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Fundamental characteristics of solids from low-temperature heat capacity

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ABSTRACT

A new approach to obtaining fundamental characteristics of solids is provided. The key element of this approach is related to solving the inverse problem of how to reconstruct phonon density of states $g(\omega)$ from low-temperature heat capacity. The original method for numerical solution of this problem allows to calculate the $g(\omega)$ dependence with correct description of its shape and correct proportion of the number of vibrational modes in different frequency intervals. This allows to accurately calculate the moments of the $g(\omega)$ and related characteristic temperatures which, being constants, unambiguously describe individual substance. Also this allows to calculate a zero-point energy of crystal with high accuracy. This, in turn, opens up the possibility for calculating the full internal energy of a solid. The knowledge of the $g(\omega)$ allows calculating the isochoric thermodynamic functions in the entire region of existence of solid phase. Special attention is paid to the estimation of the accuracy of the characteristics obtained. The capacities of the approach are demonstrated on a model object and a real-world object, the latter is represented by a single-crystal lithium molybdate. The described approach is universal and opens up new possibilities for studying solids. The proposed computer algorithm can be used to numerical solve other types of inverse problems that include the integrated form.

1. Introduction

Development of new methods for defining properties of substances based on their key characteristics has always been and remains an important element in the research methodology. Therewith, it is important to consider key characteristics that can be obtained experimentally with high accuracy. The low-temperature heat capacity of solid is among such characteristics. State-of-art setups allow measuring the heat capacity within the range of helium to room temperatures with the accuracy that can be at the level of 0.1% including both a systematic and an accidental error. It is known that it is adiabatic method [1] that allows such accuracy [2] of data received in wide range of low temperatures. Reference documents present a method [3,4] that may be applied to receive thermal properties of nanoparticles. Study of nanoscale and massive objects and comparison of their thermal and vibrational properties is of interest, since it may provide a more detailed understanding of the nature behind emergence of new properties in nanosystems [5].

The knowledge of the temperature dependence of heat capacity is the starting point in calculating energy, entropy, and other important characteristics of solids. In general, when considering the energy of solids, we deal with a system, which is composed of lattice, electronic, and magnetic subsystems. However, when considering a wide range of temperatures, the main and decisive contribution to the energy of solids is made by nuclear vibrations. These vibrations are described well within the phonon formalism taking into account their quantum-statistical distribution, which determines a decrease in the heat capacity to zero at low temperatures and is an inherent property of all solids.

The heat capacity is associated in a known manner with the phonon density of states, which, being a bridge between the microscopic and macroscopic properties of the substance, belongs to the fundamental characteristics of solids. The existing problem (that has not been fully solved so far) is related to the solution of the inverse problem of the Bose system spectrum reconstruction based on its heat capacity [6]. The urgency of solving this problem is quite obvious, since this will provide a new tool for obtaining information about the major characteristics of solids. Furthermore, its solution can be potentially used to solve other types of inverse problems that include the integrated form.

In this paper, we bridge the gap by providing a new and original method for numerical solution of the inverse problem concerning

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the reconstruction of the phonon density of states $g(\omega)$ based on the data on the low-temperature heat capacity. The possibility to obtain a number of fundamental characteristics of a solid (the density of states, moments of the $g(\omega)$ spectrum, zero-point energy, etc.) is demonstrated. The ability to obtain and the accuracy of these characteristics are demonstrated on a model object and a real-world object. For the real-world object a single-crystal lithium molybdate (Li_2MoO_4) is taken.

2. Heat capacity and phonon density of states

It is well known that the data on temperature dependence of heat capacity allows calculating a number of phonon spectrum characteristics. Thus, it is possible to obtain quantitative information about the acoustic branch of the crystal lattice vibrations from the lattice component of the heat capacity in the low-temperature region (see, e.g., [7,8]). In addition, the cut-off frequency of the crystal vibrational spectrum can be calculated or evaluated from the heat capacity. Such capacity is commonly associated with the description of the heat capacity within some model representations of $g(\omega)$ spectrum, among which the Einstein [9], Debye [10] and Tarasov [11] models, or their combinations (e.g., [12]), are often used. Even moments of the phonon density of states $g(\omega)$ and the effective cut-off frequency can also be calculated from the heat capacity by the method based on high-temperature expansion of the heat capacity [13].

The heat capacity $C_V(T)$ in the harmonic approximation is related to the phonon density of states $g(\omega)$ by the following expression:

$$C_V(T) = 3Nk_B \int_0^\infty g(\omega)\Psi(\omega, T)d\omega \quad (1)$$

where

$$\Psi(x) = \frac{x^2 e^{-x}}{(1-e^{-x})^2}; \quad x = \frac{\hbar\omega}{k_B T};$$

and where $\Psi(x)$ is the Einstein function, N – the number of atoms, k_B – Boltzmann constant, $\hbar$ – Planck's constant. Function $g(\omega)$ in expression (1) is normalized to unity:

$$\int_0^\infty g(\omega)d\omega = 1 \quad (2)$$

In paper [6], the existence of solution (but not the solution itself) of the inverse problem aimed at finding the unknown subintegral function $g(\omega)$ in Eq. (1), when the left-hand side of this equation is known, was shown for the first time. A number of attempts have been made to find a simple solution to this inverse problem [14–18]. However, no method that would allow practical implementation of solution to this problem for a wide range of objects has been provided in the literature so far. It appears that the method [19,20] proposed by us can be implemented in a fairly straightforward manner, has a number of undeniable advantages and is adapted for studying important characteristics of solids.

To solve the inverse problem, we rely upon the knowledge of the isochoric heat capacity in a wide range of low temperatures. It is apparent that, in this case, the reconstructed density of states $g(\omega)$ according to Eq. (1) will characterize the excitation spectrum of the ground state of crystal lattice, i.e. the excitation spectrum at zero temperature.

For all solids heat capacity at constant pressure $C_p(T)$ and at constant volume $C_V(T)$ below a certain temperature are characterized by a negligible value. The difference between $C_p(T)$ and $C_V(T)$ can be within the experimental uncertainty limits up to the temperatures at which the entropy of the solid has maximum gain. Therefore, to solve the problem can be used experimentally obtained data on the heat capacity $C_p(T)$. If electronic, magnetic, and other components are present in the experimental heat capacity, it is necessary to give correct consideration for these components in separating the phonon heat capacity.

3. Phonon density of states calculation

The phonon density of states calculation includes three steps. At the first step a zero approximation $g_0(\omega)$ is chosen that correctly describes the behavior of $g(\omega)$ at low and cut-off frequencies. The choice of $g_0(\omega)$ is made so that it describes well the asymptotic behavior of heat capacity (at $T \to 0$ and $T \to \infty$), but the description for medium temperatures is not satisfactory. Selection of the $g_0(\omega)$ can be implemented by different methods; however, as noted in paper [20], it is essential to take into account the behavior of $g(\omega)$ at the asymptotic upper bound, i.e. when the heat capacity is well described at high temperatures (above the point of inflection of the heat capacity curve) when selecting the cut-off frequency ω_c. Note that introducing the cut-off frequency is the most important element since it reduces the degree of incorrectness of the problem being solved and significantly reduces the solution uncertainty.

At the second step, the zero approximation is refined by an iterative process, where the number of vibration modes is redistributed over frequencies. By changing the shape of zero approximation of the density of states, such redistribution of vibration modes ultimately reduces the difference between the calculated and the experimental heat capacities in middle temperature region. The iterative process continues until the difference in heat capacities drops below the pre-specified value. In our case, this value is experimental uncertainty of measuring heat capacity.

At the third step, a number of calculations with different values of zero approximation parameters and/or iterative process parameters are averaged. The averaging procedure significantly reduces the random component, which is present in each individual solution. Firstly, this results in a more accurate description of the density of states $g(\omega)$, and, secondly, this allows us to observe and estimate the degree of uncertainty of the solution we obtain.

While various solutions were obtained with different frequency subintervals in paper [20], we obtain a series of solutions with equal subintervals through using different algorithms for iterative process implementation in the current paper. This allows obtaining a series of solutions that reproducibly describe the basic spectrum shape, being different in details only. Note that the use of the same frequency subintervals to obtain a series of solutions considerably simplifies the entire calculation procedure and allows determining the averaged values of the $g(\omega)$ spectrum and their uncertainties with higher accuracy.

3.1. Choosing zero approximation

We used zero approximation $g_0(\omega)$ which has a constant density of modes over the whole frequency range below the cut-off frequency to calculate the phonon density of states. This kind of spectrum was first considered in the paper published by Tarasov [11]. Note that we do not use the low-frequency asymptotic of the phonon density of states when selecting $g_0(\omega)$. The feasibility of this is related to the fact that we obtain the same computational procedure for $g(\omega)$ reconstruction in the entire frequency interval, from 0 to ω_c, which considerably simplifies the problem-solving algorithm. Moreover, the use of such zero approximation $g_0(\omega)$ can be justified by the asymptotically unambiguous determination of the density of states $g(\omega)$ within the range of low frequencies by the $C_V(T)$ dependence [21]. As follows from [21], at small values of $\hbar\omega/(k_B T)$, the phonon density of states is proportional to the deriva-