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Self-consistent modeling of thermal and elastic properties of unconventional superconductor $PuCoGa_5$

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ABSTRACT

A self-consistent thermodynamic model of $PuCoGa_5$ is developed, which for the first time takes into account the anharmonicity of both acoustic phonons, described within a Debye model, and optical phonons, considered in an Einstein approximation. Within the framework of this model, we have calculated the temperature dependencies of lattice contributions to heat capacity, bulk modulus, volumetric coefficient of thermal expansion, Debye and Einstein temperatures and their Grüneisen parameters. The electronic heat capacity of $PuCoGa_5$ is obtained, which demonstrates an unusual temperature dependence with two maxima. In addition, it is shown that an abnormal low temperature behavior of the bulk modulus of $PuCoGa_5$ is not caused by the effects of lattice anharmonicity and is most likely due to the valence fluctuations, which is in agreement with previous studies.

1. Introduction

The strongly correlated compound $PuCoGa_5$ undergoes a transition to the superconducting state, which is followed by the appearance of diamagnetism, the disappearance of electrical resistance and the formation of an anomalous maximum heat capacity (the C/T relation)—all near the same temperature, $T_c \approx 18.5$ K [1,2]. In [3] from point-contact spectroscopy measurements it was shown that the order parameter, appearing in the system of strongly correlated f-electrons in the superconducting state, is characterized by d-wave symmetry, which points to the spin-fluctuation mechanism of superconductivity. On the other hand, anomalous extreme near the transition temperature recently have been revealed in the temperature dependencies of elastic constants and bulk modulus of $PuCoGa_5$ [4]. It is shown in [4] that the observed behavior of elastic constants of $PuCoGa_5$ (as well as some compounds of 4f-metals) is most likely caused by the valence fluctuations of plutonium atoms, which in the absence of instability to superconductivity, could lead to the phase transition with the change of valence at temperatures near 8 K. It is also noted that the temperature dependencies of elastic constants of $PuCoGa_5$ are affected by the significant anharmonicity of its complicated crystal lattice, the nature of which (in particular, its connection with valence fluctuations) is not yet established. Phonon dispersion curves of $PuCoGa_5$ have been calculated in [5] using *ab initio* methods and overall are in good agreement with the experimental data obtained by inelastic x-ray scattering [6, 7], although experimental data on the optical branches are somewhat limited. However, these studies did not consider the anharmonicity of acoustic and optical phonons and their effect on thermal and elastic properties of $PuCoGa_5$. Moreover, the lattice heat capacity at constant volume obtained in [5] at some temperatures exceeds the experimental data at constant pressure, which does not allow a correct estimation of the electronic heat capacity of $PuCoGa_5$ to be made.

Recently published experimental data on the temperature dependencies of elastic constants of $PuCoGa_5$ in a wide temperature range [4] alongside the available experimental data on the heat capacity and information from *ab initio* calculations [5] enabled us to construct a self-consistent thermodynamic model of the thermal and elastic properties of $PuCoGa_5$. Within the framework of this model, we account for the anharmonicity of both acoustic and optical phonons, which is necessary in order to calculate the temperature dependencies of bulk modulus, lattice heat capacity at constant pressure and coefficient of thermal expansion of $PuCoGa_5$. It is also crucial for the correct estimations of the electronic heat capacity, which is important for analysis of the fluctuation effects appearing in the vicinity of the superconducting temperature.

2. Model description

In order to build a self-consistent model of the crystal lattice of $PuCoGa_5$, the extended Debye model [8] is clearly insufficient,

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since it is necessary to account for possible anharmonicity of both acoustic and optical phonons. Therefore, let us write down the thermodynamic potential (TDP) of the crystal lattice in the additive form

$$\Phi = \Phi_0 + \Phi_{ac} + \Phi_{opt}, \tag{1}$$

where $\Phi_0=\Phi_0(P)$ is the 'constant' part of TDP, which does not depend on temperature but is a function of pressure, and Φ_{ac} and Φ_{opt} are terms reflecting the contributions of acoustic and optical vibrations of the crystal lattice, respectively. The portion of the TDP contributed by the acoustic phonons is defined in terms of the extended Debye model [8]

$$\Phi_{ac}(\theta_D, T) = 3R\left(\frac{3}{8}\theta_D + T\phi(z)\right). \tag{2}$$

Here $z=\theta_D/T$, $R=8.31441$ J/(K mol) is the universal gas constant, $\phi(z) = \ln(1 - e^{-z}) - D(z)/3$ (where $D(z)$ is the Debye integral) and θ_D is the Debye temperature, which is expressed via molar volume V and bulk modulus B

$$\theta_D = \frac{\hbar}{k_B}\left(6\pi^2 N_A\right)^{1/3}\sqrt{\frac{3}{\mu}}\,\Xi^{1/2}B^{1/2}V^{1/6}, \tag{3}$$

where $\hbar$, N_A and k_B are the Planck, Avogadro and Boltzmann constants, respectively; $\Xi(\sigma)$ is a function of the Poisson coefficient σ; and μ is the molar mass of the compound.

The optical modes are described with the Einstein approximation:

$$\Phi_{opt}(\theta_E, T) = \frac{(3n-3)R\theta_E}{2} + (3n-3)RT\ln\left(1 - e^{-\theta_E/T}\right), \tag{4}$$

where n is the number of atoms in the unit cell (in the case of $PuCoGa_5$, $n=7$) and θ_E is the Einstein temperature, which depends on the molar volume V in accordance with the expression

$$\theta_E = \theta_{E0}\left(\frac{V}{V_0}\right)^{-\gamma_{\theta E0}}\exp\left[\frac{\gamma_{\theta E1}}{q'}\left(1 - \left(\frac{V}{V_0}\right)^{q'}\right)\right], \tag{5}$$

wherein θ_{E0} and V_0 are the "starting" (extrapolated to $T=0$K) values of the Einstein temperature and molar volume, $\gamma_{\theta E0}$, $\gamma_{\theta E1}$ and q' are the input parameters of the model. The expression (5) can be obtained directly by integration over the volume of the Grüneisen parameter $\gamma_{\theta E} = -\frac{V}{\theta_E}\left(\frac{d\theta_E}{dV}\right)_T$ for the Einstein temperature, which according to [9,10] can be defined as

$$\gamma_{\theta E} = \gamma_{\theta E0} + \gamma_{\theta E1}\left(\frac{V}{V_0}\right)^{q'}. \tag{6}$$

As can be seen from (6), unlike the classical Grüneisen theory, $\gamma_{\theta E}$ depends on volume and, as a consequence, on temperature, which is essential for the correct description of the temperature dependence of the bulk modulus.

According to eqs. (1–5) the characteristic Debye θ_D and Einstein θ_E temperatures, entering the definition of the phonon part of TDP, explicitly depend on volume (θ_D is also a function of the bulk modulus B), which, in turn, is calculated on the basis of TDP. This allows us to construct an iterative procedure for self-consistent calculations of $\theta_D(T)$ and $\theta_E(T)$ and also of temperature dependencies of thermal and elastic properties of a compound. This procedure simultaneously accounts for the effects of anharmonicity of acoustic and optical phonons.

The expressions for the molar volume and bulk modulus can be represented in the additive form

$$V = \left(\frac{\partial\Phi}{\partial P}\right)_T = V_0 + V_{ac} + V_{opt} \tag{7}$$

$$B = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T = B_0 + B_{ac} + B_{opt} \tag{8}$$

where B_0 and V_0 are the 'starting' values of the bulk modulus and molar volume, which correspond to the 'constant' part of TDP Φ_0 and of the Helmholtz free energy (FE) F_0 (the integral representation of which has the same form as the TDP and differs only in the set of variables). The expressions for the contributions of the acoustic and optical modes are obtained by differentiating the corresponding parts of TDP and FE.

Thus, for the contributions of acoustic modes to the molar volume and bulk modulus we obtain

$$V_{ac}(T) = \frac{3R\theta_D\gamma_{\theta D}}{B}\left(\frac{3}{8} + \frac{D(z)}{z}\right), \tag{9}$$

$$B_{ac}(T) = \frac{3R}{V}\left\{\frac{3}{8}\gamma^*_{\theta D}\ \theta D - T[\gamma^*_{\theta D}\ C_{VR}(\theta_D/T) - \gamma^*_{\theta D}\ D(\theta_D/T)]\right\}. \tag{10}$$

The formulas for the components of the molar volume and bulk modulus associated with the influence of the optical modes have the following form

$$V_{opt}(T) = \frac{(3n-3)R\theta_E\gamma_{\theta E}}{B}\left[\frac{1}{2} + \frac{1}{e^{\theta_E/T} - 1}\right], \tag{11}$$

$$B_{opt}(T) = \frac{(3n-3)R\theta_E}{2V}\gamma^*_{\theta E} + \frac{(3n-3)R\theta_E}{V}\left[\frac{\gamma^*_{\theta E}}{e^{\theta_E/T} - 1} - \gamma^2_{\theta E}\frac{\theta_E}{T}\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}\right]. \tag{12}$$

The expression for the molar lattice heat capacity at constant pressure (i.e., including the anharmonic effects)

$$C_{ph} = -T\frac{\partial^2\Phi}{\partial T^2}$$

also consists of two terms:

$$C_{ac}(T) = 3R\left\{C_{VR}(z)\left[1 - \frac{1}{z}\left(\frac{\partial\theta_D}{\partial T}\right)_P\right]^2 - T\left[\frac{3}{8} + \frac{D(z)}{z}\right]\left(\frac{\partial^2\theta_D}{\partial T^2}\right)_P\right\}, \tag{13}$$

where $C_{VR}(z)$ is the standard Debye heat capacity, normalized to $3R$, and

$$C_{opt}(T) = (3n-3)R\left\{T^2\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}\left(\frac{1}{T}\left(\frac{\partial\theta_E}{\partial T}\right)_P - \frac{\theta_E}{T^2}\right)^2 + T\left(\frac{1}{2} + \frac{1}{e^{\theta_E/T} - 1}\right)\left(\frac{\partial^2\theta_E}{\partial T^2}\right)_P\right\}. \tag{14}$$

The γ_f and γ^*_f parameters, appearing in Eqs. (8)–(13), are generalized Grüneisen parameters of the first and second order, which for a thermodynamic quantity $f=f(T,V)$ at constant temperature are defined as

$$\gamma_f = -\frac{V}{f}\left(\frac{\partial f}{\partial V}\right)_T,\quad \gamma^*_f = \frac{V^2}{f}\left(\frac{\partial^2 f}{\partial V^2}\right)_T. \tag{15}$$

In the case of the Debye temperature, $\gamma_{\theta D}$ and $\gamma^*_{\theta D}$ are expressed through the Grüneisen parameters for the bulk modulus, γ_B, γ^*_B, and for the function depending on the Poisson coefficient γ_Ξ, γ^*_Ξ (see Eq. (3)). The values of γ_B and γ^*_B are defined during the self-consistent cycle and change with temperature, however their starting values