THE CONFIGURATIONAL HEAT CAPACITY OF FULLERITE OVER THE REGION OF SCL ↔ FCCL PHASE TRANSITION

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1. Introduction

Experimental investigation of temperature dependence of heat capacity of solid-phase fullerite shows the availability of abrupt change of capacity in the region of temperature T_o =249-260 K [1, 2]. Below temperature T_o fullerite has simple cubic lattice (*scl*), above this temperature it has face-centered cubic lattice (*fccl*) and in the area of temperature T_o the first-kind phase transition from *scl* phase to *fccl* phase occurs. The orientation ordering takes place in fullerite at ~ 260 K that was experimentally studied in papers [3, 4].

Below the statistical-thermodynamical calculation of configurational heat capacity of ordering twocomponent fullerite from fullerenes C_{60}, C_{70} has been performed within the approximation of pair interaction of fullerenes by the method of average energies in the model of spherically symmetric rigid balls [5] and the capacity evaluation has been made over the region of *scl* ↔ *fccl* phase transition.

2. Theory

For solving the problem the free energies f_1, f_2 of *scl* and *fccl* phases for one site (fullerene) of crystal lattice and the internal configurational energies ε_1, ε_2 of studied phases have been determined by which the capacities can be defined as

$$C = \frac{\partial \varepsilon_1}{\partial T} = -\frac{3}{2}\omega_1\eta_1\frac{d\eta_1}{dT} \qquad \text{for } scl \text{ phase,} \qquad (1)$$

$$C = \frac{\partial \varepsilon_2}{\partial T} = -\omega_2\eta_2\frac{d\eta_2}{dT} \qquad \text{for } fccl \text{ phase,} \qquad (2)$$

where ω_1, ω_2 are ordering energies of phases, η_1, η_2 are order parameters of these phases.

From the condition of equilibrium state of system the order parameters and their depen dences on temperature and fullerite composition: $\eta_1 = \eta_1 (T, c_1)$, $\eta_2 = \eta_2 (T, c_2)$ have been found. The ordering temperatures of *fcl* and *fcc*l phases are functions of ordering energies and concentrations c_1, c_2 of fullerenes C_{60}, C_{70}

$$kT_1 = 6\omega_1 c_1 c_2, \qquad (3)$$

$$kT_2 = 4\omega_2 c_1 c_2. \qquad (4)$$

In view of derived equations (3), (4) the equation for configurational heat capacity C_i (C_1 or C_2) has been written as

$$\frac{C_i}{k} = \frac{1}{4}\eta_i \ln\frac{(c_1+\frac{1}{2}\eta_i)(c_2+\frac{1}{2}\eta_i)}{(c_1-\frac{1}{2}\eta_i)(c_2-\frac{1}{2}\eta_i)} \Bigg/ \left[\frac{T}{T_i}c_1c_2\frac{c_1c_2-\frac{1}{4}\eta_i^2}{(c_1^2-\frac{1}{4}\eta_i^2)(c_2^2-\frac{1}{4}\eta_i^2)}-1\right],$$

$$i = 1;\ 2\ . \qquad (5)$$

Formula (5) determines the dependence of configurational heat capacity correspondingly of *scl* phase at *i* =1 and *fccl* phase at *i* =2 on temperature and concentrations c_1, c_2 of fullerite.

For fullerite of stoichiometric composition (c_1, c_2 =0,5) the formula (5) is simplified and assumes the form

$$\frac{C_i}{k} = \frac{1}{2}\eta_i \ln\frac{1+\eta_i}{1-\eta_i} \Bigg/ \left(\frac{T}{T_i}\frac{1}{1-\eta_i^2}-1\right), \qquad i = 1; 2\ . \quad (6)$$

As this takes place, we find the ordering temperatures as follows:

$$kT_1 = \frac{3}{2}\omega_1, \qquad kT_2 = \omega_2, \qquad (7)$$

and the equations of equilibrium states of phases in term of the result (7) transform to the relation

$$\frac{T}{T_i}\ln\frac{1+\eta_i}{1-\eta_i} = 4\eta_i\,. \qquad (8)$$

The derived formulae (6), (8) allow us to elucidate the character of temperature dependence of configurational heat capacity of *scl* and *fccl* phases of fullerite of stoichiometric composition over the region of temperatures of phase transition from one phase to another.

3. Result and discussion

For elucidation of temperature dependence of configurational heat capacity of fullerite of stoichiometric composition the theory proposes that phase transition occurs in ordered phases, when $\eta_1 \neq 0$ and $\eta_2 \neq 0$. So, it is believed that temperature T_o (kT_o=0,022 eV) of *scl* ↔ *fccl* phase transition is below the ordering temperatures T_1, T_2 of these phases. In this case it is possible that the ordering temperature of one phase can be both above and below the ordering temperature of another phase, i.e.

$$T_o < T_1, T_2, \quad 1)\ T_1 > T_2, \quad 2)\ T_1 < T_2\ . \qquad (9)$$

We consider the both cases.

The temperature T_o of studied phase transition can be defined from equality of free energies f_1, f_2:

$$kT_o = [2(e_2 - e_1) + \frac{1}{2}(3\omega_1\eta_1^2 - 2\omega_2\eta_2^2)]/(\Delta_1 - \Delta_2), \quad (10)$$

where values $\Delta_i = \Delta_1$, Δ_2 for fullerite of stoichiometric composition are determined by formula

$$\Delta_i(\eta_i) = (1+\eta_i)\ln\frac{1+\eta_i}{2} + (1-\eta_i)\ln\frac{1-\eta_i}{2}. \quad (11)$$

The experimental values of temperature T_o of phase transition (T_o=249-260 K, kT_o=0,022 eV) allow us to evaluate the ordering tempera tures T_1, T_2 according to (9), the ordering ener gies ω_1, ω_2 according to (7), the energetic parameters e_2-e_1 according to (10) and the order parameters η_1, η_2, as η_1=0,73; 0,4; η_2=0,6.

According to the chosen values of ordering temperatures T_i=T_1, T_2 and numerical values of order parameters for all temperatures, the character of temperature dependence of configurational heat capacity has been elucidated and the peculiarities of this dependence has been established over the region of *scl* ↔ *fccl* phase transition.

The plots C(T) (Fig.1) have been constructed in the neighbourhood of *scl* ↔ *fccl* phase transition for cases *a*) $kT_1>kT_2$, when $\eta_1>\eta_2$ and b) $kT_1<kT_2$, when $\eta_1<\eta_2$.

As Fig.1 shows, the heat capacity increases with rise in temperature and undergoes the discontinuous change at the temperature T_o of *scl* ↔ *fccl* phase transition and at the temperature T_2 of phase transition of order-disorder type in *fccl* phase.

The obtained results of the theory are in gratifying agreement with experimental data.

4. Conclusions

The elaborated theoretical calculation makes it possible to elucidate the character of temperature dependence of configurational heat capacity of *sc*l and *fccl* phases of fullerite and to reveal the possible peculiarities of this dependence over the temperature T_o area of phase transition of fullerite from *scl* to *fccl* phase. The consideration of fullerenes C_{60}, C_{70} ordering determines the possibility of manifestation of two steps on the plots of temperature dependence of heat capacity. As this takes place, the abrupt change of capacity in the point $T=T_o$ can both increase and decrease the capacity value in dependence on the relationship between ordering temperatures in *scl* and *fccl* phases, at the disordering of fullerite the configurational heat capacity goes to zero. The obtained results of theory are in satisfactory agreement with experimental data.

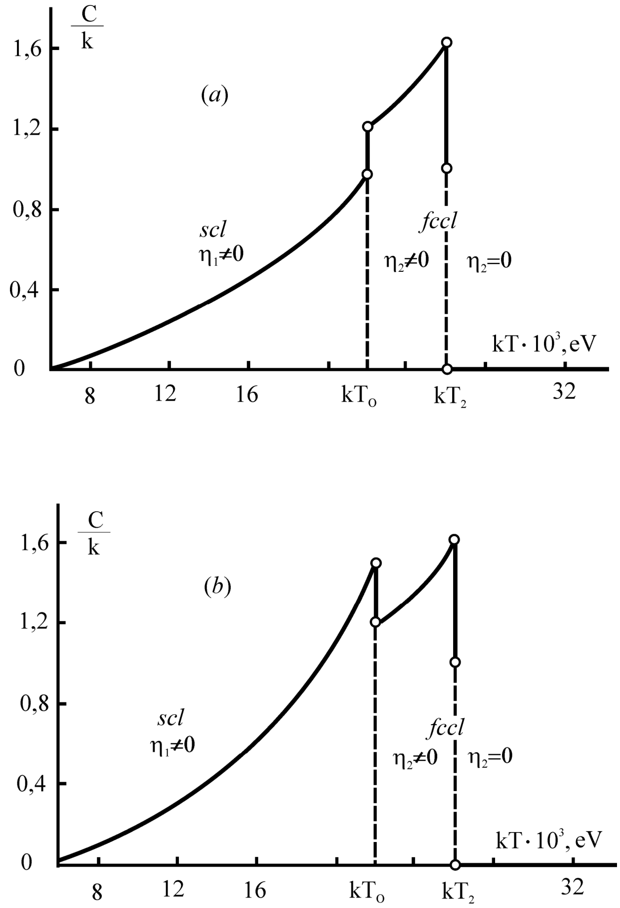

Fig. 1. The configurational heat capacity of fullerite of stoichiometric composition as a function of temperature in the neighbourhood of scl ↔ fccl phase transition.
a) $kT_1 > kT_2$, when $\eta_1 > \eta_2$,
b) $kT_1 < kT_2$, when $\eta_1 < \eta_2$.
The steps of heat capacity of *scl* ↔ *fccl* phase transition at the temperature kT_o and order-disorder phase transition at the temperature kT_2 in *fccl* phase are marked off by circles.

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