by a much smaller helium concentration dependence. Moreover, the broadening appears to be anisotropic as indicated by the data for the (002) and (211) reflections. The values for the (110) reflection being statistically less significant lie between. The data for the $TaT_{0.115}$ platelet are less accurate but complement reasonably the $TaT_{0.04}$ concentration dependence. However, within the experimental error there is no indication of any anisotropy in the $TaT_{0.115}$ sample. As in Fig. 1 the vertical arrows in Fig. 2 mark the helium concentration at which the fracture of the platelets occurred. Here again, the macroscopic breakup does not seem to influence the microscopic line broadening behavior.

B. Phonon measurements

A few acoustic phonons were investigated in a $TaT_{0.05}$ single crystal which at the time of the measurement had a helium concentration of ~ 0.4 at. %. For comparison the same phonon scans were also performed in a Ta single crystal of similar size. In comparison to the pure Ta single crystal the mosaic spread of the $TaT_{0.05}$ sample was somewhat broadened. The investigation of the charged crystal turned out to be difficult since the intensities of the phonons were considerably reduced. A typical transverse acoustic phonon is shown in Fig. 3 together with the (002) Bragg reflection on a logarithmic scale both for $TaT_{0.05}$ and pure Ta. The intensity of the phonon in $TaT_{0.05}$ is by an order of magnitude lower than that in pure Ta, however, without significant change of width and position. Several phonons belonging to the TA[001] and to the $T_2A[110]$ branch were investigated. The results are shown in Fig. 4 as a function of the reduced wave vector q. The reduction of the intensity clearly increases with decreasing q and can well be described by a fit to $1/q^2$.

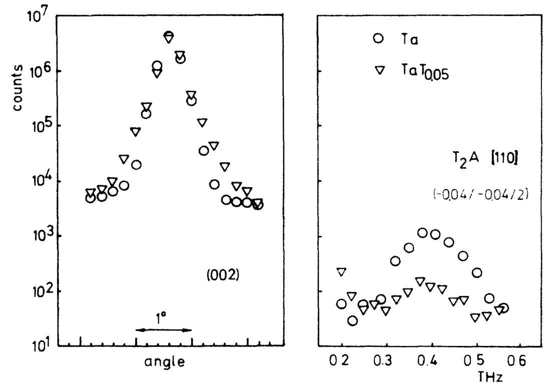

FIG. 3. Comparison of scattering intensities between pure Ta and $TaT_{0.05}$ single crystals. Each crystal has a volume of approximately 1 cm^3. Intensities are given on a logarithmic scale and are normalized to equal counting time. On the left rocking curves of the (002) Bragg reflection, on the right a typical phonon ($T_2A[\xi\xi 0]$, $\xi=0.04$). The Bragg intensities in the two crystals are approximately the same apart from some broadening in the $TaT_{0.05}$ sample. The phonon intensity in the $TaT_{0.05}$ crystal is about ten times lower by contrast with the pure Ta sample, however, there is no significant change in energy and linewidth.

IV. DISCUSSION

The evolution of polycrystalline TaT_x systems during more than two years reaching a final helium concentration of ~ 1.2 at. % was investigated by measuring the positions and widths of Debye-Scherrer lines. An increase of the lattice parameter was observed though considering only the decrease of tritium concentration a contraction of the unit cell would be expected. From the experimentally observed value $d(\Delta a/a)_{\rm obs}/dc_{\rm He}$ one can deduce the total lattice expansion induced by the increasing helium concentration by correcting for the known tritium loss,

$$d(\Delta a/a)_{\rm tot}/dc_{\rm He} = d(\Delta a/a)_{\rm obs}/dc_{\rm He} - d(\Delta a/a)/dc_T$$

yielding $d(\Delta a/a)_{\rm tot}/dc_{\rm He} = 0.150 \pm 0.04$ (see Fig. 1). This value may be compared to recent values for the relative

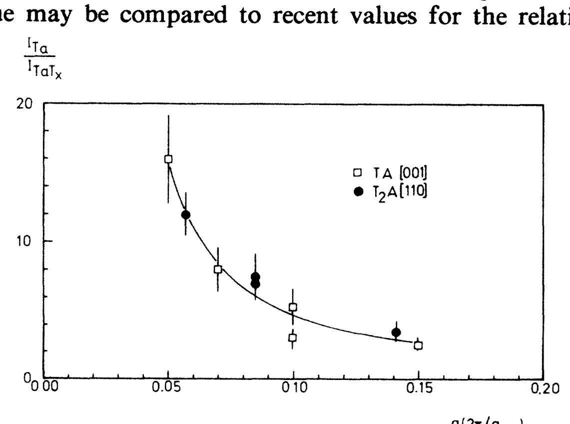

FIG. 4. Intensity ratio of phonons measured in pure Ta and $TaT_{0.05}$ as a function of the reduced wave vector q. Several phonons of the TA[001] and the T_2A[110] branch were investigated. The full line represents a fit calculated on the assumption that the intensity ratio approaches unity for large q and yielding $I_{\rm Ta}/I_{\rm TaT} = 1 + 0.036/q^2$.

length change $\Delta L/L$ obtained by dilatometric methods[6] which gave $d(\Delta L/L)/dc_{\rm He} = 0.173$. According to Simmons and Balluffi[7] the net fractional increase of vacancy-type defects $\Delta N/N$ is given by

$$\Delta N/N = c_v - c_i = 3(\Delta L/L - \Delta a/a) ,$$

where c_v and c_i are the respective overall concentrations of defects of vacancy and interstitial type. Since within the experimental error the values for $\Delta a/a$ obtained in the present experiment and $\Delta L/L$ as given by Schober *et al.*[6] are very close to each other we conclude that $c_v - c_i$ will be rather small. This implies that interstitials mostly form dislocation loops which affect $\Delta L/L$ and $\Delta a/a$ in like manner.

Crystal lattice defects, generally, may influence both the position and the width of the experimentally determined Debye-Scherrer lines.[8] Defects with limited dimensions, however, e.g., interstitials, vacancies and also He bubbles do not induce line broadening effects, but contribute to the change of the observed line position. Thus, the change of the lattice parameter is rather an integral measure of the lattice deformation. On the other hand, line broadening indicates a degrading of the long-range coherence of the lattice and therefore reveals the presence of extended crystal defects, i.e., dislocations and dislocation networks, evolving with He concentration. The results for the $TaT_{0.04}$ sample exhibiting a larger width in the elastically softer (002) direction than that found for the (211) reflection even point to an anisotropic line broadening behavior. This anisotropic broadening is not observed for the $TaT_{0.115}$ crystal. At present, it is not possible to decide whether this is due to the greater statistical errors or due to the different response of the $TaT_{0.115}$ system to helium bubble formation. Indeed, in view of the larger unit cell of the $TaT_{0.115}$ sample leaving more space for the helium atoms a somewhat different defect structure may develop. This last argument is further supported by the fact that the $TaT_{0.04}$ system exhibiting smaller unit cell dimensions and showing the anisotropic line broadening already broke at a much lower helium concentration. It should be noticed, however, that both platelets were destroyed at rather small helium concentrations below 1%.

In view of the complicated defect structure of the TaT_x single crystal it is *a priori* not too surprising to find that lattice vibrations are affected. Most commonly the problem of phonon-defect interaction is treated by using an approach which on principle maintains the concept of coherent one-phonon scattering, yet as a consequence of anharmonicity leads to a characteristic frequency shift $\Delta\omega$ and broadening of the linewidth Γ. The uncertainty in the phonon energy $\Gamma \sim 1/\tau$ is directly related to the finite lifetime τ of the phonon resulting from scattering at the respective defects.

The present experiment, however, contains two conspicuous features which to some extent deviate from the above concept: the q dependence of the measured phonon intensities and the absence of any significant line broadening.

Contrary to the well-known case of static inhomogeneities[8] characterized by an increase of the damping Γ with some power of q, in the present experiment it is the low-q phonons for which the attenuation is most pronounced (see Fig. 4). Given the resolution of the spectrometer configuration used the line broadening of these phonons corresponding to an attenuation by about ~ 10 should clearly be visible. However, despite the marked decrease of intensity only a very weak increase of the line width can be observed, if at all. This is of peculiar interest since the relation $\Gamma \sim 1/\tau$ is quite general and holds independently of the particular reason giving rise to anharmonicity.

A qualitative explanation of this finding as suggested by the experimental results can be given in the following way. The fact that the Bragg intensities of the $TaT_{0.05}$ crystal are only slightly different from those observed in pure Ta shows that elastic scattering still occurs coherently in the loaded crystal. This can be understood by remembering that pointlike defects (as the helium bubbles are) and dislocation loops are accompanied by distortion fields falling off with the square of the distance and therefore do not affect long-range coherence. At least this is true for Bragg scattering where (apart from the Debye-Waller factor) a purely static description of the crystal lattice is sufficient.

In the case of phonon scattering the situation is different. In order that a phonon can be created a dynamical coupling between neighboring atoms must be present allowing for a coherent movement of atoms at least over a distance of the order of the phonon wavelength. If the crystal is severely damaged by helium bubbles and extended dislocation networks this dynamical coupling can be largely impeded. The crystal then splits into many small regions which when viewed "statically" still scatter coherently, yet dynamically act as different crystallites scattering independently of one another. The phonons developing in these regions have a maximum wavelength depending on their respective size which in turn explains why the intensity of low-q phonons is most affected. In view of the experimental data one may conclude that in the present case the diameter of the coherent "grains" limited by bubbles and dislocation networks will typically be several tens of atoms.

A supposedly related phenomenon recently was observed by Stedman[9] in the vicinity of the low-temperature phase transition in sodium. There, similarly, a marked reduction of phonon intensities without noticeable broadening was observed whereas the Bragg intensities remained practically unaltered. The finding was interpreted in terms of reduced long-range coherence due to the development of lattice defects closely associated with the phase transformation.

Presently, most theoretical approaches to phonon-defect interactions formally treat defects within the framework of perturbation theory. Obviously, in the present case as with the mentioned phase transition in sodium this view is no longer applicable. In the case of very large and extended defect structures comprising a significant proportion of the crystal volume defects can no longer be described simply as perturbation of an essentially coherent matrix but must enter the model from the very beginning. The experimental results provide evidence that this situation prevails in TaT_x crystals damaged to such a degree that macroscopic fracture occurs and possibly likewise near first-order phase transitions where nuclei of the new phase act as defects which gradually extend to the entire crystal volume.

It seems worth mentioning that the phonon intensity decrease in the loaded crystal can be described very well by a fit to $1/q^2$ (see Fig. 4). However, this may be accidental and given the present knowledge about the details of defect structures in metal-helium systems any quantitative model would be rather speculative.

Two interesting points which should be investigated in further experiments are following.

(a) The phonon intensity decrease was explained above by a simple qualitative model. As a consequence of this picture the incoherent inelastic scattering cross section should increase in order to make up for the loss in coherent scattering intensity. No attempt was undertaken in the present investigation to verify this presumption.

(b) It is by no means clear whether the observed q dependence of the phonon scattering intensity extends fully to the long-wavelength limit. It is easily conceivable that for very long wavelengths the crystal lattice again becomes sufficiently coherent to facilitate the propagation of lattice vibrations. These probably will be sound waves which can be described in the continuum approximation.

Note added in proof. After having submitted the present paper we received a manuscript by R. Lässer, K. Bickmann, H. Trinkaus, and H. Wenzl entitled "Evolution of the Lattice Spacing and Damage in Tantalum Tritide." In their work the change of lattice parameter and linewidths in TaT_x as a function of time is investigated by x-ray diffraction. The results are interpreted as evidence for the presence of an evolving dislocation network already at very low helium concentrations. A detailed comparison of the two investigations requires a more extensive discussion and will be part of a later communication.

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