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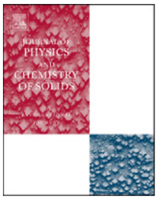

Non-Debye behaviours of heat capacities of cubic II–VI materials

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On the basis of an appropriate *four*-oscillator version of a representative dispersion-related hybrid model we perform detailed analyses of isobaric heat capacity data available for cubic ZnS, ZnSe, ZnTe, CdTe, HgSe, and HgTe. Characteristic non-Debye behaviours of the $C_p(T)$ data sets under study, which are manifested above all in form of non-monotonic dependences (maxima) of the respective $C_p(T)/T^3$ curves in the cryogenic region, are described in terms of two Einstein oscillators for short-wave transversal acoustic (TA) phonons in combination with relatively weak components of Debye and non-Debye type due to long-wave acoustic phonons. This prominent non-Debye feature is represented alternatively in the form of non-monotonic dependences (minima) of conventional Debye temperature curves, $\Theta_D(T)$. The close correlation between the low-temperature asymptotic (decreasing vs. increasing) sections of $\Theta_D(T)$ vs. $C_p(T)/T^3$ curves is described by simple algebraic formulae. The maxima positions of the latter are shown to be nearly proportional to the centre of gravity positions of the respective TA phonon spectra sections. The inherent non-Debye nature of the whole phonon density of states (PDOS) spectra is shown to find its global expression in characteristic snakelike shapes of the equivalent, moment-related phonon energy curves.

1. Introduction

For almost a whole century, the development of the theory and of experimental investigations of heat capacities of solids was largely dominated by an enormous number of papers referring primarily to the well-known Debye theory [1–7]. The main cause of the predominant consideration of this simple model may be ascribed to some remarkable initial successes consisting, above all, in a plausible explanation of the commonly expected cubic asymptotes, $C_p(T\to 0)\propto T^3$ [1–9], for limiting lattice heat capacities in solids. Moreover, this model was found to be capable of providing, especially for a variety of *cubic metals* [1–3], some satisfactory simulations of $C_p(T)$ dependences from cryogenic to room temperatures, by adopting even fixed values for material-specific Debye temperatures, Θ_D. On the other hand, in contrast to such initial successes, no satisfactory simulations of $C_p(T)$ dependences could be provided in analogous way (at fixed Θ_D) e.g. for Si and Ge [10–15] and large varieties of binary III–V [13,15,16–28] and II–VI [13,15,19,29–41] materials.

The inherent *non*-Debye nature of PDOS spectra of these materials is clearly revealed by the results of the conventional numerical assessment procedures consisting in point-by-point transformations of given $C_p(T)$ values into corresponding Debye temperature values (see e.g. [3–7,9,14,15,17]). Actually, these transformations are leading as a rule to respective sets of $\Theta_D(T)$ values that turned out to be *strongly* dependent on T, especially in the cryogenic region [10–41] (see also below). The wealth of corresponding $\Theta_D(T)$ estimations published during the past 50 years shows, among other things, that it is largely useless to cultivate nowadays the obviously illusionary idea [42–45] of fitting $C_p(T)$ data for various binary materials (like GaN [44] or MgO and ZnO [45]) strictly on the basis of the original Debye model [1], with a constant Θ_D (merely by increasing enormously the accuracy of numerical calculations [42–45] of the respective Debye function integrals).

Further indications for a global non-Debye nature can be readily found e.g. via partial analyses of given $C_p(T)$ data sets using the exponential series representation for heat capacities [46]. A significant advantage of this unconventional analysis scheme [46] (as briefly sketched in Section 2) is due to the fact that it enables good analytical and numerical simulations of large sections of given $C_p(T)$ curves *without* involving one or the other type of a hypothetical ansatz for the phonon density of states (PDOS) spectral function, $g_P(\varepsilon)$. We show in Section 2 that the actual shapes of $C_p(T)$ functions, for the materials under study, are qualitatively largely different from the conventional pattern implied by Debye's very special model, $g_D(\varepsilon)\propto\varepsilon^2$ [1,14]. This observation gives a clear evidence of an inherently *non*-Debye character of the heat capacity behaviours in consideration. Unfortunately, this elegant analysis procedure [46] is not applicable to very low temperatures (regions

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where the magnitudes of $C_p(T)$ are lower than about 20% of the classical Delong–Petit limiting value). More elaborate analytical models of non-Debye type are thus required for duly comprehensive descriptions of heat capacity behaviours, from $T=0$ to room temperature.

A principal alternative to Debye's fictitious PDOS model function [1] is well known to be given by Einstein's suggestion of a single discrete peak [47]. Generalizations of this obviously oversimplified model in the form of certain combinations of *several* discrete peaks, with properly adjusted weights, have been repeatedly found [39,48–50] to be capable of providing good simulations of given $C_p(T)$ data sets, from cryogenic to room temperatures. In particular, such multiple Einstein oscillator constellations are capable of simulating (at least roughly) the generally observed *non-monotonic* behaviours (occurrences of maxima [12,41,51–57]) of $C_p(T)/T^3$ curves somewhere in the cryogenic region, provided that the positions of the first Einstein peaks, ε_1, are chosen to be located close to the first special points of the respective material-specific PDOS spectra (e.g. $\varepsilon_1 \approx \hbar v_{TA}(L)$ or $\varepsilon_1 \approx E_2(low)$, for binary materials with zinc-blende or wurtzite structure [58], respectively). At the same time it is obvious that, in view of the known $T\to 0$ plateau behaviour of the Einstein functions (see below), such exclusively discrete $g_P(\varepsilon)$ model functions are a priori incapable of providing *finite* magnitudes of the respective $C_p(T)/T^3$ functions [12,41,51–57] in the $T\to 0$ limit.

It is thus a matter of principle that physically adequate descriptions of the whole $C_p(T)$ curves, including their well established $T\to 0$ limiting behaviour, $C(T\to 0)\propto T^3$ [1–9,15], can be given only on the basis of properly devised *hybrid* model expressions for PDOS functions [14,59], $g_P(\varepsilon)$. These are generally consisting of combinations of certain *continuous* components for low-energy tail regions [3,11,14,59] with conveniently chosen sequences of *discrete* (Einstein) oscillators. The corresponding analytical framework [59] is briefly sketched in Section 3. We display in Section 4 a specialized *four*-oscillator-based version of this hybrid model, which turns out to be appropriate for comprehensive numerical analyses of $C_p(T)$ data sets available for cubic II–VI materials (ZnS [57], ZnSe [33,60], ZnTe [40], CdTe [29,30,33], HgSe [56], and HgTe [56]). Various characteristic facets of non-Debye behaviour of the $C_p(T)$ data sets under study are discussed in Section 5.

2. Foundations of non-Debye vs. Debye model descriptions

Within the frame of the harmonic regime, the temperature dependence of the *isochoric* heat capacity per mol, $C_{Vh}(T)$, is generally given by [46,59]

$$C_{Vh}(T)=3n_A R\kappa_P(T) \tag{1}$$

where R is gas constant, n_A is the number of atoms per molecule of the material in question (i.e. $n_A=2$ for binary materials), and $\kappa_P(T)$ is a material-specific heat capacity shape function. The latter is generally given by an integral of the form [46,59]

$$\kappa_P(T)=\int d\varepsilon g_P(\varepsilon)\left(\frac{\varepsilon}{2k_BT}\Big/\sinh\left(\frac{\varepsilon}{2k_BT}\right)\right)^2\Big/\!\!\Big/\int d\varepsilon g_P(\varepsilon) \tag{2}$$

where $g_P(\varepsilon\equiv\hbar\omega)$ represents the PDOS spectral function [3,4,10,50,61]. (Note that the high temperature $T\to\infty$ limiting value of Eq. (2) is unity, $\kappa_P(T\to\infty)=1$, in accordance with the known Dulong–Petit limiting value of $C_{Vh}(T\to\infty)=3n_AR$ for the respective isochoric heat capacity (1).)

It had been shown in Refs. [14,46] that the experimentally measured, *isobaric* heat capacities can be represented in good approximation on the basis of the heat capacity shape function $\kappa_P(T)$ (2) in combination with a certain Taylor series expansion for the high temperature behaviour [46]

$$C_p(T)=3n_AR\kappa_P(T)[1+\kappa_P(T)(A_1T+A_2T^2+\ldots)]. \tag{3}$$

The latter involves a set of empirical expansion coefficients, $A_1,A_2,\ldots$, which are accounting for the material-specific deviations of $C_p(T)$ from $C_{Vh}(T)$. The respective differences, $C_p(T)-C_{Vh}(T)>0$, can generally be ascribed to combinations of lattice expansion and anharmonicity effects, and their magnitudes use to increase monotonically with temperature. Within the present study, however, we confine ourselves throughout to analyses of $C_p(T)$ data sets limited to temperatures below 400 K, where the corresponding

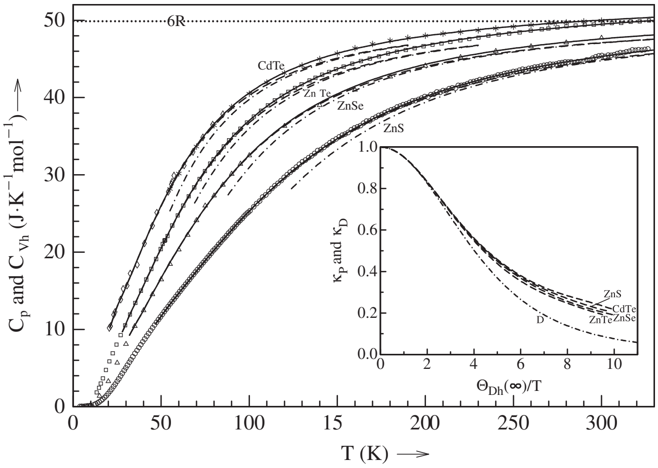

Fig. 1. Partial fittings of $C_p(T)$ data sets for ZnS (○ [57]), ZnSe (△ [60]), ZnTe (□ [40]), and CdTe (* [29], ◇ [30]) on the basis of the exponential series representation (5) for $\kappa_P(T)$ (———C_p Eq. (3); - - - - -C_{Vh} Eq. (1)). Shown are also limited sections of the fictitious temperature dependences, $C_D(T)$, as resulting from Debye's $\kappa_D(T)$ model function (4) with *fixed* (limiting) Debye temperatures, $\Theta_D\to\Theta_{Dh}(\infty)$ (see Table 1; – – – $C_{Vh}\to C_D$, due to Eqs. (1) and (4)). In the inset are visualized the qualitative differences between the actual material-specific dependences of non-Debye shape functions, κ_P (5), and the dependence of Debye's fictitious shape function, κ_D (4), on the ratio of limiting Debye vs. lattice temperatures, $\Theta_{Dh}(\infty)/T$.

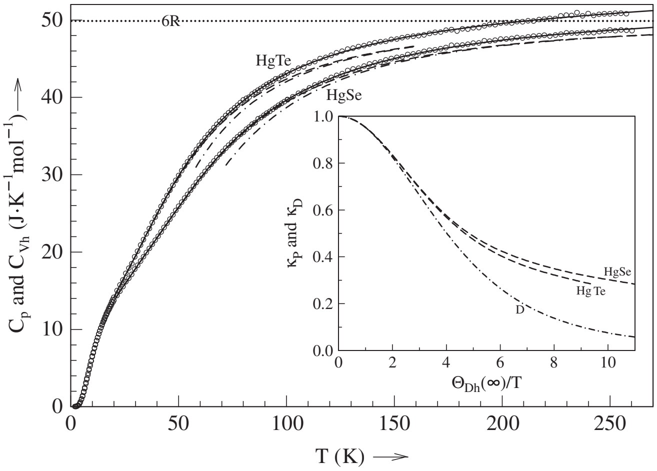

Fig. 2. Partial fittings of $C_p(T)$ data sets for HgSe (○ [56]) and HgTe (○ [56]) on the basis of the exponential series representation (5) for $\kappa_P(T)$. (———C_p Eq. (3); - - - - -C_{Vh} Eq. (1)). Shown are also the fictitious temperature dependences, $C_D(T)$, as resulting from Debye's $\kappa_D(T)$ model function (4) with *fixed* (limiting) Debye temperatures, $\Theta_D\to\Theta_{Dh}(\infty)$ (see Table 1; – – – $C_{Vh}\to C_D$, due to Eqs. (1) and (4)). In the inset are visualized the qualitative differences between the actual material-specific dependences of non-Debye shape functions, κ_P (5), and the dependence of Debye's fictitious shape function, κ_D (4), on the ratio of limiting Debye vs. lattice temperatures, $\Theta_{Dh}(\infty)/T$.