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Precision dilatometry of Nb, Ta, and Lu tritides

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Applying buoyancy dilatometry at room temperature to $NbT_{0.0253}$ and strain-gauge dilatometry at room temperature and 78 K to $TaT_{0.0744}$ and $LuT_{0.15}$, respectively, we have measured the swelling of these tritides due to the transmutation of T to ^3He in the first two years after T charging. For all three tritides almost linear swelling is found, indicating approximately constant ^3He densities in bubbles. The corresponding values for the volume requirement of a ^3He atom in a bubble are around 8 Å^3. Associated pressure values are derived with the aid of an equation of state for ^3He adapted to recent high-pressure x-ray-diffraction measurements on solid ^4He. With increasing ^3He concentration the pressure seems to converge to about 0.2 of the shear modulus of the metal, in accordance with recent theoretical results concerning the threshold pressure for dislocation-loop punching by bubbles.

I. INTRODUCTION

Because of the transmutation of tritium into helium, metal tritides change their composition continuously. Above the temperature where the ^3He interstitial atoms formed upon transmutation become mobile, their diffusional clustering results in bubbles.[1–4] At temperatures where metal lattice vacancies are not yet available ^3He bubble formation and growth can only occur by metal self-interstitial emission[5] or dislocation-loop punching.[6–9]

^3He precipitation results in swelling[10–14] since the ^3He atoms in bubbles require more space than the T interstitial atoms in the matrix lattice from which they originate. Actually, swelling data represent the most direct information on ^3He densities and associated pressures in bubbles.

Quantitatively, the relative length and volume change is given by the volume charge per T-decay event and host-atom volume, $(\Delta v/\Omega)_{T\to He}$, times the atomic ^3He concentration c_{He}:[12]

$$3\Delta L/L \approx \Delta V/V \approx c_{He}(\Delta v/\Omega)_{T\to He}$$
$$= c_{T,0}(\Delta v/\Omega)_{T\to He}[1-\exp(-\lambda t)] \ , \quad (1)$$

where $c_{T,0}$ is the initial tritium concentration, λ the decay constant (1.774×10^{-9} s^{-1}), and t the time. The metal-atom volume, Ω, in a tritide of tritium concentration c_T increases with respect to its value in the pure metal according to

$$\Omega=\Omega_0[1+c_T(\Delta v_T/\Omega_0)] \ , \quad (2)$$

where Δv_T is the volume change upon introducing a tritium atom into the alloy. For a small elastic relaxation of the bubbles containing ^3He, the volume change per decay event may be split up approximately as[12]

$$\Delta v_{T\to He}=(\tilde{v}_{He}/\Omega)\Delta\tilde{v}_I-\Delta v_T \ , \quad (3)$$

where $\tilde{v}_{He}$ is the effective volume requirement of a ^3He atom in a bubble within this approximation and $\Delta\tilde{v}_I$ is the volume change per self-interstitial transferred from the bubble to interstitial positions or to dislocations, grain boundaries, and surfaces. For the latter cases, $\Delta\tilde{v}_I$ is close to Ω, in the former case it may be somewhat larger. The exact value of the atomic ^3He volume, including bubble relaxation corrections, v_{He}, is the quantity we want to determine here.

Previously we have reported values of the effective volume $\tilde{v}_{He}$ for the metals Ta, Nb, V, and Lu deduced from a series of first-generation experiments.[12–14] These values are now estimated to have an accuracy of $\pm$(15–20 %). Based on refined techniques and growing experience in performing swelling experiments, we have made an effort to produce a new set of considerably more accurate second-generation data for the metals Nb, Ta, and Lu. For that purpose we have also used, for the first time, *density measurements* as an independent technique to measure helium densities in tritides in addition to the well-established strain-gauge dilatometry. The data obtained are sufficiently accurate to test recent modifications in the theory of bubble growth by dislocation-loop punching.[8,9]

II. EXPERIMENTS

Ultrahigh-vacuum-annealed Nb, Ta, and Lu samples of approximate size $5\times5\times0.25$ mm^3 were charged with T in the Jülich tritium facilities using standard gas phase charging techniques to atomic T concentrations of 0.0253, 0.0744, and 0.15, respectively. These values were corrected for isotopic impurities in the tritium gas. The latter was analyzed by gas chromatography.[15]

A. Density measurements of $NbT_{0.0253}$

We have recently developed a buoyancy method to measure the density of bulk hydrides or tritides with accuracies in the low 10^{-5} region.[15] In brief, the samples were accurately weighed with a 10-μg resolution in air or methylene iodide or dibromoethane. The balance and the immersion bath had to be thermostated to ±0.01 °C.[16] The tritium inventory of the $NbT_{0.0255}$ sample was 75 Ci ($2.775\times10^{12}Bq$). The density of that sample was measured for ~600 d at intervals of about 3–4 weeks.

B. Strain-gauge dilatometry of $TaT_{0.0774}$ and $LuT_{0.15}$

Two strain gauges were applied to opposite faces at corresponding points of rather thick (250 μm) tritide plates with M-Bond 610 cement. A curing temperature of 170 °C (1 h) was used. The above two active strain gauges were diagonally incorporated into a complete Wheatstone bridge to eliminate possible effects of slight bending of the plate. The remaining two reference resistors were made from strain gauges applied as above to thick annealed SS 304 pieces. The detection threshold is estimated to about 2×10^{-6}.

The $TaT_{0.15}$ sample with its two strain gauges and the reference resistors were suspended in an inert oil bath thermostated to 26.0±0.05 °C. The $LuT_{0.15}$ sample together with the reference resistors were suspended in liquid nitrogen in a Dewar. Thus, sample and reference resistors were constantly kept at ~ −195±0.5 °C during the aging experiment (~300 d). Strain measurements occurring in the two tritides were taken every other day under microprocessor control.

III. RESULTS

A. Density measurements of $NbT_{0.0253}$

The reduced density of $NbT_{0.0253}$, $\rho(t)/\rho(0)$, is plotted in Fig. 1 versus time up to about 550 d after T charging. The straight line representing a linear least-squares fit to the measuring points shows that the density decreases almost linearly with time.

B. Strain-gauge dilatometry of $TaT_{0.0774}$ and $LuT_{0.15}$

Figure 2 shows the relative length change or strain of the $TaT_{0.0774}$ sample measured at room temperature for

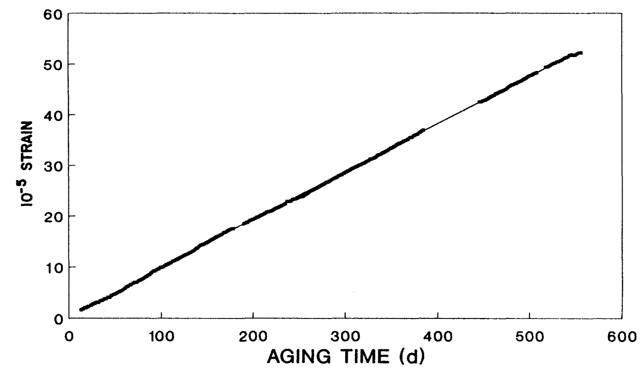

FIG. 2. Relative length change of $TaT_{0.0744}$ vs aging time as measured at room temperature with strain gauges.

about 500 d. An approximately linear increase with time is visible. Figure 3 shows the length change of the $LuT_{0.15}$ sample as measured at −195 °C for about 300 d. After a transient of about 30 d the increase is again essentially linear.

IV. DISCUSSION

^3He interstitial atoms are, as other interstitials, mobile in metals down to relatively low temperatures. It has been shown that ^3He is mobile in Lu above 26 K.[17] For the two other metals, Nb and Ta, ^3He may be safely expected to be mobile at room temperature. There exists experimental and theoretical evidence[4,7,13] that under such conditions bubble nucleation is complete even below 10^{-4} ^3He. After the nucleation stage, most of the ^3He produced will be contained in bubbles. Consequently, our swelling data provide information on ^3He densities within these bubbles.

According to Eq. (1), the primary quantity resulting from our data is the volume change per T decay event given by the experimental quantity $\Delta V/(Vc_{He})$. From this, an approximate value for the volume requirement of a ^3He atom in a bubble, $\bar{v}_{He}$, follows from Eq. (3). The

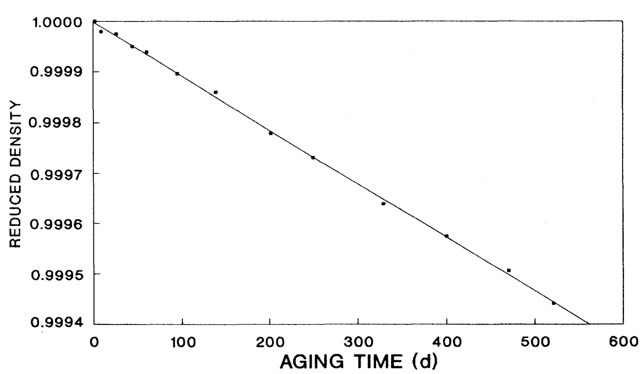

FIG. 1. Reduced density of $NbT_{0.0253}$, $\rho(t)/\rho(0)$, vs aging time. The density of the tritide was measured using a high-precision buoyancy technique (Ref. 16). The straight line represents a linear least-squares fit.

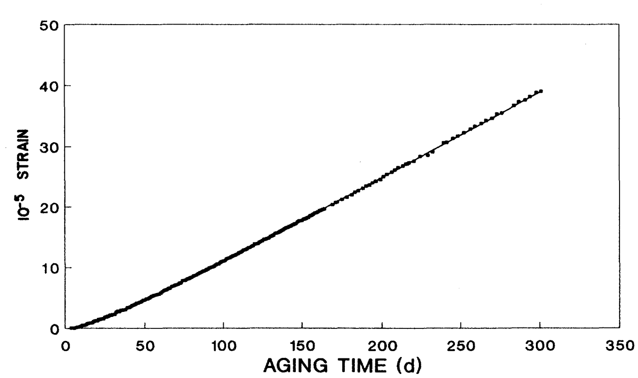

FIG. 3. Relative length change of a $LuT_{0.15}$ sample vs aging time as measured at −195 °C using strain gauges with known k factors at that temperature.

linear increase of the sample dimensions with time indicates that both quantities are approximately constant during the periods investigated.

In the following, we attempt to draw conclusions from the c_{He} dependence of v_{He} on the bubble size dependence of the pressure within the bubble which has not been clear up to date from a theoretical point of view. Since for constant $\tilde{v}_{\mathrm{He}}$ the bubble radius r_B would be proportional to $c_{\mathrm{He}}^{1/3}$ we have plotted $\Delta V/(Vc_{\mathrm{He}})$ versus $c_{\mathrm{He}}^{1/3}$ in Figs. 4–6.

Such plots strongly magnify the low c_{He} regions where the experimental uncertainties are still rather high. For the buoyancy and the strain gauge dilatometry, these initial uncertainties seem to have different origins. In the former case, they are due to the experimental sensitivity limit. In the latter case, comparison with previous measurements[14] indicates stochastic deformations of the samples in the early stage. A possible reason for this could be T diffusion controlled relaxation of small accidental initial stresses resulting from clamping the samples. For Nb and Ta the corresponding relaxation times would, however, be significantly shorter than the observed transients. We think that the latter are correlated with mechanical instabilities manifesting themselves in irregular acoustic emission.[13] Note that a rather limited number of dislocations, i.e., less than 100, are required to produce the observed stochastic deformations.

The conclusion of this discussion is that for the strain-gauge dilatometry the data below about 5×10^{-4} ^{3}He do not provide reliable information. Redefining the zero point by extrapolating the data between 30 and 50 d back to the beginning we have tried to reduce this initial uncertainty somewhat. Fortunately, its effect decreases with increasing c_{He} as indicated by the estimated error bars in Figs. 4–6.

Beyond the initial uncertainties, Figs. 4–6 provide the following information. The volume change per decay event does not change very much with $c_{\mathrm{He}}^{1/3}$. The increase in the second half of the investigated $c_{\mathrm{He}}^{1/3}$ ranges is about 3%, 5%, and 14% but certainly less than 10%, 10%, and 25% in the case of Nb, Ta, and Lu, respectively. The

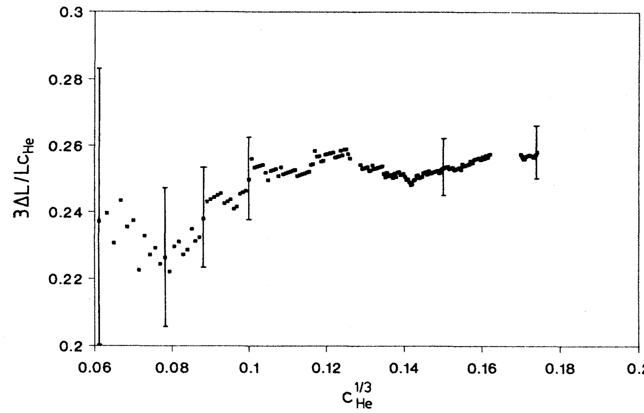

FIG. 5. $3\Delta L/(Lc_{\mathrm{He}})\approx\Delta V/(Vc_{\mathrm{He}})$ vs $c_{\mathrm{He}}^{1/3}$ for $\mathrm{TaT}_{0.0744}$.

values of $(\Delta V/\Omega)_{\mathrm{T}\to\mathrm{He}}$ at the end of our measuring periods and the corresponding values of $\tilde{v}_{\mathrm{He}}/\Omega$ and $\tilde{v}_{\mathrm{He}}$ resulting from them by assuming $\Delta\tilde{v}_I=1$ in Eq. (3) are listed in Table I together with the estimated trends, $\Delta\tilde{v}_{\mathrm{He}}/\tilde{v}_{\mathrm{He}}$, and their absolute upper bounds (in parentheses) for the second half of the $c_{\mathrm{He}}^{1/3}$ range.

From the ^{3}He densities, the pressures within the bubbles can be deduced by using an appropriate equation of state (EOS) for ^{3}He. Recent high-pressure x-ray-diffraction measurements on solid ^{4}He at 300 K (Ref. 18) allow us to provide more reliable values than in the past. We use the procedure described in Ref. 7 for deriving an EOS for solid and fluid He to interpolate and extrapolate the existing data and to correct them for isotropy. In Table I the approximate pressure values corresponding to $\tilde{v}_{\mathrm{He}}$ are listed together with the estimated relative decrease, $-\Delta\tilde{p}/p$ (and its absolute upper bound), for the second half of the $c_{\mathrm{He}}^{1/3}$ range. Also given are the ratios of the approximate pressure to the shear modulus of the metal, μ, controlling shear along the glide cylinder of the expected dislocation-loop punching process (⟨111⟩ and ⟨001⟩ directions in bcc and hcp, respectively).

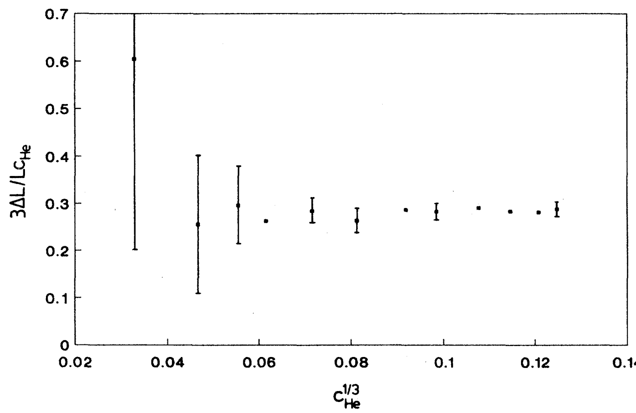

FIG. 4. $3\Delta L/(Lc_{\mathrm{He}})\approx\Delta V/(Vc_{\mathrm{He}})$ vs $c_{\mathrm{He}}^{1/3}$ for $\mathrm{NbT}_{0.0253}$.

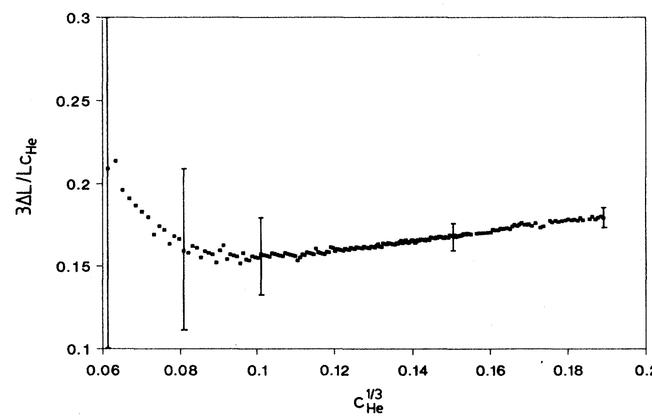

FIG. 6. $3\Delta L/(Lc_{\mathrm{He}})\approx\Delta V/(Vc_{\mathrm{He}})$ vs $c_{\mathrm{He}}^{1/3}$ for $\mathrm{LuT}_{0.15}$.

TABLE I. Parameters characterizing the transmutation of T to ^{3}He in the Nb, Ta, and Lu tritides.

Specimen	$NbT_{0.0253}$ (299 K)	$TaT_{0.0744}$ (299 K)	$LuT_{0.15}$ (78 K)
$(\Delta v/\Omega)^{final}_{T\rightarrow He}$	0.285±0.017	0.255±0.008	0.178±0.007
$(\Delta v/\Omega_0)_T$	0.175±0.003[a]	0.156±0.003[a]	0.107±0.01[b]
$\tilde{v}_{He}/\Omega$	0.460±0.018	0.411±0.009	0.285±0.012
Ω_0 (Å^3)	17.99	18.01	29.52
$\tilde{v}_{He}$ (Å^3)	8.31±0.32	7.49±0.17	8.55±0.36
$\Delta\tilde{v}_{He}/v_{He}$	+2% (<6%)	+3% (<6%)	+9% (<16%)
$\tilde{p}$ (GPa)	7.9±1.2	11.0±1.1	6.0±0.9
$-\Delta\tilde{p}/\tilde{p}$	+6% (<20%)	+10% (<20%)	+30% (<60%)
μ (GPa)	47	63	28
$\tilde{p}/\mu$	0.168±0.026	0.175±0.017	0.214±0.032
v_{He} (Å^3)	7.89±0.32	7.10±0.21	8.00±0.48
p (GPa)	9.2±1.5	12.8±1.5	7.4±1.5
p/μ	0.196±0.031	0.203±0.024	0.264±0.053

[a]Reference 16.
[b]Reference 19.

Corrections to the approximation resulting from Eq. (3) by assuming $\Delta\tilde{v}_I=1$ have been discussed in some detail in Ref. 12. One correction relates to the value of $\Delta\tilde{v}_I$ depending somewhat upon the type of site to which the self-interstitials are transferred from the bubbles. Meanwhile, x-ray-diffraction studies of the lattice damage due to ^{3}He bubble formation in a Ta tritide[20] have shown that in the whole range investigated by us the generated self-interstitials are incorporated into an evolving dislocation network. The decrease in v_{He} estimated from the deviation of $\Delta\tilde{v}_I$ from Ω for the reported evolution of the dislocation density is smaller than 1% and will, therefore, be neglected in the following.

A more important correction is associated with the elastic relaxation of the bubbles which is given by[12]

$$\delta v_{He}/v_{He}\approx 0.3\hat{p}/\mu \ , \tag{4}$$

where $\hat{p}\approx 0.8p$ is the value of the pressure in excess of the value due to the surface tension, $\approx 0.2p$, whose uncertainty increases somewhat the estimated error ranges. The values of v_{He}, p, and p/μ following from Eq. (4) and the estimated error ranges are listed in the last three lines of Table I. Note that in the Ta and Lu tritides the ^{3}He in the bubbles is in the solid state.

On the basis of these results we are now able to discuss theoretical predictions concerning the pressure necessary for dislocation-loop punching.[6–9] Equating the total decrease in the free energy of a bubble of radius r associated with punching out a prismatic dislocation loop of the same radius and Burgers vector b, with the formation free energy of this loop, Greenwood, Foreman, and Rimmer[6] (GFR) obtained a necessary condition for loop punching which we write as

$$p\geq\frac{\mu b}{2\pi(1-\nu)r}\ln(r/r^*)$$
$$\text{with } r^*=r_0\exp[-4\pi\gamma(1-\nu)/\mu b] \ , \tag{5}$$

where ν is Poisson's ratio, γ is the surface free energy, and r_0 is the core radius of the dislocation line.

For small loops, an interpolation between the formation energies of small self-interstitial clusters and of large dislocation loops yielded the approximate condition[7]

$$p\geq(2\gamma+\mu b)/r \quad \text{for } 2\lesssim r/b\lesssim 10 \ . \tag{6}$$

For larger bubbles, the elastic interaction of the bubble and the loop establishes a barrier against their separation resulting in a size-independent threshold pressure above the values given by Eqs. (5) and (6).[8] A recent detailed analysis[9] showed that the maximum pressure first decreases with increasing radius, roughly according to Eq. (6), but then converges to an asymptotic value around 0.2μ which is close to the theoretical shear strength.

Obviously, the latter findings are confirmed by the absolute pressure values deduced from our data, in particular when these are considered in relation to the values for the relative decrease of the pressure. Thus, the highest-pressure values, found for the Lu tritide, are correlated with the strongest relative decrease in the pressure. This result indicates very low bubble sizes, probably in the subnanometer range, corresponding to an extremely high bubble density as expected for the low temperature applied to the Lu tritide.

For a definite conclusion we consider the GFR criterion, Eq. (5), in some more detail. Since there is considerable uncertainty concerning the value of r^* we could try to explain our finding by properly choosing the latter. For instance, large pressure values are obtained for extremely small r^*. In this case, however, the pressure would approximately decrease as $1/r$. On the other hand, a vanishing relative decrease of p with r is found for $r/r^*=e$. For bubbles in the nanometer range as expected for the Nb and Ta tritides at the end of our measuring periods, the corresponding pressure is, however, significantly below the values deduced for these tritides. This feature of Eq. (5) becomes particularly clear by correlating the relative decrease of p with increasing r with p and r

$$d \ln p / d \ln r = -1 + \frac{\mu b}{2\pi(1-\nu)} \frac{1}{pr} . \quad (7)$$

According to Eq. (7), the relative decrease of p with increasing r increases with decreasing p, just opposite to the correlation deduced from our data. We, therefore, can safely rule out the GFR criterion as being operative. On the other hand, our data provide striking evidence for the refined criterion[8,9] accounting for a possible barrier against the loop-punching process.

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