

Stability of non-centrosymmetric phases in tetra-coordinated of LD TM intercalates

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On the basis of comparison of temperature dependences of lattice parameters of CuCrSe_2 and $\text{Cu}_{0.5}\text{ZrSe}_2$ in the temperature region including transition between phases with centrosymmetric and non-centrosymmetric distribution of copper on positions tetrahedrally coordinated by selenium. It is concluded that the critical factor that ensures the stability of the non-centrosymmetric copper distribution is the covalent interaction between copper and selenium sublattices. This effect is not related to the anisotropy of the elastic constants of the lattice and can be observed in other layered structures with copper tetrahedrally coordinated by chalcogen.

Keywords: Thermal Expansion Coefficient; dichalcogenides; intercalation; delafossite; phase transition

Introduction

For a number of years, phases with the delafossite [1] structure described by the general chemical formula ACrX_2 ($\text{A}=\text{Cu}, \text{Ag}; \text{X}=\text{S}, \text{Se}$), have attracted much attention. The basis of these materials are CrX_2 layers, where chromium, which forms a triangular lattice, is in an octahedral environment of the chalcogen. Between the layers is metal A, whose atoms coordinated by the chalcogen. These positions form two planes parallel to the plane of CrX_2 layers and shifted relative to the center of the interlayer gap. In the high-temperature phase, which is also

called superionic due to the high diffusional mobility of atoms of metal A, the atoms of this metal are uniformly distributed between the positions of both tetra-planes. The lattice is centrosymmetric (CS) and is described by the space group $P\bar{3}$. Cooling leads to the situation that the atoms of metal A are concentrated in only one of the tetra-planes. Such a lattice is non-centrosymmetric (NCS) and is described by the group $P3$.

The non-centrosymmetric of the low-temperature phase provides the possibility of ferroelectric ordering. The magnetic ordering of the chromium sublattice is mainly antiferromagnetic. However, it is impossible to organize proper antiferromagnetic ordering in a triangular lattice. Therefore, frustrations, disturbances of the correct antiferromagnetic periodicity, are formed in the chromium sublattice. The point of transition to the ferroelectrically ordered state $ACrX_2$ coincides with the point of ordering of these frustrations and the formation of ferrimagnetic order. Moreover, these two orders – electric and magnetic are closely related, so that switching the direction of electric momentum leads to switching the direction of magnetization. Such materials are called multiferroics [2] and they are of great applied interest.

An outstanding and well-known example of this family of materials is $CuCrSe_2$ [3]. Here, at temperatures below $90^\circ C$, the stability of the non-centrosymmetric distribution of copper occupying positions in only one of the tetra-planes is observed (space group $R3m$).

Of course, the question arises about the reason of stability of such non-centrosymmetric ordering. If in the centrosymmetric distribution the influence of atoms located on different sides of the observed position compensate each other, then in the non-centrosymmetric case some external factors are required to ensure the stability of such a structure. What can they be?

The first idea that comes to mind is the influence of anisotropy of elastic constants of layered lattices of transition metal dichalcogenides (LDTM). One can roughly estimate the anisotropy of elastic constants using the coefficient of thermal expansion in crystallographic directions. Indeed, in some cases the Young's modulus along the basic plane is several times higher than in the direction normal to it [4].

It is known that TEC (Thermal Expansion Coefficient) is related to compressibility by the following relation [5]:

$$\beta = \gamma \frac{C_V}{V} \chi_T, \quad (1)$$

where β – volumetric TEC, γ – Gruneisen parameter, C_V – heat capacity at constant volume and χ_T – isothermal compressibility. Characteristic Debye temperatures of layered materials are in the region of 150–250 K [6, 7]. Therefore, the heat capacity near room temperature and above it can be taken as constant. Thus, the TEC is directly proportional to the isothermal compressibility.

Among them is $CrSe_2$ [8] where the temperature dependence of the lattice parameters shows an anomalous form, which does not allow us to use the usual approach to estimate the Young's modulus. This is due to the fact that $CrSe_2$ itself is chemically unstable and decays upon heating to form Cr_2Se_3 . Although

by thermal analysis methods the decomposition is registered at a temperature of 625 K, however, the signs of decomposition appear already starting from a temperature of 185 K. At lower temperatures it is possible to estimate the ratio of Young's modules along and across the layer as 3:1.

The instability of CrSe_2 required us to compare the elastic constants and stability of the non-centrosymmetric intercalant distribution for CuCrSe_2 , a material that is quite stable.

On the other hand, the elastic constants in isostructural materials depend on the mass of the atoms that compose them. The weighting of atoms leads to a decrease in the vibrational frequencies and, consequently, to a decrease in the lattice elasticity. Therefore, for comparison we have chosen the recently synthesized material CuZrSe_2 [9] (space group $P\bar{3}m1$). In this material, copper is also distributed between tetra-coordinated positions, which makes its structure similar to that of CuCrSe_2 (see Figure 1) and at room temperature it exhibits a non-centrosymmetric distribution of copper occupying only one tetra-plane. However, this phase is found to be thermally unstable and decays at temperatures above about 200°C . Therefore, it is not possible to determine the TEC in the elevated temperature region. However, lowering the Cu concentration to the composition $\text{Cu}_{0.5}\text{ZrSe}_2$ stabilizes this phase. Therefore, we chose this composition for a comparative study with CuCrSe_2 to investigate the relationship between the elastic constants and the stability of the Cu non-centrosymmetric ordering.

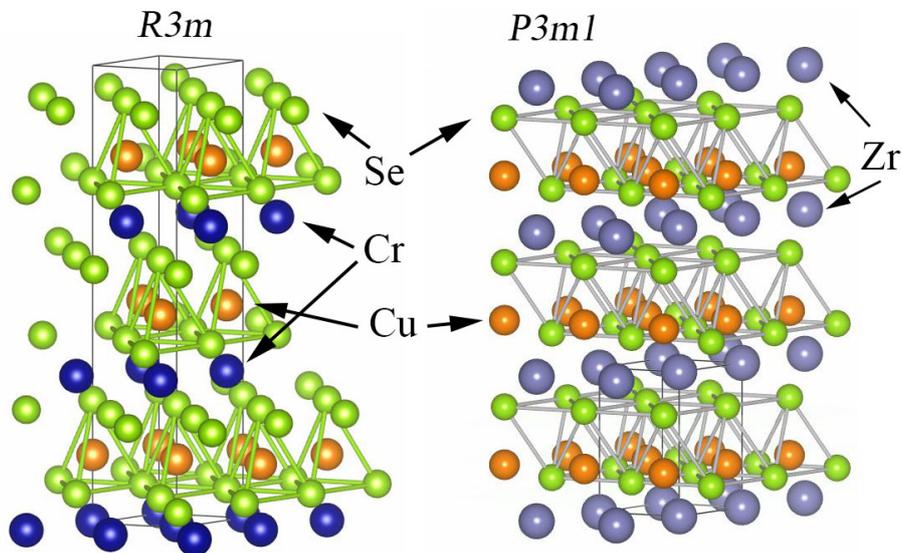


Figure 1. On the right panel fragment of crystal structure for $P\bar{3}m1$ space group (dichalcogenides), on the left panel for $R3m$ space group (delafossite).

Moreover, the effect of the non-centrosymmetric distribution of the intercalant on the elastic constants of the lattice is interesting. Obviously, such a distribution should increase the polarizability of the lattice and, consequently, reduce its stiffness. The answer to these questions we tried to obtain in the present work by comparing the thermal expansion coefficient along the crystallographic directions for CuCrSe_2 and $\text{Cu}_{0.5}\text{ZrSe}_2$.

Experiment

The polycrystalline sample of CuZrSe_2 was synthesized using previously prepared ZrSe_2 and metallic copper. ZrSe_2 was obtained from the elements: Zr (iodine purification, 99.95%) plates of size $0.3 \times 10 \times 10$ mm (VSMPO-AVISMA) and Se (after double distillation in a vacuum, 99.99%). The appropriate amount of Zr and Se with a total sample mass of 3 g was sintered at 1000°C for 7 days in sealed quartz ampoules evacuated to 10^{-5} Torr in a tube furnace with a temperature gradient not exceeding 1 deg/cm. The CuZrSe_2 sample was obtained using thermal intercalation procedure at room temperature [10, 11]. More details on the synthesis procedure can be found in [12].

The CuCrSe_2 polycrystalline samples were synthesized from the elements: Cr (X99, 99%), Cu (electrolytic copper OSCh 19-4 purity 99.99) and Se (high purity, 99.99%, after double distillation in a vacuum). The appropriate amount of the elements was sintered at 1150°C for 7 days in sealed quartz ampoules, evacuated to 10^{-5} Torr. After that the ampoules were opened, the samples were ground, pressed, and again annealed under the same conditions for a week for homogenization.

Low temperature diffractograms were measured on Shimadzu XRD 7000 Maxima diffractometer, $\text{CuK}\alpha$ radiation, scattering angle range $10\text{--}90^\circ$, speed 1 deg/min, step 0.02 deg, Bragg-Brentano focusing (CCU Ural-M). High temperature diffractograms were measured at the MCX beam-line of Elettra-Synchrotron Trieste (Italy) [13]. More information about experiment can be founded in [12, 14].

The parameters of crystal structure was indexed using the GSAS II software package [15].

Results and discussion

An example of the obtained diffraction patterns is shown in Figure 2. According to the obtained X-ray diffraction patterns shown in Figure 2, at low temperatures (RT and below) the systems are in the NCS phase ($R\bar{3}m$ for CuCrSe_2 and $P3m1$ for CuZrSe_2), and at high temperatures (300°C) they are in the CS phase ($R\bar{3}m$ for CuCrSe_2 and $P\bar{3}m1$ for CuZrSe_2).

Since the values of lattice parameters for $\text{Cu}_{0.5}\text{ZrSe}_2$ and CuZrSe_2 are different, it is more appropriate to give their temperature dependence in the form of the absolute value of the parameter change as a function of temperature. In this form, the temperature dependences of changes in the lattice parameters and unit cell volume are shown in Figure 3.

For the changing of the parameter a , several areas can be identified for each of the samples. For CuCrSe_2 there are two linear regions with almost unchanged parameter a (labeled as 1 and 4 in Figure 3) and a region with decreasing parameter a with increasing temperature (region labeled as 3). Accordingly, for regions 1 and 4 TEC is around 0, and for region 3 TEC is negative: $\text{TEC} = -1.33 \cdot 10^{-5}$. This dependence may indicate that the transition between the CS

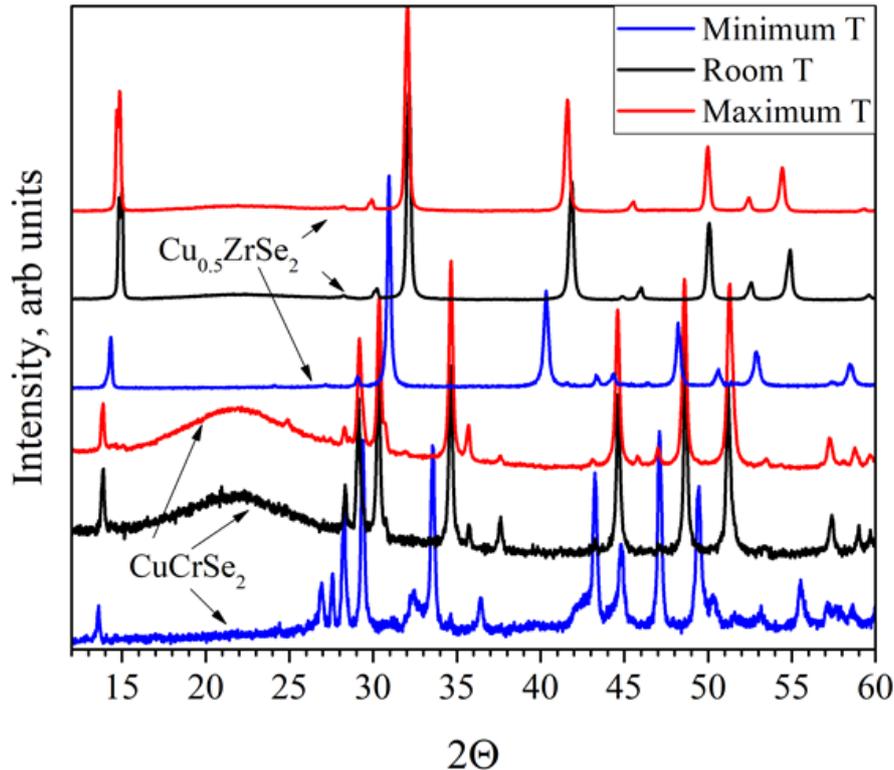


Figure 2. X-ray diffraction patterns for CuCrSe_2 (at -150°C , Room Temperature and 300°C) and for $\text{Cu}_{0.5}\text{ZrSe}_2$ (at -178°C , Room Temperature and 300°C).

and NCS phases is a second-order phase transition. Indeed, the temperature dependence of the unit cell volume, see Figure 3c, does not show a sharp break, but smoothly changes. Such a dependence indicates that the transition of Cu atoms into the same tetra-plane occurs gradually and there is a wide temperature region of unequal filling of crystallographic positions in both tetra-planes. The beginning of the transition to the NCS phase upon heating occurs at about room temperature and is completed at about 200°C .

At the same time, for $\text{Cu}_{0.5}\text{ZrSe}_2$, a discontinuous change in the unit cell volume and a sharp break in the lattice parameters at 79°C for c and 170°C for a are observed. For the region above 170°C , the TEC is also about 0, and for the lower temperature site $\text{TEC}=1.4 \cdot 10^{-5}$.

It is noteworthy that the TEC along the a direction is practically zero for both phases in the CS-phase, while the TEC along c increases compared to the NCS-phase. This allows us to conclude that the NCS ordering does not decrease the lattice hardness along the basis plane, contrary to what is intuitively expected. At the same time, the bulk TEC even decreases. All this suggests that the reason for the NCS-ordering may be not the optimization of elastic distortions, but covalent bonds between tetra-coordinated copper atoms. Certainly, the difference in the behavior of the TEC along the a and c axes indicate the involvement of elastic interactions as well. However, the coincidence of the temperatures of the final stabilization of the CS phase in the lattices of such significantly different transition metal atom masses as Zr and Cr and, consequently, polarizability, shows that the elastic interaction does not play the main role here. It calls attention to the fact that in the known superionic conductor Cu_2Se the transition to the

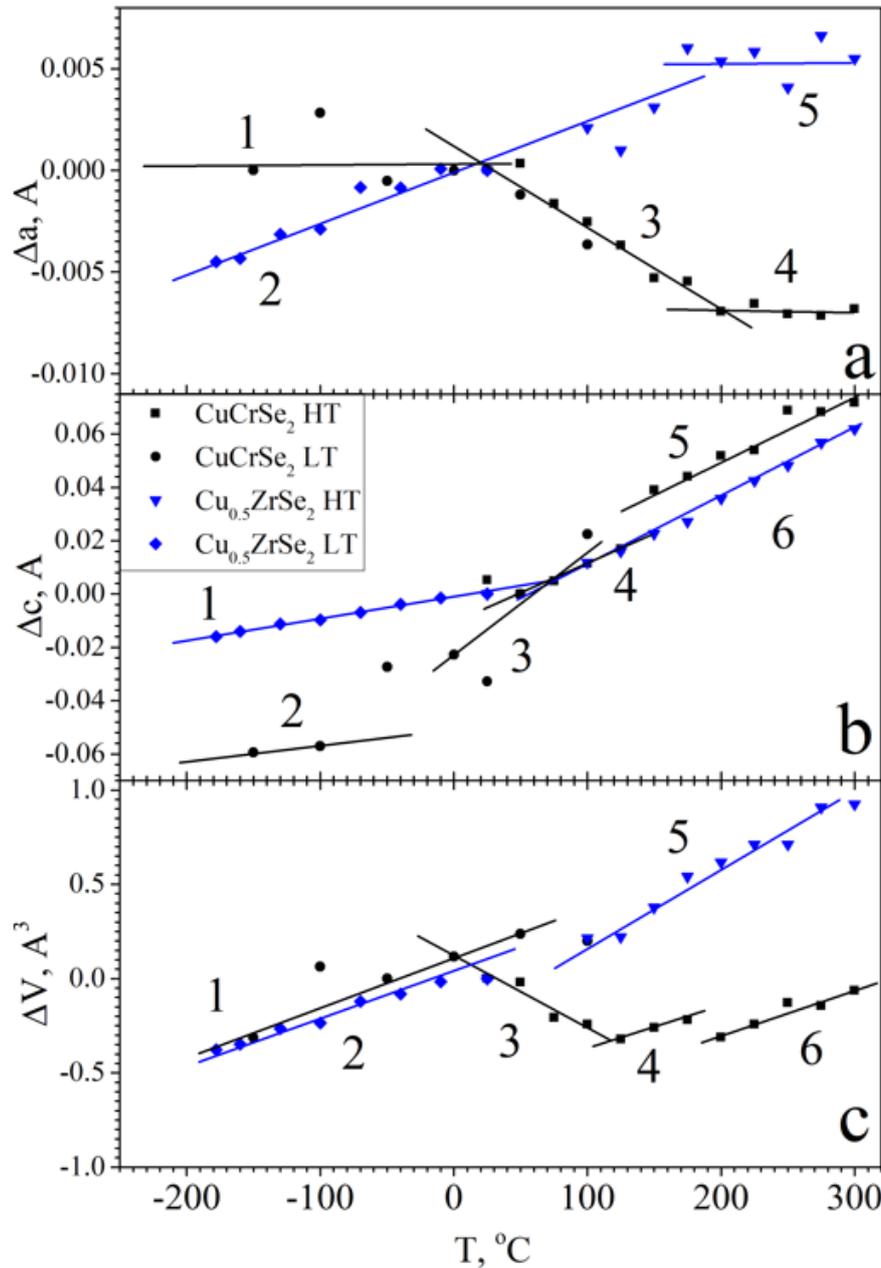


Figure 3. Temperature dependences of lattice parameters a (a), c (b) and unit cell volume V (c) for $\text{Cu}_{0.5}\text{ZrSe}_2$ and CuCrSe_2 . Areas with approximately linear TEC behavior are drawn with lines for clarity.

superionic state occurs in the temperature range $80\text{--}150^\circ\text{C}$ [16], which actually coincides with the observed transition point in the discussed $\text{Cu}_{0.5}\text{ZrSe}_2$ and CuCrSe_2 materials. Obviously, this transition should be attributed not to the elastic interaction, but to the peculiarities of the covalent bonding of copper with the selenium tetrahedral environment.

It should be noted that in the Cu_2Se superionic phase Cu atoms are also tetrahedrally coordinated by the Se ones. The average Cu-Se distance in the NCS-phase is 2.454 \AA as compared to 2.324 \AA in the CS-phase. The Cu-Se distance in the NCS phase is less than 2% different from one in Cu_2Se , which is 2.488 \AA [17]. Thus, the coordination of Cu in the NCS phase is significantly closer to that in Cu_2Se . It can be assumed that the formation of a cohesive network

of the crystallographic positions which are tetrahedrally coordinated by the Se atoms stabilizes the structural fragment similar to Cu_2Se .

Conclusions

Our data allow us to connect the non-centrosymmetric distribution of copper in materials with delafossite structure not with the anisotropy of elastic constants, as it seemed intuitively, but with the covalent interaction between tetrahedrally coordinated selenium copper atoms. This explains the reason for the absence of such ordering in ACrX_2 materials, $\text{A}=\text{Li, Na, K}$; $\text{X}=\text{S, Se}$. Indeed, the bonding of alkali metals to the lattice is almost completely ionic, so that the covalent interaction in the sublattice of metal A coordinated by chalcogen is negligibly weak.

On the other hand, the plane consisting of selenium tetrahedrons containing copper reproduces the local copper environment close to that observed in Cu_2Se . That is, a layer of material similar to binary copper chalcogenide is formed. Therefore, the nature of the transition metal forming the host lattice, Cr or Zr, is not important. Probably, compounds based on HfSe_2 intercalated with copper are also capable of exhibiting the NCS phase.

Acknowledgements

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References

- [1] J.-P. Doumerc et al., *Materials Research Bulletin* **21** (1986) 745–752. [[CrossRef](#)]
- [2] M. Fiebig et al., *Nature Reviews Materials* **1** (2016) 16046. [[CrossRef](#)]
- [3] A. Gagor et al., *Materials Chemistry and Physics* **146** (2014) 283–288. [[CrossRef](#)]
- [4] G.A. Wiegers, *Physica B+C* **99** (1980) 151–165. [[CrossRef](#)]
- [5] S.I. Novikova, *Thermal expansion of solids* (Nauka/Interperiodica, Moscow, 1974) 291 p. (In Russian) [[WebLink](#)]
- [6] R.A. Yakshibaev et al., *Fiz. Tverd. Tela* **29** (1987) 1220. (In Russian) [[GoogleScholar](#)]
- [7] A.N. Titov et al., *Physics of the Solid State* **49** (2007) 1532–1535. [[CrossRef](#)]
- [8] C.F. van Bruggen et al., *Physica B+C* **99** (1980) 166–172. [[CrossRef](#)]
- [9] A.S. Shkvarin et al., *Journal of Materials Chemistry C* **8** (2020) 8290–8304. [[CrossRef](#)]
- [10] E.G. Shkvarina et al., *The Journal of Chemical Physics* **147** (2017) 044712. [[CrossRef](#)]
- [11] E.G. Shkvarina et al., *Acta Crystallographica Section C* **74** (2018) 1020–1025. [[CrossRef](#)]

- [12] E.G. Shkvarina et al., Journal of Solid State Chemistry **328** (2023) 124307. [[CrossRef](#)]
- [13] L. Rebuffi et al., Zeitschrift für anorganische und allgemeine Chemie **640** (2014) 3100–3106. [[CrossRef](#)]
- [14] E.G. Shkvarina et al., Journal of Solid State Chemistry **330** (2024) 124497. [[CrossRef](#)]
- [15] B.H. Toby, R.B. Von Dreele, Journal of Applied Crystallography **46** (2013) 544–549. [[CrossRef](#)]
- [16] X.-X. Xiao et al., Chinese Physics B **20** (2011) 087201. [[CrossRef](#)]
- [17] S.A. Danilkin et al., Journal of Alloys and Compounds **361** (2003) 57–61. [[CrossRef](#)]