



Isochoric Specific Heat and Anharmonicity for Liquid Potassium

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1. Introduction

Liquid alkali metals are assumed to be nearly 'harmonic liquids' with small anharmonicity. The Grüneisen constant, which is of order 1.5, and $1 \leq C_p/C_V \leq 1.5$ are the features of these liquids. An inelastic neutron scattering experiment for liquid potassium at temperatures of 340, 440 and 550 K was performed and frequency spectrum (FS) of oscillations of potassium's atoms was obtained [1]. Neutrons with initial energy of 4 meV were used and the average energy of potassium atoms' oscillations was about 7 meV [1]. The temperature dependence of the spectrum is small compared to the energies of the spectral components in the temperature range studied, the Grüneisen constant has been found to be 1.3. This temperature dependence indicates an anharmonicity in oscillations of potassium atoms and makes possible the evaluation of the isochoric specific heat, C_V , at the same time.

2. Theoretical background

The internal energy of a system per one mole can be represented via a system's FS as following:

$$U(T) = E_0 + 3N_A \int_0^{\infty} \varepsilon g(\varepsilon) f(\varepsilon, T) d\varepsilon, \quad (1)$$

$g(\varepsilon)$ is the frequency spectrum, N_A is the Avogadro number, ε is excitation energy, i.e. change of neutron energy in the scattering process, and the function $f(\varepsilon, T)$ is:

$$f(\varepsilon, T) = \left[\exp(\varepsilon/k_B T) - 1 \right]^{-1} + 1/2, \quad (2)$$

k_B is the Boltzmann constant. Taking into account the revealed deformation of $g(\varepsilon)$ with temperature the specific heat per one mole is:

$$C_V(T) = \frac{\partial U(T)}{\partial T} = 3N_A \int_0^{\infty} \left[\frac{\partial g(\varepsilon)}{\partial T} f(\varepsilon, T) + g(\varepsilon) \frac{\partial f(\varepsilon, T)}{\partial T} \right] \varepsilon d\varepsilon. \quad (3)$$

The first term in square brackets represents the anharmonic contribution to the specific heat.

3. Results

At three temperatures of our experiment $g(\varepsilon)$ has been represented by the following [1]:

$$g(\varepsilon) = g_L(\varepsilon) + g_T(\varepsilon) = \frac{4\varepsilon^2}{\sqrt{\pi}} \left[\frac{A_L}{\varepsilon_L^3} \exp(-\varepsilon^2/\varepsilon_L^2) + \frac{A_T}{\varepsilon_T^3} \exp(-\varepsilon^2/\varepsilon_T^2) \right]. \quad (4)$$

A_L and A_T are weight coefficients independent of temperature, ε_L and ε_T are excitation energies corresponding to the peaks of components, $g_L(\varepsilon)$ and $g_T(\varepsilon)$, respectively. The dependence of $g_i(\varepsilon)$ ($i = L, T$) and ε_i on temperature is an evidence of anharmonicity. The function $\partial g(\varepsilon, T)/\partial T$ and the anharmonic contribution in Eq. (3) can be defined now (Fig.1).

The second term in Eq. (3) represents harmonic component and if $\varepsilon \ll k_B T$ (that is really the case) it is approximately that of the Dulong-Petit law: $C_V^{har} \approx 3N_A k_B$.

Before comparing the result with known data [2] it should be remembered that the FS, $g(\varepsilon, T)$, does not contain a diffusion component of the total mobility of atoms. Only

inelastic contribution to neutron scattering pattern was considered to obtain FS [1]. So now the diffusion contribution is to be considered, and C_V takes the form:

$$C_V(T) \cong (1 - S_d) \left(C_V' - \frac{3}{2} N_A k_B T \frac{\partial S_d}{\partial T} \right) + \frac{3}{2} N_A k_B S_d. \quad (5)$$

Here C_V' is the specific heat of Eq. (3), and S_d is relative part of diffusive modes in the FS.

For solid potassium near the melting point the anharmonic contribution has been found [3]:

$$C_V^{an}(T) = 3 N_A k_B T A, \quad (6)$$

where $A = 1.7 \cdot 10^{-4} \text{ K}^{-1}$. Being extrapolated to temperatures from 340 to 550 K this contribution is shown on Fig.1. More appropriate comparison comes with the result [4] where the anharmonicity has been considered as a small correction to harmonic law connected with the structure of liquid that finally yields the upper limit of the anharmonic contribution:

$$C_V^{an} \leq 1.5 N_A k_B S_m(T). \quad (7)$$

$S_m(T)$ is the structure factor, $S(q)$, at $q = (18\pi^2 n)^{1/3}$ [2], n is particle density. It is seen on Fig.1 that our result as regards to the anharmonic contribution, C_V^{an} , is consistent with both [3] and [4]. Total specific heat, C_V , calculated with Eq. (5) matches in general the reference data [2] but are 1 to 1,5 J/mole K smaller. Configurational contribution caused by thermal expansion of metal and restructuring corresponding to the expansion could be taken into account. It does not exceed 1.5 J/mole K in the considered temperature range.

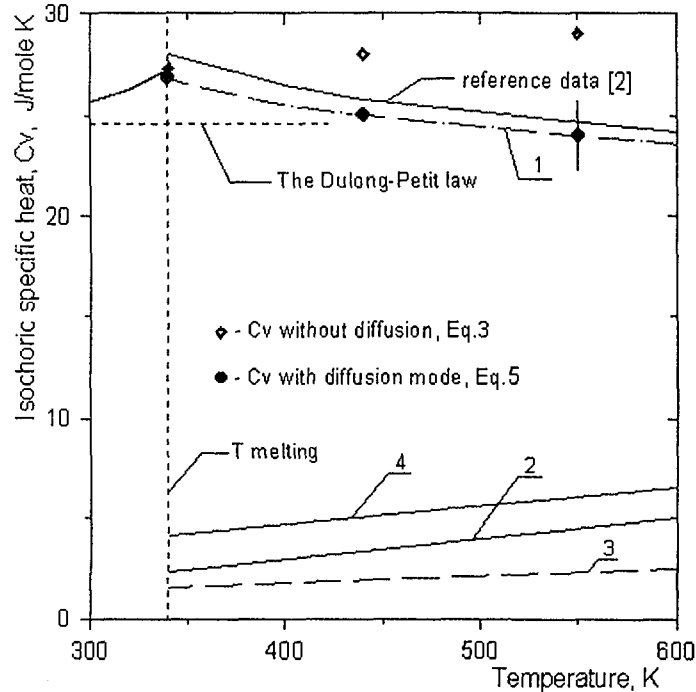


Fig.1. Isochoric specific heat for liquid potassium.

- 1 – approximation curve;
- 2 – anharmonic contribution, C_V^{an} , of Eq. (3);
- 3 – extrapolation of data [3], Eq. (6);
- 4 – upper limit of the anharmonic contribution, Eq. (7).

References

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