THE HEAT CAPACITY AND PHASE TRANSITION IN $CoFe_2Se_4$ CRYSTALS

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The heat capacity of $CoFe_2Se_4$ crystals in interval 55-300K is investigated. The $C_p(T)$ dependence reveals the anomaly showing on the presence of ferromagnetic phase transition in interval 108-135K. The anomaly maximum value is at $T_c \approx 128$K temperature. The values of ΔQ energy and ΔS entropy of phase transition, the coefficients of thermodynamic potential are obtained. The small value $\frac{\Delta S}{R} = 0{,}22$ testifies to the effect that this transition is to transitions of displacement type. The behavior of anomalous heat capacity near T_c is satisfactory described by Landau's theory of phase transitions.

The neutron diffraction studies [1] show that $CoFe_2Se_4$ is ferromagnetic compound with Curie temperature T_c = 125K which has the monoclinic structure (space group $C_{2/m} = C_{2h}^3$) with $M_3\square X_4$-type of ordered vacancy (□ is vacancy). The superstructure vacancy in $CoFe_2Se_4$ corresponds to NiAs lattice type.

The heat capacity of $CoFe_2Se_4$ in interval 55-300K is investigated in the present paper. The semi-crystal samples of $CoFe_2Se_4$ are synthesized by melting of corresponding components in evacuated quartz ampoules. The X-ray structure analysis allows us to define the nature of homogeneous phase and lattice parameters of $CoFe_2Se_4$ samples at investigation a=0,615 nm, b=0,355nm, c=1,095 nm and β=91°55' which coincide with data [1].

The heat capacity of $CoFe_2Se_4$ crystals is measured on adiabatic calorimeter installation used earlier in [2]. The absolute error in temperature definition is ±0,01 K. The relative error in heat capacity definition at T>50K doesn't exceed 0,3%.

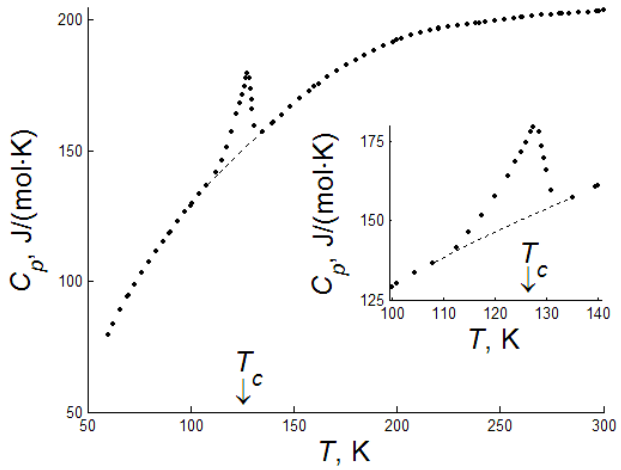

Fig. 1. $C_p(T)$ dependence for $CoFe_2Se_4$.

The investigation results of heat capacity of $CoFe_2Se_4$ crystals are presented on fig.1. As it is seen from fig.1, $C_p(T)$ dependence reveals the anomaly showing on the presence of ferromagnetic phase transition in 108-135K interval [1]. The anomaly maximum value is at temperature $T_c \approx 128$K.

The excess heat capacity exists higher than T_c in interval 128-135K in symmetric phase. The extrapolation $C_p(T)$ (the dotted line on fig.1) in 108-135K is carried out with the help of approximation by cubic splines and the regular (ΔC_{p0}) and anomalous (ΔC_p) deposits of heat capacity (fig.1) are divided where $\Delta C_p = C_p - C_{p0}$ that allows us to define and analyze the phase transition characteristics of $CoFe_2Se_4$ crystal. The anomaly value in T_c region is 19% of its regular part.

The changes of (ΔQ) energy and (ΔS) entropy connected with phase transition are defined by the integration of cubic interpolated $\Delta C_p(T)$ and $\frac{\Delta C_p(T)}{T}$ splines and correspondingly in 108-135K interval. The ΔQ and ΔS values are presented in the table. The small value $\frac{\Delta S}{R} = 0{,}22$ testifies to the effect that this transition is to transitions of displacement type.

The series of character peculiarities: the small jump at T_c and anomaly which is asymmetric one relatively to transition temperature, is revealed on temperature dependence of heat capacity of $CoFe_2Se_4$ near T_c is revealed. The phase transition at T_c can be considered as the transition of II type.

These peculiarities are probably connected with the fact that $CoFe_2Se_4$ has the defect structure and vacancies can appear in both metal sublattices (Co or Fe). In [1] it is established that the one half of Fe atoms are in free planes (001) whereas the other Fe atoms and Co atoms are statistically distributed in filled planes. Using this fact as foundation, the cation distribution in $CoFe_2Se_4$ can be presented as $Fe^{3+}[Co^{2+}Fe^{3+}]Se_4^{2-}$. However, the opportunity of this fact, that bivalent iron ions (Fe^{2+}) are also presented in $CoFe_2Se_4$ towards Fe^{3+}, can't be excluded.

The simultaneous presence of three different ions (Fe^{2+}, Fe^{3+} and Co^{2+}) in $CoFe_2Se_4$ makes difficult the nature of magnetic exchange, in sublattices and between them and probably causes the appearance of magnetocrystalline anisotropy. Thus the fuzzy character of magnetic phase transition in $CoFe_2Se_4$ is connected with spontaneous magnetostrictive strain caused by defects and Co^{2+}, Fe^{2+} Fe^{3+} ions also [1].

In transition point region at T_c close to critical one the thermodynamic potential can be expanded into power series over order parameter by the following formula [3]:

$$\Phi = \Phi_0 + A\eta^2 + B\eta^4 + D\eta^6, \qquad (1)$$

where $A = a(T - T_k)$. Here for phase transition of II type. The transition temperature T_c and stability threshold T_k in this case are identical ones, i.e. $T_c = T_k$ [3].

The minimization of thermodynamic potential for excess heat capacity in low-symmetric phase is:

$$\Delta C_p = \frac{a^2 T}{2\sqrt{B^2 - 3AD}}.$$

Transforming this formula one can show [4] that $\left(\frac{\Delta C_p}{T}\right)^{-2}$ value at temperature lower than T_c is temperature function of the following type:

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \frac{4B^2}{a^4} + \frac{12D}{a^3}(T_c - T). \qquad (2)$$

The $\left(\frac{\Delta C_p}{T}\right)^{-2}$ dependence on T for $CoFe_2Se_4$ is presented on fig.2, it is linear in 122-127,5K interval, i.e. up to T_c that shows on absence of significant contribution of correlative effects to heat capacity. From equation (2) we obtain the two relations between coefficients of equation (1) which are presented in table.

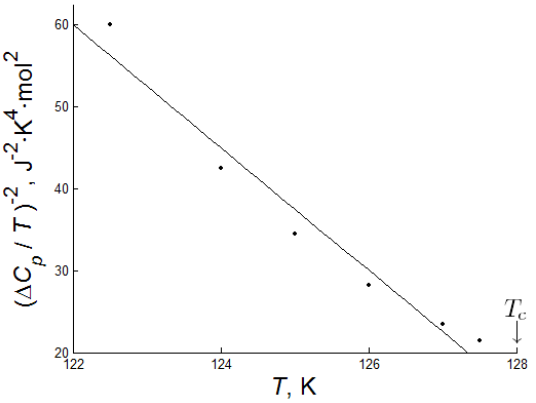

Fig. 2. Temperature dependence $\left(\frac{\Delta C_p}{T}\right)^{-2}$ for $CoFe_2Se_4$.

Thus we can make the following conclusions on the base of experimental data analysis on heat capacity of $CoFe_2Se_4$:

1) The phase transition at $T_c \approx 128$K is revealed;

2) Small entropy change characterizes it as the transition of displacement type;

3) The behavior of anomalous heat capacity near T_c is satisfactory described by Landau theory of phase transitions.

$\Delta Q, \frac{\text{J}}{\text{mol}}$	$\Delta S, \frac{\text{J}}{\text{mol}\cdot\text{K}}$	$\frac{\Delta S}{R}$	$\frac{a^2}{B}, \frac{\text{J}}{\text{mol}\cdot\text{K}^2}$	$\frac{a^3}{D}, \frac{\text{J}^2}{\text{mol}^3\cdot\text{K}^3}$
227	1,84	0,22	0,516	1,6

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$CoFe_2Se_4$ KRİSTALINDA İSTİLİK TUTUMU VƏ FAZA KEÇİDİ

İndiki işdə $CoFe_2Se_4$ kristalının istilik tutumu 55–300K intervalında tədqiq edilmişdir. $C_p(T)$ asılılığının 108–135K intervalında ferromaqnit faza keçidinin mövcud olmasını göstərən anomaliya aşkar olunur. Anomaliyanın maksimal qiyməti $T_c \approx 128$K temperaturunda yerləşir. Enerjinin ΔQ və entropiyanın ΔS dəyişmələri, termodinamik potensialın əmsalları təyin olunmuşdur. $\frac{\Delta S}{R} = 0{,}22$ kiçik qiyməti bu keçidin yerini dəyişmə tipinə aid olduğunu göstərir. T_c yaxınlığında istilik tutumunun anomaliyasının özünü aparması Landaunun faza keçidlər nəzəriyyəsi ilə qənaətbəxş təsvir edilir.

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ТЕПЛОЕМКОСТЬ И ФАЗОВЫЙ ПЕРЕХОД В КРИСТАЛЛАХ $CoFe_2Se_4$

В настоящей работе исследована теплоемкость кристаллов $CoFe_2Se_4$ в интервале 55–300K. Зависимость $C_p(T)$ обнаруживает в интервале 108–135K аномалию, указывающую на наличие ферромагнитного фазового перехода. Максимальное значение аномалии находится при температуре $T_c \approx 128$K. Определены изменения ΔQ энергии и ΔS энтропии фазового перехода, коэффициенты термодинамического потенциала. Малая величина $\frac{\Delta S}{R} = 0{,}22$ указывает на то, что этот переход относится к переходам типа смещения. Поведение аномальной теплоемкости вблизи T_c удовлетворительно описывается теорией фазовых переходов Ландау.

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