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# TRENDS IN THE HIGH-TEMPERATURE HEAT CAPACITIES OF TERNARY CHALCOPYRITE SEMICONDUCTORS

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The anharmonic contribution to the heat capacity of any chalcopyrite semiconductor $A^IB^{III}C_2^{VI}$ or $A^{II}B^{IV}C_2^V$ is evaluated. It is shown that the degree of lattice anharmonicity decreases with increasing atomic weight of the constituent atoms of the compounds, and there is no essential difference in the degree of lattice anharmonicity of the two groups of compounds. Except for $CdGeAs_2$, the trend in the Grüneisen constants is the same.

In studies of the thermal expansion behaviour of the ternary compounds $A^IB^{III}C_2^{VI}$ ($A^I$ = Cu, Ag; $B^{III}$ = Al, Ga, In; $C^{VI}$ = S, Se, Te), it has been established that the thermal expansion coefficients remain temperature-dependent up to the highest temperatures investigated ([1–3] and references cited therein). In terms of the perturbation theory, this means that higher-order anharmonic contributions to the interatomic forces play an important role in establishing the thermal properties of these compounds. In the $A^{II}B^{IV}C_2^V$ compounds ($A^{II}$ = Zn, Cd; $B^{IV}$ = Si, Ge, Sn; $C^V$ = P, As), which also crystallize in the chalcopyrite structure, the situation seems to be different from that in the semiconductors $A^IB^{III}C_2^{VI}$. In most cases, temperature-independent thermal expansion coefficients have been found at elevated temperatures ([4] and references cited therein), the only exception being $CdGeP_2$, which exhibits a thermal expansion behaviour like that in the compounds $A^IB^{III}C_2^{VI}$ [5]. These results suggest the conclusion that lattice anharmonicity effects are generally less pronounced in the compounds $A^{II}B^{IV}C_2^V$ than in the semiconductors $A^IB^{III}C_2^{VI}$. It was the aim of the present work to acquire further insight into the lattice anharmonicity effects of these ternary compounds by measuring and analysing their heat capacities at elevated temperatures.

## Experimental

The compounds $A^IB^{III}C_2^{VI}$ used in the experiments were prepared by fusion of stoichiometric mixtures of the elements, while the semiconductors $A^{II}B^{IV}C_2^V$ were grown from the vapour phase. X-ray analysis was used to confirm the structures and the lattice parameters of the compounds and to

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ensure that the materials were single phases. The molar heat capacities at constant pressure $C_p$ were measured in the temperature range $T = 300$–500 K by using a SETARAM DSC 111 heat flow calorimeter. After careful calibration of the calorimeter using a sapphire single-crystal, the absolute values of $C_p$ could be determined with an accuracy of about ± 1 J/mol·deg [6].

## Results and discussions

The measured $C_p$ of the $A^IB^{III}C_2^{VI}$ compounds $CuInS_2$, $CuInSe_2$ and $CuInTe_2$ are shown in Fig. 1. We see that the $C_p$ of all these compounds

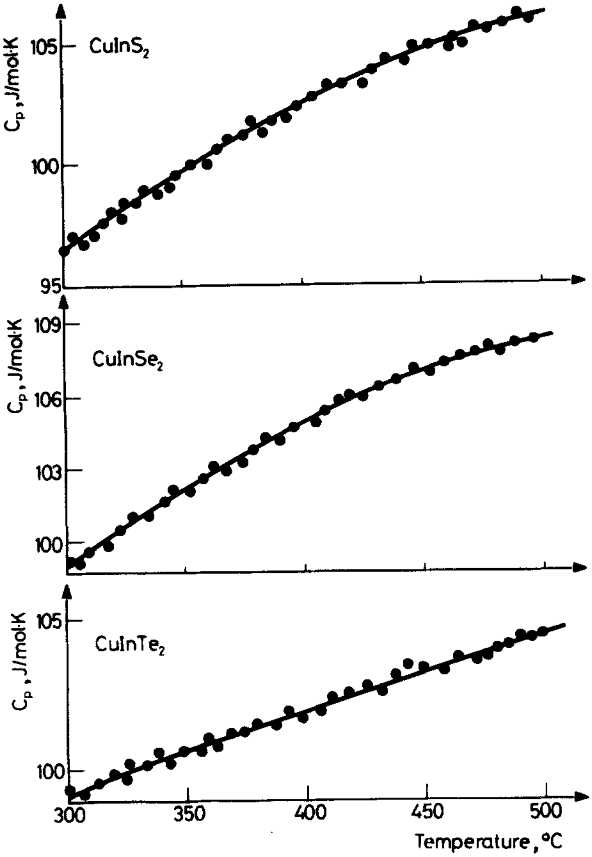

Fig. 1 Temperature dependence of the heat capacity in $CuInS_2$, $CuInSe_2$ and $CuInTe_2$

becomes distinctly larger than the upper bound of $C_p$ in the harmonic approximation of $C_{ph}$ $(T \to \infty) = 12\,R = 99.77$ J/mol·deg, which can only be explained by lattice anharmonicity effects. In the cases of the $A^{II}B^{IV}C_2^V$ compounds $CdSiP_2$, $CdGeP_2$ and $CdSnP_2$ (Fig. 2), we have the same effect for $CdSnP_2$. For the other two compounds, we have $C_p$ values of 100 J/mol deg for $CdGeP_2$ and 98 J/mol·deg for $CdSiP_2$ at 500 K, but the tendency to a further increase of $C_p$ with increasing temperature is obvious from the $C_p$ data given in Fig. 2. Thus, it is evident that the lattice anharmonicity effects must be taken into account in analyses of the $C_p$ values of all compounds.

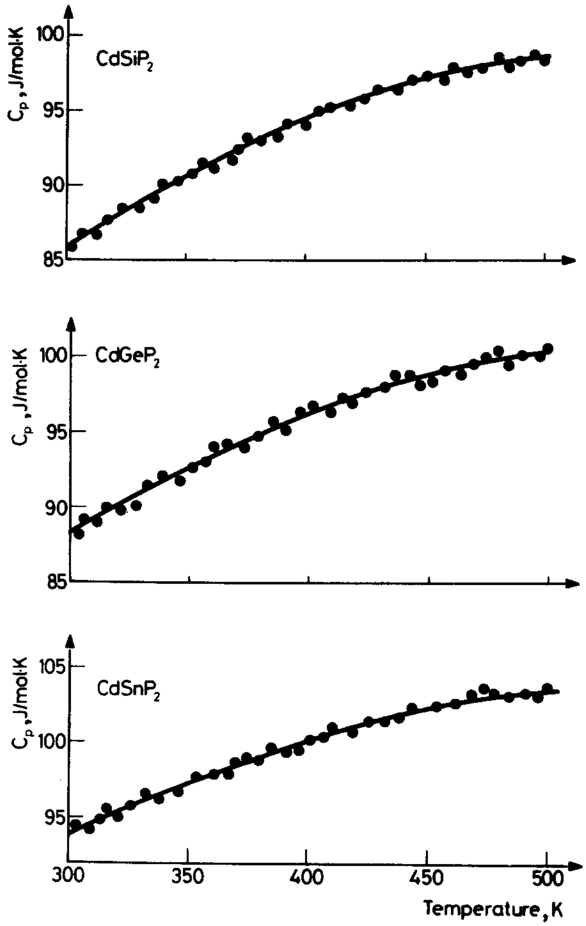

Fig. 2 Temperature dependence of the heat capacity in $CdSiP_2$, $CdGeP_2$ and $CdSnP_2$

Since the temperature range considered in the present study is well below the melting temperatures of the compounds, it can be assumed that perturbation can be used to describe the contribution $\Delta C_p$ to the heat capacity due to lattice anharmonicity [7]. Then, $\Delta C_p$ is given by a polynomial in the temperature $T$, and the total heat capacity of the compounds can be written in the form

$$C_p(T) = 12\left\{ F(\theta/T) + \sum_{k=1}^{N} c_k T^k \right\} \tag{1}$$

where $\theta_D$ is the Debye temperature and $F(X_D)$ the Debye function describing the temperature-dependence of $C_p$ in the harmonic approximation. However, if the harmonic part of $C_p$ is calculated in this manner, the temperature-dependence of $\theta_D$ must be taken into account [8]. Unfortunately, of the compounds investigated, the temperature variation of $\theta_D$ has only been reported for $CuInS_2$ so far [9]. For this reason we tried to analyse our data with relation (1) by setting $\theta_D$ equal to the Debye temperature $\theta_o$ for the low temperature $T \to 0$. The polynomial in $T$ will then not give the correct magnitude of the anharmonicity contribution to $C_p$, but it can be expected that the qualitative trends in the degree of the lattice anharmonicity are described correctly.

Using the $\theta_o$ values from [10–12], we fitted relation (1) to the measured heat capacities (Figs 1 and 2) with the parameters $N$ and $c_k$ as adjustable parameters. We found that a value of $N = 3$ must be used in all cases. The resulting coefficients $c_k$ are given in Table 1. For comparison, the results of the analogous analyses of the $C_p$ data for $ZnSiP_2$ and ZnSiAs [13], $ZnSiAs_2$ [14] and $CdGeAs_2$ [15] are also included in Table 1. Within each compound family, the compuonds are arranged with ascending molecular mass $m$.

The following trends are obvious from Table 1. First, we always have $c_1 < 0$, $c_2 > 0$, $c_3 < 0$. Secondly, the absolute magnitudes of the coefficients $c_k$ decrease with increasing molecular mass within each compound family. Thirdly, the order of magnitude of the coefficients $c_k$ is the same in both compound families for compunds with comparable molecular masses. Then, if the absolute magnitudes of the coefficient $c_k$ are considered as a measure of the degree of lattice anharmonicity, we come to the conclusions that

i) lattice anharmonicity effects become less pronounced with increasing molecular mass $m$; and
ii) there is no essential difference in the degrees of lattice anharmonicity of the compounds $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$.

**Table 1** Molecular mass *m*, parameters of relation (1) and Grüneisen constants $\gamma$ of the compounds investigated

| Compound | $m$ | $\Theta_o$, K | $c_1$, $10^{-4}K^{-1}$ | $c_2$, $10^{-6}K^{-2}$ | $c_3$, $10^{-9}K^{-3}$ | $\gamma$ (300K) |
|---|---|---|---|---|---|---|
| $TnSiP_2$ | 155.40 | 445 | $-21.59$ | 10.32 | $-11.87$ | 1.25 |
| $CdSiP_2$ | 202.43 | 390 | $-15.08$ | 6.33 | $-6.51$ | 1.19 |
| $CdGeP_2$ | 246.93 | 340 | $-14.85$ | 6.29 | $-6.43$ | 1.09 |
| $ZnSiP_2$ | 243.30 | 347 | $-12.87$ | 5.68 | $-5.89$ | 0.96 |
| $CdSnP_2$ | 293.03 | 280 | $-9.85$ | 4.47 | $-4.58$ | 0.69 |
| $ZnSnAs_2$ | 333.90 | 266 | $-5.76$ | 3.24 | $-3.63$ | 0.59 |
| $CdGeAs_2$ | 334.83 | 241 | $-3.22$ | 1.56 | $-1.34$ | 0.75 |
| $CuInS_2$ | 242.49 | 273 | $-8.21$ | 4.11 | $-4.34$ | 1.05 |
| $CuInSe_2$ | 336.28 | 222 | $-7.68$ | 4.06 | $-4.30$ | 0.79 |
| $CuInTe_2$ | 433.56 | 191 | $-5.38$ | 2.63 | $-2.67$ | 0.73 |

To obtain additional evidence in favour of these suppositions, we have evaluated the volume Grüneisen constants

$$\gamma = \frac{\alpha \cdot V_m B}{C_p} \tag{2}$$

of all compounds by using the volume expansion coefficients $\alpha$ from [16], the bulk moduli $B$ from [17, 18] and the $C_p$ data from this study. The resulting values for 300 K are given in Table 1 too. We see that, except for $CdGeAs_2$, the trend in $\gamma$ is the same as in the absolute magnitudes of $|c_k|$, which confirms our conclusion.

For $CuInS_2$, $CuInSe_2$ and $CuInTe_2$, we also estimated the anharmonic contribution $\Delta C_p$ to the heat capacity for the temperature range from 300 to 500 K. In the case of $CuInS_2$, the harmonic of $C_p$ was calculated by extrapolating the $\theta_D(T)$ values from [9] to the temperatures above 300 K. For $CuInSe_2$ and $CuInTe_2$, the variation of $\theta_D$ with $T$ was estimated according to the relations given in [8, 19], by using the interatomic force constants from [20]. The resulting $\Delta C_p$ curves are shown in Fig. 3 as a function of the reduced temperature $T/\theta_\infty$, where $\theta_\infty$ is the Debye temperature in the high-temperature limit $T \to \infty$ ($\theta_\infty = 388$ K for $CuInS_2$ [9, 19], 275 K for $CuInSe_2$ and 218 K for $CuInTe_2$). We see that the onset of $\Delta C_p$ shifts to higher reduced temperatures on going from $CuInS_2$ to $CuInSe_2$ and $CuInTe_2$, which means that the degree of lattice anharmonicity decreases in this compound sequence. We note that this trend is again in

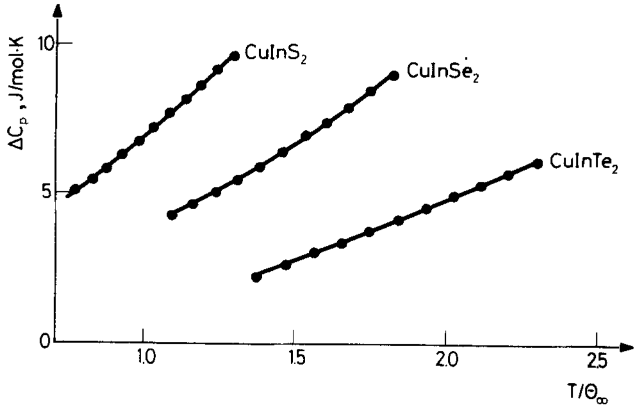

Fig. 3 Temperature dependence of the anharmonic contribution $\Delta C_p$ to $C_p$ for $CuInS_2$, $CuInSe_2$ and $CuInTe_2$

agreement with that deduced from the $c_k$ values and the Grüneisen constants of Table 1. For the compounds $A^{II}B^{IV}C_2^V$ no estimate of the true $\Delta C_p$ $(T)$ behaviour can be made, because neither constants have yet been reported.

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**Zusammenfassung** — Der anharmonische Beitrag zur Wärmekapazität verschiedener Halbleiterverbindungen $A^IB^{III}C_2^{VI}$ und $A^{II}B^{IV}C_2^V$ vom Chalkopyrit-Typ wird bestimmt. Es wird gezeigt, dass die Gitteranharmonizität mit steigender relativer Atommasse der Bestandteile der Verbindungen abnimmt und dass keine wesentlichen Unterschiede in der Gitteranharmonizität beider Gruppen von Verbindungen bestehen. Der Trend der Grüneisen-Konstanten ist der gleiche, ausgenommen bei $CdGeAs_2$.

**РЕЗЮМЕ** — Оценен ангармонический вклад в теплоемкость халькопиритных полупроводников $A^IB^{III}C_2^{VI}$ и $A^{II}B^{IV}C_2^V$. Показано, что степень решеточной ангармоничности уменьшается с увеличением атомного веса элементов, составляющих данные соединения, и что для обоих групп соединений нет особого различия в степени решеточной ангармоничности. Постоянные Грюнайзена одинаковые для всех соединений, за исключением $CdGeAs_2$.