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# Low-temperature thermal expansion in sphalerite-type and chalcopyrite-type multinary semiconductors

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## Abstract

The lattice parameters and linear thermal expansion coefficients  $\alpha_a$  and  $\alpha_c$  of multinary  $2(\text{ZnX})_x(\text{CuB}^{\text{III}}\text{X}_2)_{1-x}$  mixed crystals (cubic  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  and tetragonal  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$ ) were determined by neutron diffraction in the temperature region 1.5–300 K. With decreasing temperature the lattice constants in the mixed crystals decrease but show a flat minimum at a certain temperature, reflecting a change in sign of the linear thermal expansion coefficient. Because of the negative linear thermal expansion coefficients, negative Grüneisen parameters may be expected in the low-temperature region and as a consequence the existence of low-energy lattice vibrational modes. For tetragonal  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  mixed crystals the lattice constants  $a$  and  $c$  vary independently with temperature, as expected from the axial symmetry of the crystal. Moreover, the linear thermal expansion coefficients follow the inequality  $\alpha_a > \alpha_c$  in the whole temperature range. The tetragonal distortion  $\Delta$  of the chalcopyrite structure ( $\Delta = 2 - c/a$ ) decreases nonlinearly with decreasing temperature and has a positive temperature coefficient  $\alpha_\Delta$  in the whole temperature range studied.

## 1. Introduction

One of the most intriguing properties of solids whose crystal structures are based on tetrahedrally coordinated ions is their negative thermal expansion. For Si, Ge and a number of  $\text{A}^{\text{III}}\text{X}^{\text{V}}$  and  $\text{A}^{\text{II}}\text{X}^{\text{VI}}$  compounds it was shown [1–5] that the thermal expansion  $3\alpha$ , where  $\alpha$  stands for the linear thermal expansion coefficient, becomes negative below 50 and 100 K. The binary compounds crystallize at room temperature in the cubic sphalerite-type structure (sg  $F\bar{4}3m$ ), each anion is tetrahedrally coordinated by the cations and vice versa. The ternary  $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{X}_2^{\text{VI}}$  semiconductors ( $\text{A} = \text{Ag}, \text{Cu}$ ;  $\text{B} = \text{Al}, \text{Ga}, \text{In}$ ;  $\text{X} = \text{S}, \text{Se}, \text{Te}$ ), crystallizing in the tetragonal chalcopyrite-type structure (space group  $I\bar{4}2d$ ), also exhibit tetrahedral coordination. The ordered substitution of the metal in II–VI compounds by two metals (I and III) doubles the identity period of the initial cubic unit cell (by definition along the crystallographic  $c$ -direction). This goes along with a tetragonal distortion  $\Delta = 2 - c/a \neq 0$  ( $a$  and  $c$  are the lattice constants) due to different interactions between A–X and B–X resulting

in different bond lengths ( $R_{\text{AX}} \neq R_{\text{BX}}$ ) and bond angles and leads to a displacement of the anions from the ideal tetrahedral site characterized by a parameter  $|u - 1/4|$  (where  $u$  is the anion  $x$  coordinate).

Solid solutions of  $\text{D}^{\text{II}}\text{X}^{\text{VI}}$  and  $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{X}_2^{\text{VI}}$  compounds ( $\text{D} = \text{Zn}$ ;  $\text{A} = \text{Cu}$ ;  $\text{B} = \text{Ga}, \text{In}$  and  $\text{X} = \text{S}, \text{Se}, \text{Te}$ ) are of interest due to possible photovoltaic applications, such as for instance the multinary semiconductors of the  $2(\text{ZnX})_x(\text{CuBX}_2)_{1-x}$  solid solution series. These series are formed by alloying Cu–III–VI<sub>2</sub> into Zn–VI. They show no complete solubility, the chemical disorder process leads to a phase separation and the formation of a large miscibility gap [17].

Measurements of thermal expansion coefficients of some  $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{X}_2^{\text{VI}}$  compounds by dilatometry or x-ray diffraction [6–15] have shown that the linear thermal expansion coefficients of the lattice parameters  $a$  and  $c$ , which are defined by  $\alpha_a(T) = \frac{1}{a(T)} \times \frac{da(T)}{dT}$  and  $\alpha_c(T) = \frac{1}{c(T)} \times \frac{dc(T)}{dT}$  are anisotropic. This can be understood in terms of the difference in the strength of the A–X and B–X bonds characterized by

different bond ionicities. Negative values have been found for  $\alpha_c$  [6–8, 11, 12, 14, 15]. It is usual to describe the thermal expansion properties of solids in terms of Grüneisen parameters  $\gamma$  [16]: a negative thermal expansion will give rise to negative Grüneisen parameters. In the case of the uniaxial chalcopyrite-type structure there are two independent Grüneisen parameters,  $\gamma_a$  and  $\gamma_c$ , which are related to the principal thermal expansion coefficients  $\alpha_a$  and  $\alpha_c$  via [12]

$$\begin{aligned} \gamma_a &= \frac{V_m}{C_p} [(c_{11}^S + c_{13}^S)\alpha_a + c_{31}^S\alpha_c] \\ \gamma_c &= \frac{V_m}{C_p} [2c_{13}^S\alpha_a + c_{33}^S\alpha_c]. \end{aligned} \quad (1)$$

Here  $V_m$  is the molar volume,  $C_p$  the molar specific heat at constant pressure and the  $c_{ij}$  are the adiabatic elastic stiffness coefficients. Moreover, it is expected that with increasing ionicity the Grüneisen parameter becomes more negative [5]. Thus a strong dependence of the Grüneisen parameter on the covalent character of the chemical bond is anticipated.

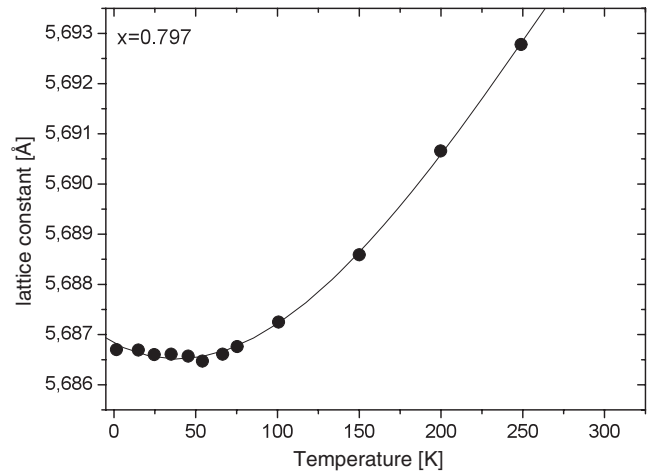
In the present work we report the results of low-temperature (temperature range 1.5–300 K) neutron diffraction studies of  $(\text{ZnSe})_x(\text{CuInSe}_2)_{1-x}$  powder samples with  $0.38 \leq x \leq 1$  (cubic mixed crystals) and of a  $(\text{ZnS})_x(\text{CuGaS}_2)_{1-x}$  powder sample with  $x = 0.06$  (tetragonal mixed crystal).

## 2. Experimental details

The powder samples were synthesized by solid-state reaction of the elements (purity >99.999%) in sealed evacuated silica tubes at  $T = 850^\circ\text{C}$  for  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  and  $950^\circ\text{C}$  for  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$ . This procedure was repeated three times with intermediate homogenizations of the samples in between by regrinding them in an agate mortar. Finally, the samples were cooled down to room temperature at a  $10 \text{ K h}^{-1}$  rate. More details about the sample preparation are described in [18, 19]. The average chemical composition of the samples was measured by energy-dispersive x-ray (EDX) analysis adapted to a transmission electron microscope, and has been reported elsewhere [18, 19].

Neutron powder diffraction experiments were performed at the Swiss Spallation Source SINQ at the Paul Scherrer Institute (Villigen) using the high-resolution powder diffractometer for thermal neutrons HRPT [20] with a wavelength of  $\lambda = 1.1545 \text{ \AA}$ . Measurements were done at room temperature and at low temperatures using a standard orange type cryostat.

The data treatment was done by Rietveld analysis using the FullProf program [21] with the sphalerite structure model for cubic mixed crystals  $((\text{ZnSe})_x(\text{CuInSe}_2)_{1-x})$  and the chalcopyrite structure model for the tetragonal mixed crystal as starting point in the refinement. Refinement parameters for the structure were the lattice constant  $a_{\text{cub}}$  as well as  $a_{\text{tetr}}$  and  $c$ , isotropic temperature factors and in case of the tetragonal mixed crystal  $((\text{ZnS})_x(\text{CuGaS}_2)_{1-x})$  also anion coordinates and cation site occupancies. For the cubic mixed crystals the cation site occupancies were kept at a fixed value during the refinement. These values were derived from the calculated



**Figure 1.** The temperature dependence of the lattice constant  $a$  for the cubic mixed crystal  $\text{Zn}_{0.797}\text{Cu}_{0.096}\text{In}_{0.106}\text{Se}$ . The solid lines correspond to a polynomial of third order in  $T$ . The given  $x$ -value refers to the mole fraction of ZnSe in  $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$ .

average neutron scattering length for the cation site ( $\bar{b}$ ), which was calculated by

$$\bar{b} = b_{\text{Zn}}\text{Zn}_{\text{Zn}} + b_{\text{Cu}}\text{Cu}_{\text{Zn}} + b_{\text{In}}\text{In}_{\text{Zn}} \quad (2)$$

with  $b_{\text{Zn}}$ ,  $b_{\text{Cu}}$  and  $b_{\text{In}}$  being the neutron scattering lengths of Zn, Cu and In, respectively [22]. Here  $\text{Zn}_{\text{Zn}}$ ,  $\text{Cu}_{\text{Zn}}$  and  $\text{In}_{\text{Zn}}$  are the mole fractions of Zn, Cu and In derived from the chemical composition of the sample.

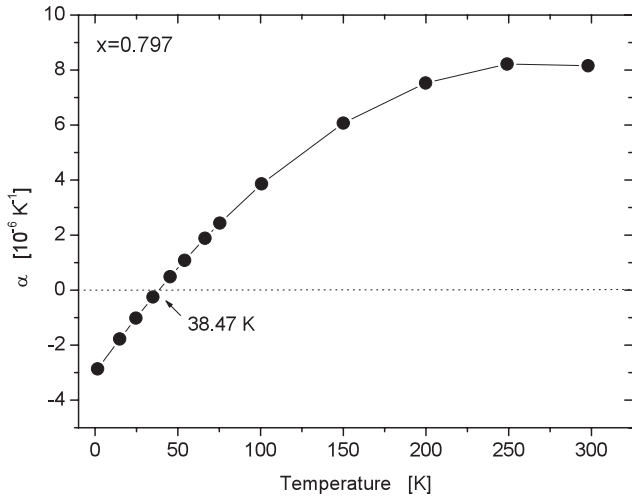
## 3. Results and discussion

### 3.1. Ternary (cubic) mixed crystals

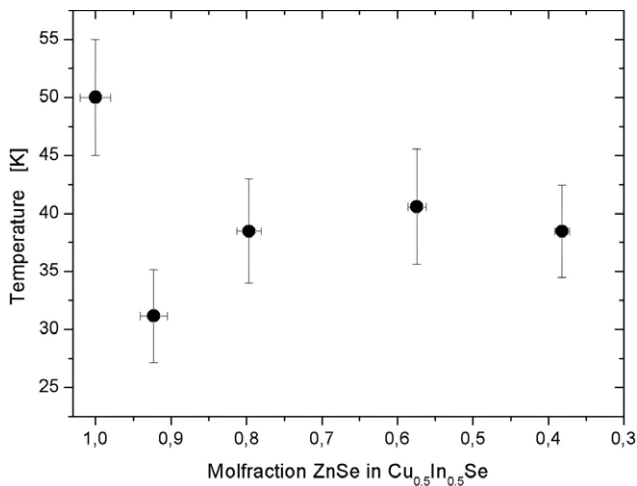
The temperature-dependent behaviour of the cubic lattice constant in the temperature range 1.5–300 K is shown as an example in figure 1 for the  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  sample with  $x = 0.797$ . A third order polynomial in  $T$  was fitted to the data. With decreasing temperature the lattice constant decreases, but shows a flat minimum at about 40 K, reflecting a change in sign of the linear thermal expansion coefficient.

Using the temperature-dependent lattice constant the linear thermal expansion coefficient  $\alpha_a$  was derived, which is shown exemplarily in figure 2 for the same sample as in figure 1.

The linear thermal expansion coefficient  $\alpha_a$  for all the  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  samples considered decreases with decreasing temperature and becomes negative in the range from 30 to 40 K (see figure 3). Below these temperatures the determination of the thermal expansion coefficient becomes less accurate, because the change in the lattice constant with temperature is nearly of the same order of magnitude as the error in the determination of the lattice parameter itself. However, it is clearly established that, first, the thermal expansion coefficient  $\alpha_a$  becomes negative below some critical temperature  $T(\alpha_a = 0)$  and, second, these critical temperatures vary with the chemical composition.



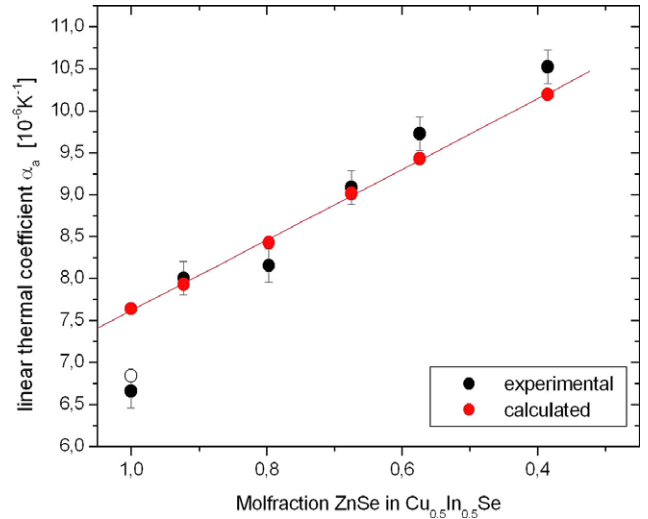
**Figure 2.** Temperature dependence of the linear thermal expansion coefficient  $\alpha_a$  for the cubic mixed crystal  $\text{Zn}_{0.797}\text{Cu}_{0.096}\text{In}_{0.106}\text{Se}$ . The dotted line marks  $\alpha_a = 0$ ; the solid line is a guide to the eye. The temperature given in the figure is the critical temperature  $T(\alpha_a = 0)$ . The given  $x$ -value refers to the mole fraction of ZnSe in  $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$ .



**Figure 3.** The critical temperature, i.e. the temperature where  $\alpha_a = 0$ , in dependence on the chemical composition.

The decrease of the critical temperature, i.e.  $T(\alpha_a = 0)$ , with alloying  $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$  in ZnSe may be discussed in terms of the ionicity of the cation–anion bonds in the mixed crystals, which can be calculated following Phillips’ definition  $f_i = 1 - \exp[-(X_A - X_B)^2/4]$  ( $X_A$  and  $X_B$  are the electronegativities of the elements A and B) [25]. Thus the ionicity of the cation–Se bond is decreasing from Zn–Se ( $f_i = 0.183$ ) to In–Se ( $f_i = 0.115$ ) and Cu–Se ( $f_i = 0.1002$ ). Because it is expected that with increasing ionicity the Grüneisen parameter becomes more negative [5], the substitution  $\text{Zn}^{2+} \leftrightarrow \text{Cu}^+ + \text{In}^{3+}$  leads to a decrease of the ionicity of the cation–Se bond. Thus the temperature for which the linear thermal expansion coefficient changes its sign, i.e.  $T(\alpha_a = 0)$ , decreases.

While comparing the temperature dependence of the linear thermal expansion coefficient  $\alpha_a$  in ZnSe and in  $(\text{ZnSe})_{2x}(\text{CuInSe}_2)_{1-x}$  mixed crystals, a similar behaviour



**Figure 4.** Comparison of the experimentally determined and calculated (equation (3)) linear thermal expansion coefficient of cubic  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  mixed crystals at room temperature. The open symbol refers to a literature value [5].

(This figure is in colour only in the electronic version)

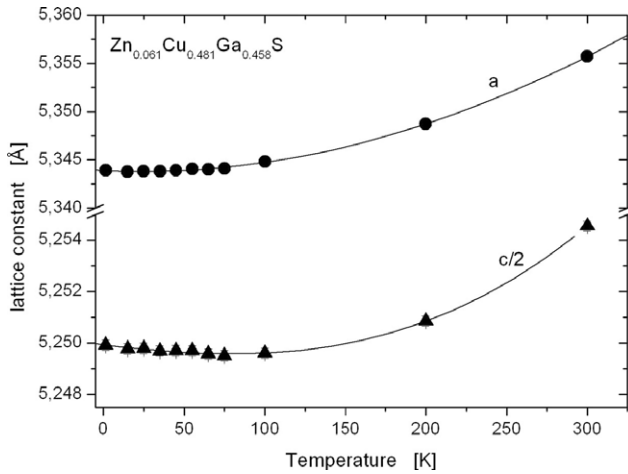
is noticed. Also for the alloys the values of  $\alpha_a$  become negative below 40 K, and negative Grüneisen parameters  $\gamma$  can be expected in this low-temperature region. So far no experimental investigation of the pressure-induced phase transitions in  $(\text{ZnSe})_{2x}(\text{CuInSe}_2)_{1-x}$  alloys is known, but the existence of the low-energy lattice vibrational modes with negative Grüneisen parameters assumed, as in ZnSe which implies a possibility for such a kind of phase transition.

A detailed analysis of the thermal expansion coefficient data of tetrahedrally coordinated  $\text{A}^{\text{IV}}$ ,  $\text{A}^{\text{III}}\text{B}^{\text{V}}$  and  $\text{A}^{\text{II}}\text{B}^{\text{VI}}$  as well as  $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{X}_2^{\text{VI}}$  and  $\text{A}^{\text{I}}\text{B}^{\text{IV}}\text{X}_2^{\text{V}}$  [9] semiconductors has shown that the average linear thermal expansion coefficients of these compounds at room temperature follow the relation [26]

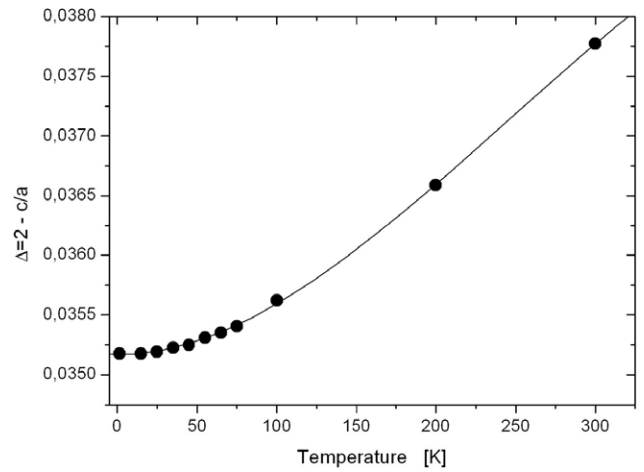
$$\alpha_L = \frac{A}{T_M} - B(d - d_0)^3 \quad (3)$$

where  $T_M$  is the melting temperature in K and  $d$  the bond length of the considered compound. The constant  $A$  has the same value,  $A = 0.021$ , for all tetrahedrally coordinated compounds. The  $d_0$  value is for a given compound family slightly different from the bond length of diamond. The factor  $B$  depends on the ionicity and was found to be nearly constant within each compound family.

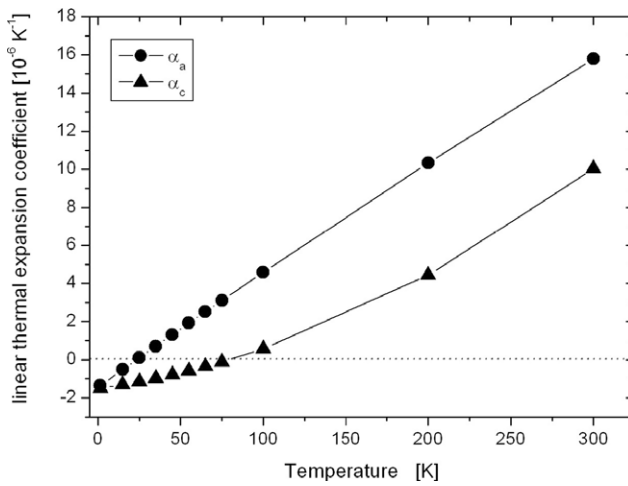
The linear thermal expansion coefficient of the cubic  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  mixed crystals was calculated using equation (3). The factor  $B$  for  $\text{A}^{\text{II}}\text{B}^{\text{VI}}$  compounds [9] was applied ( $3.3 \times 10^{-6} \text{ K}^{-1}$ ). The values for the bond length  $d$  were determined by the Rietveld analysis of the neutron diffraction data, and the melting point of the mixed crystals was taken from [27]. A comparison of the calculated and experimentally determined linear thermal expansion coefficient at 300 K reveals a good agreement (see figure 4). Thus, it can be concluded that equation (3) is also valid for mixed crystals which adopt one of the tetrahedrally coordinated structures of the compound families listed above.



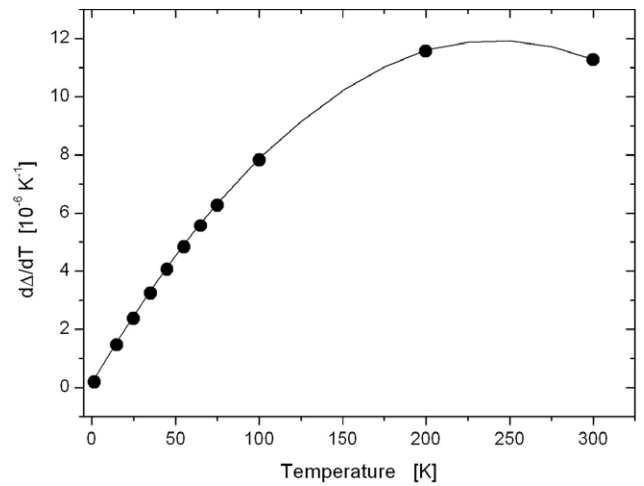
**Figure 5.** The temperature dependence of the lattice constants  $a$  and  $c$  for the tetragonal mixed crystal  $\text{Zn}_{0.061}\text{Cu}_{0.481}\text{Ga}_{0.458}\text{S}$ . For better visibility the values for  $c/2$  are shown. The solid lines correspond to a polynomial of third order in  $T$ .



**Figure 7.** The tetragonal distortion  $\Delta = 2 - c/a$  in dependence on temperature for the tetragonal mixed crystal  $\text{Zn}_{0.061}\text{Cu}_{0.481}\text{Ga}_{0.458}\text{S}$ . The solid lines correspond to a polynomial of third order in  $T$ .



**Figure 6.** Temperature dependence of the linear thermal expansion coefficients  $\alpha_a$  and  $\alpha_c$  for the tetragonal mixed crystal  $\text{Zn}_{0.061}\text{Cu}_{0.481}\text{Ga}_{0.458}\text{S}$ . The dotted line marks the point when both linear thermal expansion coefficients change their sign; the solid line is a guide to the eye.



**Figure 8.** Temperature dependence of the thermal expansion coefficient  $\alpha_\Delta$  for the tetragonal mixed crystal  $\text{Zn}_{0.061}\text{Cu}_{0.481}\text{Ga}_{0.458}\text{S}$ . The solid line was calculated from equation (3) using the  $\alpha_a$  and  $\alpha_c$  values evaluated above.

### 3.2. Quaternary (tetragonal) mixed crystals

The temperature-dependent behaviour of the tetragonal lattice constants  $a$  and  $c$  in the range 1.5–300 K is shown for the  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  sample with  $x = 0.061$  in figure 5. A third order polynomial in  $T$  was used to describe the data. With decreasing temperature both lattice constants decrease, but show a flat minima, at about 25 K for the parameter  $a$  and at about 80 K for the parameter  $c$ . This independent temperature variation can be expected from the axial symmetry of the crystal.

Using the temperature-dependent lattice constants  $a(T)$  and  $c(T)$  the linear thermal expansion coefficients  $\alpha_a$  and  $\alpha_c$  were derived. The resulting variation of  $\alpha_a$  and  $\alpha_c$  is shown in figure 6. It is noticeable that the thermal expansion coefficients always follow the inequality  $\alpha_a > \alpha_c$ , independent

of temperature. This means that the tetragonal distortion  $\Delta$  of the chalcopyrite structure has a positive temperature coefficient  $\alpha_\Delta$ :

$$\alpha_\Delta = \frac{1}{\Delta(T)} \frac{d\Delta(T)}{dT} = \frac{c}{a} (\alpha_a - \alpha_c). \quad (4)$$

Figure 7 shows the temperature-dependent behaviour of the tetragonal distortion  $\Delta$ , whereas figure 8 shows the thermal expansion coefficient  $\alpha_\Delta$ . The  $\Delta$  values decrease nonlinearly with decreasing temperature, and adopt positive values in the whole temperature range studied. A third order polynomial in  $T$  was used to describe the data.

Comparing our results for the quaternary mixed crystal with other ternary Cu–III–VI<sub>2</sub> compounds, an interesting common behaviour can be noted. For all Cu–III–VI<sub>2</sub> compounds (with the exception of  $\text{CuInTe}_2$ ), it has been established that they show the same inequality:  $\alpha_a > \alpha_c$  [12].

So far, no experimental determination of the adiabatic stiffnesses  $c_{ij}$  and of the molar specific heat at constant pressure,  $C_p(T)$ , in the temperature range of interest have been reported neither for tetragonal  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  mixed crystals nor for  $\text{CuGaS}_2$ , which prevents a quantitative analysis of the temperature dependence of the Grüneisen parameters  $\gamma_a$  and  $\gamma_c$ . However, from figure 5 it can be assumed that both  $\gamma_a$  and  $\gamma_c$  are positive above about 90 K and negative below 25 K. Since  $\gamma_a$  and  $\gamma_c$  are weighted averages of the respective principal Grüneisen mode parameters  $\gamma_{ai}$  and  $\gamma_{ci}$  in which the contribution of the  $\gamma_{ji}$  of each normal mode of the lattice to  $\gamma_j$  is weighted by its contribution to the total specific heat [16], the occurrence of negative values of  $\gamma_a$  and  $\gamma_c$  at low temperatures implies the existence of low-energy lattice vibrational modes with negative mode Grüneisen parameters in tetragonal  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  mixed crystals. This result is in accordance with the fact that  $\text{CuGaS}_2$  undergoes a pressure-induced phase transition from the chalcopyrite structure to the denser rock-salt structure at 16 Gpa [23, 24], which is also closely related to low-energy lattice modes with negative Grüneisen parameters. Unfortunately there is no knowledge on the pressure-induced phase transitions or lattice vibrations in tetragonal  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  mixed crystals so far. Thus, no further detailed discussion of this point can be given at present.

#### 4. Conclusions

Our measurements show that multinary  $2(\text{ZnX})_x(\text{CuB}^{\text{III}}\text{X}_2)_{1-x}$  mixed crystals exhibit the same type of low-temperature behaviour as the corresponding binary Zn–VI and ternary Cu–B<sup>III</sup>–VI<sub>2</sub> compounds. With decreasing temperature the lattice constants in ternary (cubic)  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  and quaternary (tetragonal)  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  mixed crystals decrease but show a flat minimum at a certain temperature, reflecting a change in sign of the linear thermal expansion coefficient.

Thus negative Grüneisen parameters  $\gamma$  can be expected in this low-temperature region. So far no experimental investigation about pressure-induced phase transitions in  $2(\text{ZnX})_x(\text{CuB}^{\text{III}}\text{X}_2)_{1-x}$  mixed crystals is known, but the existence of low-energy lattice vibrational modes with negative Grüneisen parameters can be assumed, similar to  $\text{ZnSe}$  or  $\text{CuGaS}_2$ , which implies a possibility of such kind of phase transitions.

In the case of cubic  $\text{Zn}_{2x}(\text{CuIn})_{1-x}\text{Se}_2$  mixed crystals the comparison of the experimentally determined linear thermal expansion coefficients (at room temperature) with calculated values (equation (3)) show a very good agreement. Thus this equation which is valid for the binary and ternary compounds, can also be applied to the multinary compounds of the same structure type.

For the tetragonal  $\text{Zn}_{2x}(\text{CuGa})_{1-x}\text{S}_2$  mixed crystals the lattice constants  $a$  and  $c$  vary independently with temperature as expected from the axial symmetry of the crystal. The linear

thermal expansion coefficients follow the inequality  $\alpha_a > \alpha_c$  independently of temperature. The tetragonal distortion  $\Delta$  of the chalcopyrite structure ( $\Delta = 2 - c/a$ ) decreases nonlinearly with decreasing temperature, and has a positive temperature coefficient  $\alpha_\Delta$  in the whole temperature range studied.

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#### References

- [1] Gibbons D F 1958 *Phys. Rev.* **112** 136–40
- [2] Novikova S I 1960 *Fiz. Tverd. Tela* **2** 2341–4
- [3] Novikova S I 1961 *Fiz. Tverd. Tela* **3** 178–9
- [4] Novikova S I and Abrikosov N Kh 1963 *Fiz. Tverd. Tela* **5** 129–30
- [5] Smith T F and White G K 1975 *J. Phys. C: Solid State Phys.* **8** 2031–42
- [6] Korczak P and Staff C B 1974 *J. Cryst. Growth* **24/25** 386
- [7] Iseler G W 1977 *J. Cryst. Growth* **41** 146
- [8] Brühl H-G, Neumann H and Kühn G 1980 *Solid State Commun.* **34** 225
- [9] Neumann H 1980 *Krist. Tech.* **15** 849
- [10] Brühl H-G, Neumann H, Pfeiffer T and Kühn G 1981 *Phys. Status Solidi a* **66** 597
- [11] Deus P, Neumann H, Kühn G and Hinze B 1983 *Phys. Status Solidi a* **80** 205
- [12] Neumann H, Deus P, Thomlinson R D, Kühn G and Hintze B 1984 *Phys. Status Solidi a* **84** 87
- [13] Neumann H 1987 *Cryst. Res. Technol.* **22** 723
- [14] Orlova N S and Bodnar I V 1987 *Cryst. Res. Technol.* **22** 1409
- [15] Orlova N S and Bodnar I V 1987 *Phys. Status Solidi a* **101** 421
- [16] Barron T K K, Collins J G and White G K 1980 *Adv. Phys.* **29** 609
- [17] Schorr S 2007 *Thin Solid Films* **515** 5985
- [18] Wagner G, Lehmann S and Schorr S 2005 *J. Solid State Chem.* **178** 3631
- [19] Schorr S, Wagner G, Görlicke D and Bente K 2007 *J. Alloys Compounds* in preparation
- [20] Fischer P, Frey G, Koch M, Könnecke M, Pomjakushin V, Schefer J, Thut R, Schlumpf N, Burge R, Greuter U, Bondt S and Berruyer E 2000 *Physica B* **276** 146
- [21] Rodriguez-Carjaval J 2001 FullProf: A Rietveld analysis program for x-ray and neutron diffraction data *Comm. Powder Diff. (IUCr) Newslett.* **26** 12
- [22] Sears V F 1992 *Neutron News* **3** 26
- [23] Werner A, Hochheimer H D and Jayaraman A 1981 *Phys. Rev. B* **23** 3836
- [24] Carlone C, Olego D, Jayaraman A and Cardona M 1980 *Phys. Rev. B* **22** 3877
- [25] Phillips J C 1973 *Bonds and Bands in Semiconductors* (New York: Academic)
- [26] Van Uitert L G 1977 *Mater. Res. Bull.* **12** 315
- [27] Korzun B 2005 private communication