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Short-range ordering of hydrogen isotopes in lutetium

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Abstract

The kinetics of short-range ordering of the hydrogen isotopes protium, deuterium and tritium in lutetium was studied by electrical resistivity measurements during isothermal annealing. The reaction order parameter decreased from above 2 to about 1 for temperatures from 160 to 190 K. The rate constant showed an apparent activation enthalpy of about 0.52 eV for tritium and slightly smaller values for the lighter isotopes. The data could be described by a model for clustering of hydrogen atoms with a binding energy per atom of about 0.5 eV, a migration enthalpy of about 0.45 eV and a reduction in the resistivity contribution per clustered atom by about 12%, compared with non-clustered atoms.

1. Introduction

Lutetium, like some other rare earth metals, shows hydrogen solubility in the 10% range down to low temperatures without precipitation of a second phase. Recently in Lu(D) the formation of deuterium pairs was found by diffuse neutron scattering [1]. A "resistivity anomaly", that is a change in the temperature dependence at around 175 K, has been tentatively ascribed to this ordering [2–4]. In the present work the kinetics of this resistivity anomaly are studied by isothermal annealing experiments. The atomic parameters for hydrogen migration and clustering are derived from a comparison with clustering models.

2. Experimental details

Lutetium of 99.99% metal purity and with less than 0.3 at.% impurities of gases and carbon was supplied by Aimes Laboratories in the form of 1 mm × 0.2 mm ribbons. Room-temperature to liquid-helium resistivity ratios ranged from 25 to 50. The devices for loading the specimens with hydrogen, deuterium and tritium have been described elsewhere [5]. The hydrogen concentration, given as the ratio r of hydrogen to metal atoms, was determined from the pressure change in the reaction volume during charging and during degassing after the measurements. Tritium concentrations determined from the mass changes were unreliable owing to oxidation of the sample surfaces. A third estimate of the concentration was obtained from the increases in resistivity (Table 1) measured at 296 K and after quenching to 4.2 K respectively. In this case, resistivity increment values ρ_H of 2.3 $\mu\Omega$ m (296 K) and 2.9 $\mu\Omega$ m (4.2 K) per unit concentration were used [4] identical for all three hydrogen isotopes. The concentrations derived from both methods show no systematic deviations but a relatively large scatter. Possible reasons for this are the absorption of gaseous impurities. As the following results are mainly based on resistivity measurements, the r_ρ values in Table 1 will be used.

Two specimens, with 15 mm gauge length, were mounted on a specimen holder, with four gilded clamps serving as current leads and voltage grips respectively. Experiments were performed in a helium bath cryostat, described in ref. 6. The helium gas pressure in the specimen chamber was 2.5×10^4 Pa. The specimens were annealed from 10 K to about room temperature in furnaces mounted on the support tube of the specimen chamber. The temperature was not raised above ambient to avoid losses of hydrogen and to keep tritium activation of the apparatus low. The specimen temperature was measured with calibrated (Au–Fe)–(Ni–Cr) and Cu–(Cu–Ni) thermocouples. The furnaces were cooled by exhaust gas from the cryostat bath, and the temperature was controlled by d.c. heaters.

Most isothermal anneals were performed at temperatures between about 160 and 190 K, *i.e.* in the temperature range of the resistivity anomaly [2–4]. Specimens were brought to the annealing temperature either by down-quenching from room temperature or by up-quenching, which means by first quenching into liquid helium (the cooling rate around 170 K, was about

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TABLE 1. Hydrogen-to-lutetium ratios r derived from measurement of the quenched-in resistivities ρ at 4.2 K and 296 K (r_ρ) and from pressure drop (r_p) during loading (in) and degassing (out) respectively where $r_\rho=[\rho(T)-\rho_{\mathrm{Lu}}(T)]/\rho_{\mathrm{H}}$ and typical resistivities of the hydrogen-free specimens are ρ_{Lu} (4.2 K) ≈ 0.019 ± 0.07 μΩ m and ρ_{Lu} (296 K) ≈ 0.69 ± 0.06 μΩ m

Specimen	ρ (4.2 K) (μΩ m)	ρ (296 K) (μΩ m)	r_ρ (4.2 K) (ρ_{H}=2.9 μΩ m[a])	r_ρ (296 K) (ρ_{H}=2.3 μΩ m[a])	r_p (in)	r_p (out)
LuH_r	0.7757	1.3783	0.259	0.280	0.180	0.254
LuD_r	0.5336	1.1141	0.175	0.159	0.180	0.156
LuT_r-1	0.6324	1.208	0.210	0.216	0.175	–[b]
LuT_r-3	0.2446	0.833	0.080	0.087	0.129[c]	–[b]
LuT_r-4	0.2893	0.866	0.095	0.097		

[a] The same value was used for all three hydrogen isotopes.
[b] For safety reasons the LuT specimens were not degassed.
[c] Only an average value is given, as two specimens were loaded simultaneously.

40 K s^{-1}) and subsequently pulling into the furnace. In both cases the approach to the annealing temperature T_a followed a logarithmic law: dT/dt (K s^{-1}) ≈ $0.05(T_a-T)$. The effects of temperature transients are slightly smaller during up-quenching owing to the lower temperatures involved. The temperature stability was better than 0.01 K. Long-term drifts of the order of 0.1 K were caused by lowering the gas pressure when the helium level in the bath dropped between filling cycles. The resistivity data were corrected for the influence of these temperature drifts.

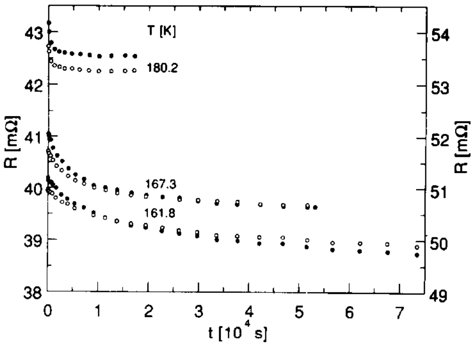

Fig. 1. Typical resistivity changes in two Lu(H) specimens (○, left-hand side ordinate; ●, right-hand side ordinate) during isothermal annealing at the given temperatures.

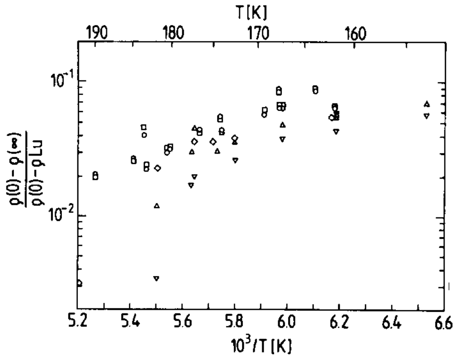

Fig. 2. Ratio of the asymptotic resistivity change to total hydrogen-induced resistivity during isothermal annealing at temperature T of LuH_r (▽), LuD_r (△), LuT_r-1 (◇) LuT_r-3 (□) and LuT_r-4 (○).

3. Results

Considerable changes in resistivity $\rho(t)$ during isothermal annealing within reasonable times were only observed at temperatures from about 150 to 200 K. Typical results are given in Fig. 1, showing a decrease of resistance at a decreasing rate, eventually attaining an asymptotic value $\rho(\infty)$. Figure 2 shows the temperature dependence of $\rho(\infty)$, plotted as $[\rho(0)-\rho(\infty)]/[\rho(0)-\rho_{\mathrm{Lu}}]$, where ρ_{Lu} and $\rho(0)$ are specimen resistivities before and after hydrogen charging respectively. A first tentative evaluation of resistivity evolution was performed using the following general kinetic equation:

$$\frac{\delta\rho/\delta t}{\rho(0)-\rho(\infty)}=-k\left(\frac{\rho(t)-\rho(\infty)}{\rho(0)-\rho(\infty)}\right)^{\beta} \tag{1}$$

The effective rate constant k and the reaction order parameter β are defined by

$$k=-\frac{\delta\rho/\delta t(0)}{\rho(0)-\rho(\infty)} \tag{2}$$

$$\beta=\log\left(\frac{\delta\rho/\delta t}{\delta\rho/\delta t(0)}\right)\Big/\log\left(\frac{\rho-\rho(\infty)}{\rho(0)-\rho(\infty)}\right) \tag{3}$$

In Fig. 3 the resistivity change rate $\delta\rho/\delta t$ is plotted in a double-logarithmic plot according to eqn. (1). The parameters k and β are then obtained from the slope and the intercept at $t=0$ (*i.e.* abscissa equal to 1) respectively. The measurement accuracy allows evaluation over relative resistivity variations of about one order of magnitude (abscissa, about 10^{-1} to 1). Above about 167 K the derived k values can be approximated by the Arrhenius laws $k=k_0\exp(-H_k/k_BT)$ with $k_0\approx3\times10^9$ s^{-1}, 5×10^{10} s^{-1} and 1×10^{12} s^{-1} and $H_k\approx0.42$ eV, 0.47 eV and 0.52 eV for protium, deuterium and tritium respectively. The values for β as a function

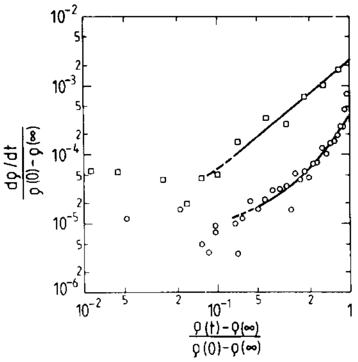

Fig. 3. Resistivity change rate of two LuT, specimens during isothermal annealing plotted according to eqn. (1). The tritium atomic ratios *r* were 0.11 ± 0.02 and the annealing temperatures 167.3 K (○) and 180.2 K (□).

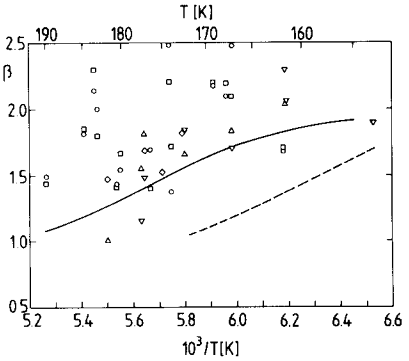

Fig. 4. Reaction order parameters β as a function of temperature T. The symbols are as in Fig. 2. The lines give calculated values as described in the text.

of temperature are summarized in Fig. 4. The data show sizable scatter but on the average decrease from above 2 at lower temperatures (about 160 K) to almost 1 at higher temperatures (about 190 K). In general the β values for hydrogen and deuterium tend to be smaller than those for tritium. Deviations from eqn. (1) occur at small times and/or low temperatures as indicated by the time dependence of the slope at lower temperatures in Fig. 3 and by the temperature dependence of β in Fig. 4. This may indicate that more than one process is involved in contrast with the assumption inherent in eqn. (1).

4. Discussion

Therefore a more detailed analysis will be performed using the following chemical rate equation, which considers clustering of mobile hydrogen atoms of atomic concentration c with a clustering parameter $n \geqslant 2$ (first term), which are subsequently growing ($m=1$) or not growing ($m=0$) (second term), and finally dissociate (third term):

$$\frac{\delta c}{\delta t} = -nk_t c^n - mk_t c[c(0)-c] + k_d[c(0)-c] \tag{4}$$

For simplicity it is assumed that trapping rate k_t and dissociation rate k_d per atom do not depend on cluster size. If only the first term were present, *i.e.* no growth ($m=0$) and no dissociation of clusters ($k_d=0$), a comparison of eqns. (1)–(4) gives

$$k = \frac{nk_t(1-\rho_2/\rho_1)[\rho(0)-\rho_{\mathrm{Lu}}]^n}{[\rho(0)-\rho(\infty)]\rho_1^{\,n-1}} \tag{2a}$$

$$\beta = n \tag{3a}$$

The hydrogen-induced resistivity is related to the concentration c of mobile atoms by

$$\rho(t) - \rho_{\mathrm{Lu}} = \rho_1 c(t) + \rho_2[c(0)-c(t)] \tag{5}$$

where ρ_1 is the resistivity contribution per unit concentration of mobile atoms and ρ_2 is the resistivity contribution per unit concentration of atoms in clusters. Evaluation of eqn. (5) for $t=0$ and for $t=\infty$ yields

$$1 - \frac{c(\infty)}{c(0)} = \frac{\rho(0)-\rho(\infty)}{\rho(0)-\rho_{\mathrm{Lu}}} \Bigg/ \left(1 - \frac{\rho_2}{\rho_1}\right) \tag{6}$$

From $c(\infty) \leqslant c(0)$ it follows that $1-\rho_2/\rho_1 \geqslant [\rho(0)-\rho(\infty)]/[\rho(0)-\rho_{\mathrm{Lu}}]$. The low temperature data in Fig. 2 then yield an upper limit $\rho_2/\rho_1 \leqslant 0.92$. Insertion of eqn. (5) into eqn. (1) shows that eqn. (1) also holds when resistivities ρ are replaced by concentrations c. This means, that for a resistivity–concentration relation such as eqn. (5), the parameters k and β also apply to the kinetics of the concentration changes.

The clustering or trapping rate k_t is given by

$$k_t = \frac{4\pi RD}{\Omega} \tag{7}$$

where R, Ω and $D = D_0 \exp(-H_m/k_B T)$ are the reaction radius, the atomic volume and the diffusion coefficient respectively of the mobile atoms. The temperature dependence of k_t is determined by the migration enthalpy H_m. From the initial change in the concentration of the mobile atoms, k_t is obtained according to eqns. (4) and (2a) by

$$k_t = -\frac{\delta c/\delta t(0)}{n[c(0)]^n}$$

$$= -\frac{\rho_1^{\,n-1}\cdot\delta\rho/\delta t(0)}{n[\rho(0)-\rho_{\mathrm{Lu}}]^n(1-\rho_2/\rho_1)} \tag{8}$$

A plot of the resistivity data according to eqn. (8) is given in Fig. 5, using $n=2$ and $\rho_2/\rho_1=0.92$ (m does not influence k_t). The slope (full line; $k_t \approx 3\times10^{10}\exp(-0.45/k_B T)$) of the Arrhenius plot in Fig. 5 gives a migration enthalpy $H_m \approx 0.45$ eV. Using $n=3$ would

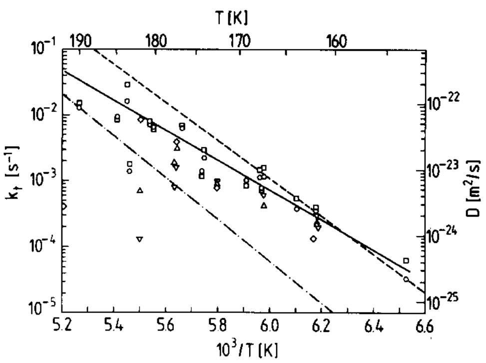

Fig. 5. Trapping rate constant k_t derived from the resistivity measurements evaluated according to eqn. (4) with $n=2$ and $m=0$. The symbols are as in Fig. 2. The data were converted to diffusion coefficients according to eqn. (7) and are fitted by the full line. The broken and chain lines indicate the diffusion coefficients of ref. 10, extrapolated from above 380 K.

increase k_t by almost an order of magnitude but would not change the slope significantly. The k_t data scatter considerably at the higher temperatures and therefore these data were rated lower in the fit. From eqn. (7) the diffusion coefficients (left-hand side ordinate in Fig. 5) are obtained by using $R=3.43\times10^{-10}$ m (nearest-neighbour distance) and $\Omega=2.95\times10^{-29}$ m^3, giving D (m^2 s^{-1})$=2\times10^{-10}$ exp(-0.45 (eV)/k_BT).

From the asymptotic concentration $c(\infty)$ of unclustered hydrogen, the ratio k_d/k_t is obtained by

$$\frac{k_d}{k_t}=\frac{n[c(\infty)]^n}{c(0)-c(\infty)}+mc(\infty)$$

$$=\frac{n[\rho(\infty)-\rho_{Lu}+(\rho_0-\rho_{Lu})\rho_2/\rho_1]^n}{[\rho(0)-\rho(\infty)](\rho_1-\rho_2)^{n-1}}$$

$$+m\,\frac{n[\rho(\infty)-\rho_{Lu}+(\rho_0-\rho_{Lu})\rho_2/\rho_1]^n}{\rho_1-\rho_2} \qquad (9)$$

The temperature dependence of k_d/k_t is given by the binding enthalpy H_b, as the dissociation rate is given by $k_d=v_0\exp(-H_{dis}/k_BT)$ and the dissociation enthalpy is given by $H_{dis}=H_m+H_b$. A plot of the data according to eqn. (9) is shown in Fig. 6, giving a binding enthalpy $H_b\approx0.5$ eV. The protium (broken line) and deuterium data exceed the tritium values (full line: $k_d/k_t\approx10^{13}\exp(-0.5/k_BT)$) by factors of about 30 and 10 respectively. Including the above results for k_t, the following pre-factors v_0 of k_d are obtained: tritium 3×10^2 s^{-1}; deuterium 3×10^3 s^{-1}; hydrogen, 1×10^4 s^{-1}.

Finally the temperature dependence of the effective reaction order parameter β introduced in eqn. (3) will be calculated by numerically solving eqn. (4). Using the above results for k_t (full line in Fig. 5) and k_d/k_t (full and broken lines in Fig. 6) gives (initial) β values, depicted by the full and broken lines in Fig. 4. Obviously only the full line, corresponding to the tritium data in Fig. 6 approaches the β values in Fig. 4. The fit is very sensitive to the assumed values of n and ρ_2/ρ_1 and could be improved by increasing n (*i.e.*, $n>2$) and/or decreasing ρ_2/ρ_1 (*i.e.*, $\rho_2\rho_1<0.92$).

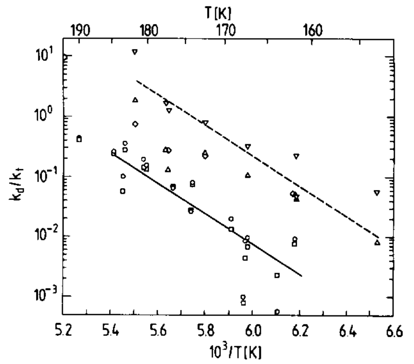

Fig. 6. Ratios of dissociation rate k_d to trapping rate k_t, derived from the resistivity measurements for tritium (——), deuterium and protium (– – –), evaluated according to eqn. (4) with $n=2$ and $m=0$. The symbols are as in Fig. 2.

5. Comparison with previous studies

The above evaluation shows that the rate constants k derived from the general kinetic equation (eqn. (1)) differ somewhat from the tapping rate constants k_t. This sheds some doubt on the migration enthalpies for hydrogen in lutetium (0.25 eV) cited in refs. 2 and 3, especially as the method by which a reaction order of 1 was derived in ref. 2 is inconclusive. Another rather low migration enthalpy (0.28 eV) was derived from nuclear magnetic resonance measurements [7]. This value was derived under the assumption of next-neighbour octahedral site occupation of hydrogen in lutetium, which is at variance with more recent indications of tetrahedral site occupation [8]. However, this is probably not the reason for the relatively low enthalpy value. From internal friction measurements [9], migration enthalpies of 0.56 ± 0.05 eV (LuH_r) and 0.64 ± 0.03 eV (LuD_r) were reported. Similar values of 0.572 ± 0.015 ($\mathrm{LuH}_{0.05}$) and 0.63 ± 0.02 ($\mathrm{LuD}_{0.05}$) were derived from Gorsky effect measurements [10] at temperatures between 380 and 540 K. Extrapolations of the data in ref. 10 are given by the broken (hydrogen) and chain (deuterium) lines in Fig. 5. This extrapolation over more than 11 orders of magnitude is in good agreement with the present diffusion coefficients. The absence of a pronounced isotope effect in the present results may be due to different impurity contents of specimens charged with different hydrogen isotopes. On the contrary a change in isotope effect as well as a decrease in the activation energy from the high temperatures in ref. 10 to the present much lower temperatures cannot be excluded.

6. Conclusions

(1) The "anomaly" in the hydrogen-induced resistivity in lutetium can within experimental error be explained by a model which includes clustering of hydrogen atoms at a rate $nk_t c^n$ with $n \geqslant 2$ and dissociation of atoms from the clusters at a rate k_d.

(2) The clustering rate constants k_t can be described by an Arrhenius law with a pre-factor 3×10^{10} s^{-1} and an activation energy of 0.45 eV, corresponding to the migration of hydrogen atoms.

(3) From the rate constants k_t, diffusion coefficients D with a pre-factor 2×10^{-10} m^2 s^{-1} and a migration energy of 0.45 eV are derived. These diffusion coefficients obtained from 160 to 190 K are in good agreement with data extrapolated from Gorsky effect measurements above 380 K.

(4) The dissociation rate constants k_d can be described by an Arrhenius law with pre-factors of the order of 10^3 s^{-1} and a dissociation energy of 0.95 eV.

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