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HIGH - TEMPERATURE SPECIFIC HEATS OF CHALCOPYRITE - TYPE SEMICONDUCTORS

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ABSTRACT

The molar specific heat was measured for any chalcopyrite - type compounds in the temperature range from 300 to 500 K. An analysis of the experimental data for $AgInS_2$ and $AgGaSe_2$ for example showed that the contribution to the specific heat due to lattice anharmonicity can be described by a polynomial of third order in the temperature.

INTRODUCTION

Recently, detailed studies of the high temperature thermal expansion of any chalcopyrite - type compounds have been reported (1, 2). In these investigations it has been established that the thermal expansion coefficients remain temperature dependent up to $T > 750$ K. This means that higher - order anharmonic contributions to the potential energy of the lattice play an important role. If the same model applied to explain the thermal expansion coefficients (3, 4) is used to derive the specific heat one finds that the contribution to the C_p due to anharmonic forces is, in general, given by a polynomial which contains terms up to the third - order in the temperature (3). To confirm this supposition is the aim of this paper.

MEASURING METHOD

The samples used in the experiments were prepared by fusion of stoichiometric mixtures of the elements.

Specific heats C_p were measured in the temperature range from 300 to 500 K using a SETARAM DSC 111. The caloric sensitivity of the system was determined by three independent methods : (i) by

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using a Joule calibration cell, (ii) from the melting points of high pure metals, and (iii) by measuring $C_p(T)$ of a cylindrical sapphire single crystal and using the data of Ginnings, and Furukawa (5). The resulting accuracy is about 1 to 2 % in this temperature range. The measurements were made using closed aluminium containers charged with about 1 g of powdered material. The best results were obtained using a stepwise temperature program with heating times of 200 s at a heating rate varying between 36 and 90 K/h followed by 400 s at isothermal conditions.

RESULTS AND DISCUSSION

The measured temperature dependence of C_p in $AgInS_2$ and $AgGaSe_2$ is shown in Fig. 1. We see that in both compounds C_p remains temperature dependent. Furthermore, it follows from our measurements that in $AgInS_2$ at $T > 360$ K and in $AgGaSe_2$ at $T > 300$ K the specific heats is larger than $C_p = 12\ R = 99.77$ J/mol•K, the upper bound of C_p in the harmonic approximation for $T \rightarrow \infty$. For other compounds one finds: $CuInTe_2\,T < 300$ K, $CuInSe_2\,T > 300$ K, $CuGaTe_2\,T \approx 350$ K, $CuGaSe_2\,T > 450$ K, and $CuGaS_2\,T > 550$ K. To analyse the temperature dependence of C_p we use the relation

$$C_p(T) = 12\ R \left\{ F(\Theta_D/T) + c_1 T + c_2 T^2 + c_3 T^3 \right\} \tag{1}$$

expected to be valid accounting for thermal expansion behavior. Here R is the molar gas constant and $F\ (\Theta_D/T)$ the Debye function describing the temperature dependence in the harmonic approximation (6). To determine the coefficients c_i in equation 1 from the experimental $C_p(T)$ curves and, thus, to derive the temperature dependence of the anharmonic contribution to the specific heat the Debye temperature Θ_D must be known from independent measurements or estimations. The rsults of the analysis are given here only for $AgInS_2$ and $AgInSe_2$. The dashed curves in Fig. 1 represent the resulting harmonic contribution $C_{ph} = 12\ RF\ (\Theta_D/T)$ for $\Theta_D\ (AgInS_2) = 239$ K and $\Theta_D\ (AgGaSe_2) = 220$ K (7). Then, analysing the anharmonic part $\Delta C_p = C_p - C_{ph}$ we found that, indeed, the temperature dependence of ΔC_p can be only described by polynomial containing terms up to at least the third order in T in analogy to the thermal expansion coefficients. The values of the coefficients c_i resulting from the least - square fit of relation 1 to the experimental $C_p(T)$ data are for $AgInS_2$ $c_1 = -9.708\ (10^{-4}K^{-1})$, $c_2 = 4.179\ (10^{-6}K^{-2})$, and $c_3 = -3.561\ (10^{-9}K^{-3})$, and for $AgGaSe_2$ $c_1 = -3.995\ (10^{-4}K^{-1})$, $c_2 = 2.391\ (10^{-6}K^{-2})$ and $c_3 = -2.571$ $(10^{-9}K^{-3})$.

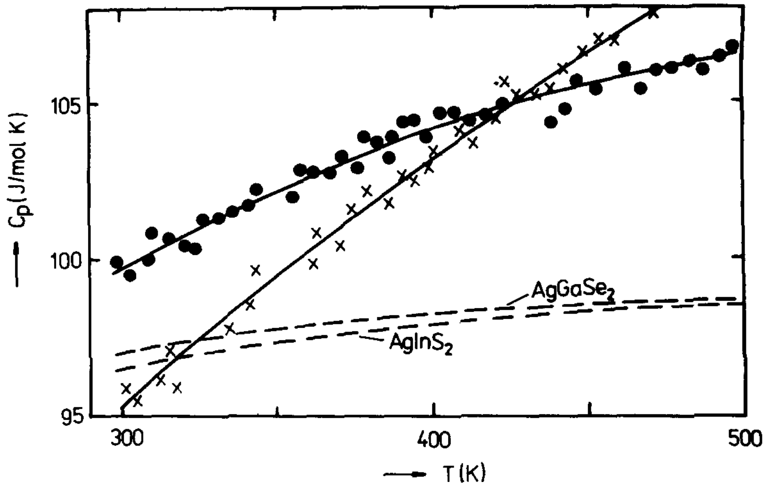

Fig. 1 Measured (o $AgInS_2$, x $AgGaSe_2$) and calculated with eq. 1 (full curves) specific heats. The dashed curves represent C_p in the harmonic approximation

Thus, we arrive at the interesting and important result that the temperature dependences of both the thermal expansion coefficients and the specific heats in $AgInS_2$ and $AgGaSe_2$ are consistent with each other regarding the expected influence of the anharmonic contributions to the potential energy of the lattice (3, 4).

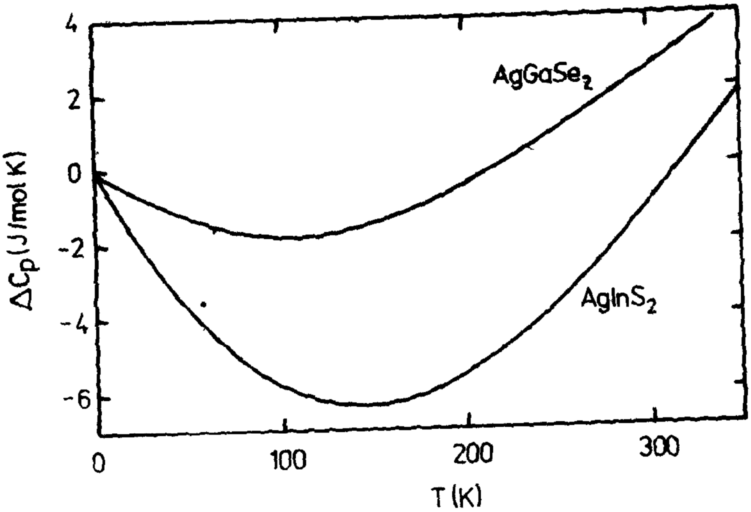

Fig. 2 Extrapolation of ΔC_p to temperatures below 300 K

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