COMMENTS CONCERNING PARAMETERS OF THE SHORT-RANGE ORDER EVOLUTION DETERMINED FROM THE DATA ON KINETICS OF A HEAT-CAPACITY RELAXATION FOR Lu–H ALLOY

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Introduction

Short-range order is the unique natural-occurring concentration heterogeneity, whose sizes are commensurate with lattice parameters of a solid solution. Kinetics of short-range order is determined by the microscopic diffusion over intersite distances. Therefore, kinetic measurements of its relaxation provide us with detailed information on the discrete diffusion mechanism such as the microscopic characteristics of atomic migrations, including probabilities and types of atomic jumps, and activation energy of diffusion. Besides, microdiffusion measurements can be performed even at room temperatures because of short time of elementary diffusion events. This means that results can be used for determining the low-temperature diffusivities and activation energies.

The relaxation of radiation diffuse-scattering intensities is a most convenient technique for the investigation of short-range order kinetics [1–3]. Another one is to study the change of physical properties affected by the short-range order evolution, for instance, the heat capacity or electrical resistivity relaxation, which enables obtaining the results with more simplicity and responsiveness.

This communication is concerned with a further theoretical analysis of the short-range order kinetics of hydrogen (H) atoms at tetrahedral interstices in h.c.p. lattice of lutetium (Lu) by means of comparison of results obtained by independent (but conditioned by the same ‘nature’) investigation methods for different characteristics—residual electrical resistance [4, 5] and heat capacity [6].

Kinetic Models

Kinetics of heat capacity (C_p) relaxation was experimentally studied in Ref. [6] for h.c.p.-Lu–H single crystal. The data about kinetics of short-range order relaxation of H in Lu can be obtained from these heat-capacity measurements during the isothermal ($T = \mathrm{const}$) annealing [6]. Changes of $dC_p(t,T)/dt$ vs. time t for LuH$_c$ during the isothermal annealing were observed at temperatures from 130 K to 180 K. During the isothermal diffusion of interstitial H atoms in h.c.p.-LuH$_c$ solution ($0 \leq c < 0.5$), reciprocal relaxation time, $1/\tau_i$, is proportional to the mobility of H atoms, $\nu_{\mathrm{H}i}$, with an efficiency factor, χ_i, as follows:

$$1/\tau_i = \chi_i (1-c)\nu_{\mathrm{H}i};$$

here $\nu_{\mathrm{H}i}$ is defined by a Boltzmann distribution,

$$\nu_{\mathrm{H}i} = \nu_{0i}\exp(-E_{\mathrm{m}i}/(k_B T)).$$

In the last expression, $E_{\mathrm{m}i}$ is the migration energy of H atoms over the i-th ‘scenario’. It corresponds to their activation energy, $E_{\mathrm{a}i}$, in a case of spatial redistribution of H atoms between the (tetrahedral) interstices ($E_{\mathrm{a}} \approx E_{\mathrm{m}i}$). So, the temperature dependence of τ_i follows the so-called Arrhenius ‘law’:

$$\tau_i = \tau_{0i}\exp(E_{mi}/(k_B T)) \text{ with } \tau_{0i} = 1/(\chi_i(1-c)\nu_{0i})\,.$$

Based on experimental results of Ref. [6], the relaxation times $\{\tau_i\}$ of heat capacity for the Lu–H were estimated within the frameworks of the first-order kinetic model,

$$\Delta C_p(t,T)/\Delta C_{p0}(T) \approx e^{-t/\tau},$$
$$dC_p(t,T)/dt \approx -\Delta C_p(t,T)/\tau,$$

and of (more realistic) second-order kinetic model,

$$\Delta C_p(t,T)/\Delta C_{p0}(T) \approx Ae^{-t/\tau_1} + (1-A)e^{-t/\tau_2},$$
$$dC_p(t,T)/dt \approx -\Delta C_{p0}(T)\left(\frac{Ae^{-t/\tau_1}}{\tau_1} + \frac{(1-A)e^{-t/\tau_2}}{\tau_2}\right);$$

$\Delta C_p(t,T) = C_p(t,T) - C_{p\infty}(T)$, $\Delta C_{p0}(T) = C_{p0}(T) - C_{p\infty}(T)$, $C_p(t,T)$ is instantaneous heat capacity (at the point of time t), $C_{p0}(T)$ is initial ($t = 0$) heat capacity and $C_{p\infty}(T)$ is equilibrium ($t \to \infty$) heat capacity at annealing temperature T, A and $(1-A)$ are ‘weights’ of the first relaxation ‘scenario’ and of the second one, respectively.

Results and Discussion

The experimental measurements for LuH$_{0.148}$ were described in Ref. [6] within the frameworks of both the first-order kinetic model and the second-order one (see, *e.g.*, Figs. 1 and 2). Using Arrhenius ‘law’, migration energies of H atoms were also estimated (see Table 1).

Changing heat capacity C_p in above-mentioned

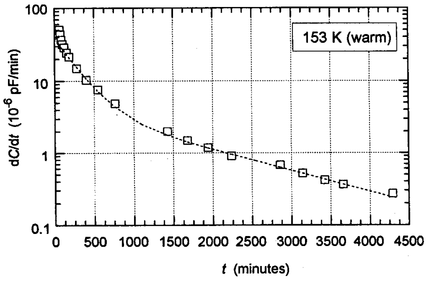

Fig. 1. dC_p/dt vs. t within the framework of the second-order kinetics model for $LuH_{0.148}$ at temperature 153 K [6].

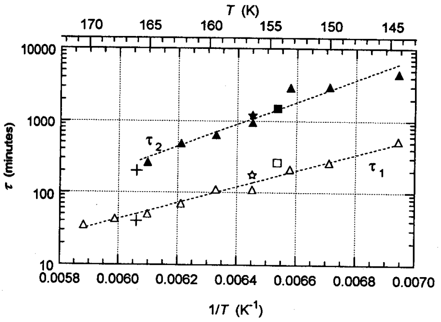

Fig. 2. Relaxation times τ vs. $1/T$ within the framework of the second-order kinetic model for $LuH_{0.148}$ [6].

equations into the residual electrical resistivity ρ, they can be reduced to corresponding kinetic models as applied to describe the results of residual resistivity measurements [5] for $LuH_{0.180}$ and $LuH_{0.254}$ (see Figs. 3 and 4). Evaluated migration energies are also listed in Table 1. Evidently on average, the presented migration energy for more concentrated $LuH_{0.180}$ solution, $(E_{m1} + E_{m2})/2 = 0.295$ eV (based on ρ data), exceeds reasonably the migration energy for less concentrated $LuH_{0.148}$ solution, $(E_{m1} + E_{m2})/2 = = 0.26$ eV (based on C_p data). Such a correlation between the increase of activation energy and the rise of c suggests that the factors determining the relaxation kinetics of two different characteristics—C_p and ρ—are associated.

Author of Ref. [6] noted that two fitting parameters, τ_1 and τ_2, are chosen for more 'high-quality' reproduction of measuring data. Nevertheless, in actual fact, the sense of these parameters is more intimate. Characterization of heat-capacity and residual-resistivity relaxation kinetics (following the short-range order evolution kinetics) for Lu–H on the whole by two relaxation times may be caused by the difference of probabilities of interstitial H-atoms' jumps along the preferential directions of 'a_0' and 'c_0' axes in h.c.p. lattice of Lu single crystal or of every crystallite in Lu polycrystal (even in spite of the isotropy of scalar C_p value).

Table 1. Migration energies for Lu–H alloy within the framework of the 1-st and 2-nd order kinetics models.

Alloy	Migration energies for the 2-nd order model, E_{m1}, eV	E_{m2}, eV	Migration energy for the 1-st order model
monocryst. $LuH_{0.148}$	0.22 [6]	0.31 [6]	
polycryst. $LuH_{0.180}$	0.30	0.29	0.33
polycryst. $LuH_{0.254}$			0.38

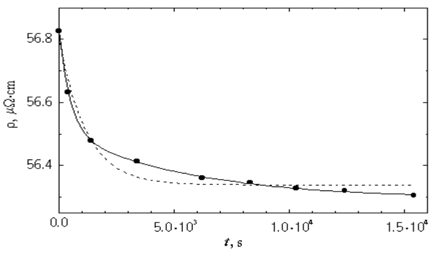

Fig. 3. Residual resistivity ρ vs. t for $LuH_{0.180}$ at temperature 180.2 K (dotted line fitted to the one τ, solid line—to the two τ-s, •—experimental data from Ref. [5]).

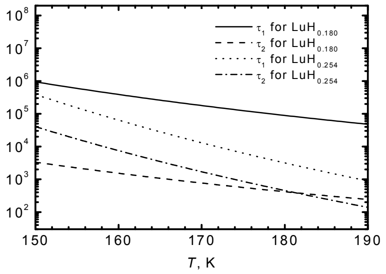

Fig. 4. Relaxation times τ vs. T within the framework of the second-order kinetic model for Lu–H. Results are calculated using resistivity measurements in Ref [5].

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