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High temperature crystal structure and chemical bonding in thermoelectric germanium selenide (GeSe)

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Abstract: The discovery of the ultra-high thermoelectric figure of merit of 2.6 in SnSe has drawn attention on other lead-free IV-VI orthorhombic semiconductors. GeSe has been predicted to possess thermoelectric performances comparable to SnSe. Here, we report a complete structural study of GeSe with temperature by means of high resolution synchrotron powder X-ray diffraction. In the orthorhombic phase, the evolution of the bond distances with temperature is shown to deviate significantly with respect to SnSe. Analysis of the chemical bonding within the Quantum Theory of Atoms in Molecules shows that GeSe is ionic with Van der Waals interlayer interactions. The signature of the N-shell lone pair of Ge is also evident from both the electron density Laplacian and the ELF topologies.

Introduction

Thermoelectric materials enable conversion of waste heat into electrical energy.^[1] The ultrahigh thermoelectric figure of merit of 2.6 has been recently reported for orthorhombic SnSe.^[2] This finding has stimulated the search for other lead-free thermoelectric candidates and orthorhombic SnS, GeS and GeSe have attracted considerable attention in view of their favorable Seebeck coefficients, power factors and low thermal conductivity.^[3] In particular, germanium selenide has been predicted to exhibit a figure of merit ranging from 0.8 at 300 K to 2.5 at 800 K.^[4] In addition to its thermoelectric performances, GeSe is inspected in view of its optic, photovoltaic and piezoelectric applications.^[5] Despite the technological importance of GeSe, only the room temperature structure including fractional coordinates and atomic displacement

parameters (ADPs) is known to date.^[6] A previous study^[7] reported the lattice thermal expansion up to the melting point at 940 K. In particular, thermal anomalies in the unit cell volume expansion were detected,^[7] the unit cell volume being constant between 670 and 770 K. Given the increased interest on the high temperature thermoelectric properties, a full structural study including atomic coordinates and ADPs is necessary for reliable theoretical investigations.

GeSe has a layered structure and high quality single crystals are difficult to grow since they cleave easily perpendicular to the long axis (*a* axis in *Pnma*), as noted for SnSe.^[8] Powder diffraction is the obvious alternative although great care has to be taken to avoid preferred orientation, which is common to layered structures such as GeSe and SnSe.^[9] The structural study of GeSe is further complicated by the very similar X-ray form factors (with ~ 6 % of difference at $\sin\theta/\lambda = 0$ for neutral Ge and Se) and neutron scattering lengths of Ge and Se (~ 3 % of difference).

In the present work we perform a complete structural study from 120 K to 940 K by means of high resolution synchrotron powder X-ray diffraction. A reconstructive phase transition to cubic rock salt is detected at 907 K for the present sample. A combined approach of Bader's Quantum Theory of Atoms in Molecules (QTAIM)^[10] and analysis of non-covalent interactions through the reduced electron density gradient^[11] shows that GeSe is formed by double layers built upon ionic bonds with a minor covalent character. Analysis of the topology of the Laplacian of the electron density reveals the formation of the lone pair of Ge upon bonding in the crystalline state. The interaction between double layers is weaker and accounted for by Van der Waals (VdW) interactions.

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Supporting information for this article is given via a link at the end of the document.

Results and Discussion

Figure 1 Structure of GeSe in the *Pnma* phase. Green and red atoms correspond to Ge and Se, respectively. Right: Coordination of Ge up to 4.0 Å at 120 K: $d_1 = 2.556(6)$ Å, $d_2 = 2.575(4)$ Å, $d_3 = 3.305(5)$ Å, $d_4 = 3.362(4)$ Å, $d_5 = 3.404(5)$ Å, $d_6 = 3.939(6)$ Å

Thermal expansion and strain

At ambient condition the structure of GeSe is orthorhombic (*Pnma*, n. 62) with $a = 10.830(10)$ Å, $b = 3.8338(3)$ Å, $c = 4.3900(6)$ Å. In particular, the structure consists of double layers held by a network of short bonds ranging from 2.5 to 3.3 Å, whereas contacts involving atoms belonging to different double layers range from 3.3 to 3.9 Å (Figure 1). This explains the very easy cleavage perpendicular to the long axis.

Figure 2 Thermal expansion of the a, b, c axes and of the unit cell volume, V , as a function of temperature (*Pnma* phase). At $T \sim 600$ K the slope of the thermal expansion of a, b, V changes. At $T = 907$ K, with the appearance of the cubic phase, the volume of the orthorhombic phase contracts. Sigma are smaller than the symbols. Numerical values are reported in the supporting information.

The cell parameters of the orthorhombic phase qualitatively reproduce the trend observed in reference^[7] i.e. the a, b axes in *Pnma* increase as a function of temperature while c features negative thermal expansion as in SnSe (Figure 2).^[8,12] The zero-

thermal expansion between 673 and 773 K previously reported^[7] is not supported by the present measurements. In this range of temperatures a slight change in the thermal expansion of the a and b axes and, therefore of the volume, is found instead. The orthorhombic cell contracts of $\sim 0.3\%$ at 907 K, in correspondence with the appearance of the cubic phase. The volume expansion coefficients of GeSe is $3.7(3) \cdot 10^{-5} \text{ K}^{-1}$ for $120 \text{ K} < T < 641 \text{ K}$ and $4.7(7) \cdot 10^{-5} \text{ K}^{-1}$ for $641 \text{ K} < T < 900 \text{ K}$.

A visible sharpening of the diffraction peaks occurs for $T > 500 \text{ K}$. Simultaneously, the scale parameter from the Rietveld refinement increases with temperature while the background decreases, suggesting that an amorphous part is becoming crystalline, which is reminiscent of phase change transition in GeTe.^[13] Peak broadening can be caused by micro-strain or crystallite size. Peak broadening is found to be caused by micro-strain through the Williamson-Hall plot^[14] and strain decreases by a factor of ~ 10 as a consequence of the annealing process (Figure 3). Analysis of anisotropic strain^[15] reveals that a significant change occurs at 650 K, with reversal of the sign of S_{040} , S_{004} and S_{022} . Analysis on an annealed powder in a capillary reveals that micro-strain is present to a much lower extent when the powder is not crushed. This means that a large amount of micro-strain was introduced in the sample preparation and it is not intrinsic to the material. Nevertheless, it is important to keep in mind the effect of such a large change of strain at high temperatures, e.g. in the mechanical stability of thermoelectric devices.^[16]

Figure 3 Left: micro-strain parameter ϵ as a function of temperature. Right: anisotropic strain parameter coefficients as implemented in JANA2006.

Although the zero-thermal expansion between 673 K and 773 K is not confirmed by the present data, in this range of temperature a change occurs in the thermal expansion, in micro-strain and in anisotropic strain. This infers that some kind of structural rearrangement, e.g. rearrangement of defects, takes place in the same range of temperature at which Wiedemeier and Siemers report thermal anomalies.^[7]

Phase transition

Asanabe and Okazaki^[17] have reported an anomaly in the electrical resistivity at around 200 K. Abrupt changes or discontinuities in electrical resistivity at 160–170 K have been confirmed by different studies.^[18,19] Raman studies have shown the appearance of new lines at 89, 201 and 226 cm^{-1} below 150 K suggesting that a structural phase transition with either increase of the unit cell or lowering of the crystal symmetry

occurs.^[20] As pointed out by some of the same authors of the aforementioned studies, no indications of any structural phase transition have been found by means of diffraction techniques.^[20,21] The electrical anomalies have been explained through a complex two impurity levels mechanism^[17] or invoking two different kinds of localized states due to stacking faults and twinning.^[19, 22] Given that no extra-peaks or anomalous isotropic ADPs are detected at 120 K, the present data support the absence of a structural phase transition down to 120 K, within the precision of the present experiment.

At 907 K a Bragg peak ascribable to the (002) peak in the $Fm\bar{3}m$ phase^[7] appears and the cubic phase co-exists with the orthorhombic phase up to the melting point at 940 K at which no diffraction peaks are present, Figure 4.

Figure 4 Diffraction pattern showing the appearance of the (002) cubic phase reflection.

Non-stoichiometry

Given the well-known non-stoichiometry of IV-VI semiconductors^[23] and the presence of a tiny quantity of elemental germanium, it could be expected that GeSe is non-stoichiometric because of germanium vacancies. Nevertheless, refinement of the occupancy of Ge suggests that the present sample is fully stoichiometric (see supporting information). Given the presence of strain, high background, the very similar form factor of Ge and Se, we cannot exclude that the data quality does not allow discerning such a small detail.

Fractional coordinates

Different structural models were tested to check the bias introduced on the structure factors in the Rietveld refinement and its influence on the final structural parameters. The final model is reported and all technical details are confined in the supporting information.

The values of fractional coordinates are in agreement with the values at room temperature published in the previous single crystal diffraction study.^[6] In $Pnma$ Ge and Se sit in the 4c (x , $\frac{1}{4}$, z) position which features a mirror plane passing through $y =$

$\frac{1}{4}$ and parallel to the xz plane. Therefore $y(\text{Ge}) = y(\text{Se})$ is fixed to $\frac{1}{4}$. At room temperature $x(\text{Ge}) = 0.12290(3)$, $z(\text{Ge}) = 0.11057(9)$, $x(\text{Se}) = 0.85491(3)$, $z(\text{Se}) = 0.50131(8)$. The evolution of fractional coordinates $x(\text{Ge})$, $z(\text{Ge})$, $x(\text{Se})$, $z(\text{Se})$ is shown in Figure 5. The atomic fractional coordinates are practically temperature-independent. This constitutes a remarkable difference with SnSe which features a displacive phase transition slightly above 800 K: in SnSe $z(\text{Sn})$ in $Pnma$ becomes zero on warming, rendering d_2 and d_3 equal in $Cmcm$.^[23a] Conversely, in GeSe, d_2 and d_3 are nearly constant with increasing temperature (Figure 6). Hence, the Ge coordination in the orthorhombic phase does not rearrange towards cubic symmetry as hypothesized in view of the similar thermal expansion of GeSe and SnSe.^[7] This outlines an important difference with SnSe, which undergoes a displacive phase transition to $Cmcm$, whereas GeSe undergoes a reconstructive phase transition to $Fm\bar{3}m$.

Figure 5 Fractional coordinates of Ge and Se as function of temperature in the $Pnma$ settings. $y(\text{Ge}) = y(\text{Se}) = \frac{1}{4}$. The fractional coordinates change with temperature is less than 0.005, i.e. negligible.

Figure 6 Temperature variation of distances around the Ge atom (symbols) in accordance to Figure 1. Full lines correspond to the analogous distances in SnSe. In SnSe, at around 805 K d_2 and d_3 become equal in the high temperature phase $Cmcm$.

Atomic displacement parameters

The ADPs account for the atomic motion due to thermal energy and/or due to disorder. Large ADPs are found for atoms loosely bonded, and in the harmonic approximation ADPs decrease with the atomic mass. As shown in the supporting information, estimation of the isotropic equivalent ADPs is model-independent as it does not depend on the peak overlapping partitioning, but only on the $\sin\theta/\lambda$ value.

Figure 7 Isotropic equivalent ADPs of Ge and Se.

At room temperature the isotropic ADPs $U_{iso}(\text{Ge}) = 0.0143(2) \text{ Å}^2$, $U_{iso}(\text{Se}) = 0.0091(4) \text{ Å}^2$ are in disagreement with $U_{eq}(\text{Ge}) = 0.0086(4) \text{ Å}^2$ and $U_{eq}(\text{Se}) = 0.0067(4) \text{ Å}^2$ obtained from single crystal X-ray diffraction,^[6] and the values are closer to the ADPs of Sn and Se in SnSe^[23a] ($U_{eq}(\text{Sn}) = 0.01313(18) \text{ Å}^2$ and $U_{eq}(\text{Se}) = 0.0115(2) \text{ Å}^2$). As in SnSe and SnTe,^[23b] the cation has a larger ADP with respect to the anion and the difference increases with increasing temperature, Figure 7. U_{iso} increases on warming, but with different slope at $T < 600 \text{ K}$ and $T > 600 \text{ K}$. This is similar to what is observed in SnSe.^[23a]

The Debye equation^[24] can be used to probe the lattice dynamics in GeSe:

$$U_{iso}(T) = \frac{3h^2T}{4\pi^2mk_B\theta_D^2} \left(\frac{T}{\theta_D} \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx + \frac{\theta_D}{4T} \right) + d^2$$

where T is the temperature, m is the atomic mass, θ_D is the Debye temperature, h is the Planck constant, k_B is the Boltzmann constant, d^2 is the disorder parameter. The Debye temperature calculated using U_{iso} obtained at $120 \text{ K} < T < 600 \text{ K}$ is $205(3) \text{ K}$ for Ge, $226(3) \text{ K}$ for Se, $214(3) \text{ K}$ if an hypothetical atom with averaged U_{iso} and mass is used. The disorder parameter, d^2 , is zero within the sigma for Ge, Se and the averaged atom, which tends to exclude the presence of static disorder. Although the Debye temperature is strictly defined for

cubic monoatomic crystals, the low Debye temperature is indicative of weak bonds.

Refinement of anisotropic ADPs in the Rietveld refinement leads to $U_{22} > U_{33} > U_{11}$ with U_{11} slightly negative at 120 K , i.e. unphysical. To limit the bias introduced in the Rietveld refinement the structure factors were extracted using isotropic ADPs, and anisotropic ADPs were subsequently refined against the extracted structure factors (see supporting information). The resulting anisotropic ADPs are depicted in Figure 8.

Figure 8 Anisotropic ADPs refined against extracted structure factors using isotropic ADPs in the Rietveld model.

Interestingly, in this latter model the components U_{ij} are very similar below 600 K and the ADPs become increasingly anisotropic with $U_{22} \approx U_{33} > U_{11}$ above 600 K . A similar behavior has been reported for SnSe from neutron single crystal diffraction and X-ray powder diffraction experiments,^[8,23a] but it is in disagreement with the anisotropic ADPs in GeSe at room temperature from single crystal X-ray diffraction^[6] ($U_{11}(\text{Ge}) = 0.0115(6) \text{ Å}^2$, $U_{22}(\text{Ge}) = 0.0037(6) \text{ Å}^2$, $U_{33}(\text{Ge}) = 0.0096(5) \text{ Å}^2$, $U_{11}(\text{Se}) = 0.0100(6) \text{ Å}^2$, $U_{22}(\text{Se}) = 0.0023(5) \text{ Å}^2$, $U_{33}(\text{Se}) = 0.0072(5) \text{ Å}^2$ in the $Pnma$ setting). Theoretical ADPs have been computed in CRYSTAL14^[25] at the experimental geometries using various functionals (PBE, PBE-D2 and PBE0) and pob-TPVZ as basis set.^[26] Although the anisotropic ADPs depend on the functional employed, there is a qualitative agreement that for Ge $U_{22} > U_{33} > U_{11}$, i.e. the potential is harder along the a -direction in $Pnma$, which qualitatively corroborates our findings, Figure 9.

Figure 9 Anisotropic ADPs of Ge and Se as a function of temperature as obtained from PBE/pob-TPVZ (circles), PBE-D2/pob-TPVZ (triangles) and PBE0/pob-TPVZ (squares).

Topological analysis of the charge density, $\rho(r)$

The topological analysis of the electron density was performed with TOPOND14^[27] on the theoretical electron density obtained by fixing the cell parameters to the experimental values at 120 K

and refining the atomic coordinates with PBE0/pob-TPVZ. The refined fractional coordinates are $x(\text{Ge}) = 0.1220$, $y(\text{Ge}) = 0.2500$, $z(\text{Ge}) = 0.10623$, $x(\text{Se}) = 0.8546$, $y(\text{Se}) = 0.2500$, $z(\text{Se}) = 0.4996$, in fair agreement with the experimental values.

Six unique bond critical points are found around the germanium atom (Table 1 and Figure 10). The first five unique bond critical points correspond to d_1 to d_5 i.e. to the shortest atomic contacts (six Ge-Se and two Ge-Ge) present in the structure. An additional bond critical point, d_6^* , is found between Se (x, y, z) and Se ($-x, -1/2+y, 1-z$), which are ~ 3.67 Å apart. No bond critical point is present in d_6 .

Figure 10 Bond critical points (3,-1) (purple) of $\rho(r)$ around the germanium atom.

Table 1. Topological descriptors at the bond critical points. They are related to Ge (x, y, z) unique interactions (d_j , $j = 1-5$) with: Se ($1/2+x, 1/2-y, 1/2-z$) in d_1 ; Se ($-x, -1/2+y, 1-z$) in d_2 ; Se ($-x, -0.5+y, -z$) in d_3 ; Se (x, y, z) in d_4 ; Ge ($-x, -1/2+y, -z$) in d_5 ; where Ge (x, y, z) = Ge (0.1220, 0.25, 0.10623) and Se (x, y, z) = Se (-0.14541, 0.25, 0.4996); Se (x, y, z) and Se ($-x, -1/2+y, 1-z$) are 3D attractors in d_6^* . $H(r_b) = G(r_b) + V(r_b)$. $\rho(r_b)$ and $\nabla^2\rho(r_b)$ are given in $\text{e} \text{Å}^{-3}$ and $\text{e} \text{Å}^{-5}$, respectively, while $G(r_b)$, $V(r_b)$ and $H(r_b)$ in $\text{kJ mol}^{-1} \text{Å}^{-3}$. Distances d_j ($j = 1-6$) and d_{bcp} (distances from Ge nucleus to bcp; for d_6^* from Se nucleus) in Å. Values in parentheses refer to the IAM electron density (which lacks d_6^* bcp).

Bond	d_j	d_{bcp}	$\rho(r_b)$	$\nabla^2\rho(r_b)$	$G(r_b)$	$V(r_b)$	$ V(r_b) /G(r_b)$	$H(r_b)$
d_1	2.556 (1.205)	1.138 (1.205)	0.41	0.76 (1.22)	447 (496)	-755	1.69	-308
d_2	2.591 (1.230)	1.160 (1.230)	0.39	0.80 (1.22)	413 (467)	-679	1.64	-265
d_3	3.285 (1.667)	1.593 (1.667)	0.11	0.76 (0.97)	137 (170)	-135	0.98	2
d_4	3.365 (1.714)	1.612 (1.714)	0.10	0.73 (0.90)	127 (150)	-120	0.95	7
d_5	3.387 (1.694)	1.694 (1.694)	0.10	0.55 (0.77)	106 (159)	-111	1.04	-4
d_6^*	3.677	1.839	0.07	0.59	97	-86	0.88	11

If judged with the classical QTAIM dichotomous classification based on the value of the Laplacian at the bond critical point, $\nabla^2\rho(r_b)$,^[10,28] the bonding between Ge and Se is of

closed shell type ($\nabla^2\rho(r_b) > 0$) and ionic (see infra the values of integrated atomic charges). However, the isolated Se atom has a positive $\nabla^2\rho(r)$ value at its outermost valence shell charge concentration maximum^[29] and the Ge atom even lacks the valence shell charge concentration relative to the 4s4p shell. Thus, the $\nabla^2\rho(r_b)$ value cannot be used as a dichotomous bond classification criterion in this case.^[28b] A more correct analysis is that of comparing the $\nabla^2\rho(r_b)$ value with that of IAM (Independent Atom Model) at the same location. If upon bonding $\nabla^2\rho(r_b)$ turns out to be less positive than the corresponding value of IAM, this can be considered as a sign of partial covalency even if $\nabla^2\rho(r_b)$ remains positive. In Table 1, data for the IAM model and relative to IAM bcp locations are reported in parentheses. It is evident that bonding implies a significant lowering of $\nabla^2\rho(r_b)$ relative to IAM, and especially so for the shorter and stronger contacts. $G(r_b)$ also decreases upon bonding, as expected. For Ge-Se interactions, the distance from the Ge nucleus to the bcp, d_{bcp} , clearly diminishes upon bonding due to the electron charge transfer from Ge to Se. When the IAM $\nabla^2\rho(r_b)$ value is taken at the same location of the “true” electron density bcp, qualitatively similar results as those reported in the Table are obtained (e.g. 1.13 and 1.04 $\text{e} \text{Å}^{-5}$ for d_1 and d_2). The value $|V(r_b)|/G(r_b)$ larger than 1 and the negative $H(r_b) = G(r_b) + V(r_b)$ indicate a partial covalent character for d_1 and d_2 . All other bond critical points may be associated to closed-shell like interactions. d_1 , d_2 , d_3 involve atoms in the same double layer whereas d_4 , d_5 , d_6^* involve two adjacent double layers. Integration over the atomic basins leads to the atomic Bader's charges, which are 0.72 e for Ge and -0.72 e for Se. It can be concluded that crystalline GeSe is formed by double layers built upon ionic bonds with a minor covalent character.

Topological analysis of the Laplacian of the charge density, $\nabla^2\rho(r)$

In principle, the analysis of the Laplacian can provide a powerful insight in locating the lone pair which is intimately linked to anharmonicity in the IV-VI compounds and therefore to their low thermal conductivities.^[30] In fact, the topological analysis of the Laplacian of the charge density is customarily used to discern local concentrations of charge density identified by a maximum in $-\nabla^2\rho(r)$ and local depletions of charge density identified by a minimum in $-\nabla^2\rho(r)$. In the case of GeSe, however, the situation is more challenging due to the “anomalous” behaviour of the electron density Laplacian in the outermost shell of the Ge and Se isolated atoms. According to such behaviour, one would so expect, upon bonding, positive rather than negative values of $\nabla^2\rho(r)$ at the Se charge concentrations and only charge concentrations relative to the 3s3p shell (M shell) around Ge.

In fact, around the Ge atom, there are four, rather than three, non-equivalent (3,-3) critical points in $-\nabla^2\rho(r)$, which belong to the Ge atomic basin, G_1 , G_2 , G_3 , G_4 , and two non-equivalent (3,-3) critical points belonging to the Se atomic basin,

S_1 , S_2 (Figure 11, Table S8). G_1 , G_2 and G_3 are 0.24 Å far from the Ge nucleus and with a slightly distorted tetrahedral arrangement, while S_1 , S_2 are 0.95 Å from the Se nucleus (compatible with charge concentration in the 4s4p shell, N shell, of Se).

Figure 11 Critical points (3,-3) in $-\nabla^2\rho(r)$ around the germanium atom.

The distances between G_i ($i=1-3$) and the Ge nucleus fit with the position of the maximum in $-\nabla^2\rho(r)$ for the M shell in the atomic germanium (0.247 Å).^[29] The fourth concentration G_4 is instead located 1.14 Å from Ge and almost collinear with G_3 (the Ge- G_3 - G_4 angle is 171.1°). G_4 is clearly associated with the lone pair of Ge belonging to the shell N, involving 4s and 4p orbitals. Upon bonding, the lone pair charge concentration due to the N shell becomes visible and it is no longer hidden by the dominance of the M shell as in the isolated atom. As supported by their almost perfect collinearity, the two charge concentrations G_3 and G_4 spot the lone pairs of Ge due to the M and N shells, respectively. No bonded charge concentrations for the N shell of Ge are recovered because of the electron charge transfer from Ge to Se. G_4 has, as expected, a positive Laplacian value (0.39 e Å^{-5}), and it is associated with a region of minimum charge depletion in the valence shell charge depletion region of the Ge atom, while S_1 , S_2 are characterized by negative Laplacian values (-1.74 and -1.59 e Å^{-5}) as charge transfer from Ge to Se is accompanied by the appearance of a charge concentration region in the Se N shell (the Ge-Se bcps, however, are displaced toward Ge, and fall in the N shell charge depletion region, see earlier). The N shell lone pair of Ge is evident in the $\nabla^2\rho(r)$ contour plot in the plane containing the Ge nucleus, its closest Se atom and G_4 . Even more evident is its detection in the corresponding Electron Localization Function (ELF)^[31] contour plot (Figure 12). Both plots show that the Ge N shell lone pair faces regions of relative charge density depletions of the neighbouring Se atoms, in a clear key-lock arrangement. $\nabla^2\rho(r)$ and ELF contour plots for the IAM model in the same plane provide further demonstration for the appearance of the N shell lone pair upon bonding (Figure

S7 and S8). Electronic charge transfer from Ge to Se and the appearance of the Ge N shell lone pair is also supported by the electron density deformation ($\rho_{\text{true}} - \rho_{\text{IAM}}$) map (Figure S9).

Upon bonding, the Ge atom becomes polarized in a direction counter to the direction of the charge transfer, as customarily found for polar interactions.^[27] In fact, the centroid of electronic charge of Ge is displaced by 0.014 Å from the Ge nucleus and it almost perfectly aligns (angle 171.0°) with the two lone pair concentrations (N and M shell), providing a further evidence for the Ge lone pair presence and location. Upon charge transfer from Ge to Se, electron density around Ge preferentially displaces and concentrates in the Ge lone pairs region (see also data in Table S8, showing that $|\nabla^2\rho(r)|$ and $\rho(r)$ are larger at G_3 than are at the other three charge concentrations G_1 and G_2).

Before concluding the analysis of the Laplacian distribution around the Ge atom, we strengthen that what we call an M-shell “lone pair” charge concentration, G_3 , could have also be classified as a core polarization (and, likewise, G_1 and G_2). The former description was preferred since the Ge atom, due to charge transfer to Se, does not show any signature of N-shell bonded concentrations and since the three M-shell charge concentrations G_1 , G_2 nicely fit with the sp^3 -like bonding arrangement around the Ge atom.

Figure 12 $\nabla^2\rho(r)$ (left) and ELF (right) contour plots in a plane containing the Ge nucleus, its closest Se atom and G_4 . Contour levels: $\nabla^2\rho(r)$ at ± 2 , ± 4 , and $\pm 8 \times 10^6 \text{ au}$, with n ranging from 0 to -3 . Red (dashed blue) lines denote positive (negative) contour values. The (3,-3) critical points in $-\nabla^2\rho(r)$ (N shell) are highlighted. For the ELF, the first blue dashed contour is the zero contour and the increase is 0.05 per contour up to 0.45. The first full red contour has the value of 0.50 and the increase is 0.05 up to 1.00

Inter-layers interactions

GeSe is partly ionic. The easy cleavage perpendicular to the longest axis indicates that the interaction between different double layers is weak. The bond critical points found in the inter-layer region are in correspondence with very low values of $\rho(r_b)$ and of atomic distances larger than 3.3 Å. Non-covalent interactions can be probed through the NCI plots^[11,32] (Figure 13). In the NCI plots, negative values of $\text{sign}(\lambda_2)\rho(r)$, colored here in red and green, indicate the presence of stabilizing contributions, while positive values of $\text{sign}(\lambda_2)\rho(r)$, colored in blue and violet, indicate the presence of steric/repulsive interactions. To gain insight on the inter-layer interactions, a calculation with PBE0/pob-TPVZ on a geometry with only half of

the double layers was performed and the corresponding NCI plot was compared with the one derived from the geometry optimization with PBE0/pob-TPVZ on the full structure. In both cases clear stabilizing contributions are found in correspondence with the d_1 and d_2 bonds, i.e. the ionic intra-layer bonds. Features of negative values of $\text{sign}(\lambda_2)\rho(r)$ in the inter-layer region are found only in the presence of the second double layer. Such inter-layer stabilizing contributions are markedly much weaker than those in the intra-layer bonding, but they constitute a clear sign of the inter-layer interaction.

Figure 13 RDG-based NCI isosurfaces corresponding to $\text{RDG} = 0.9$ a.u. The surfaces are colored on a red-green-blue-purple scale $-0.050 < \text{sign}(\lambda_2)\rho(r) < 0.045$ a.u. Left: NCI isosurface plot obtained by removing one double layer for each cell; blue regions indicate destabilizing contributions. Right: NCI plot obtained in the full cell showing stabilizing features (red arrows) in the inter-layer region.

Conclusions

A full structural study of GeSe has been carried out from 120 K up to the melting point. The lattice thermal expansion and the ADPs of GeSe have been proven to be very similar to SnSe. In particular: i) the c axis in $Pnma$ features negative thermal expansion, ii) the isotropic equivalent ADP of the cation is larger than the anion and the increase of ADPs with temperature deviates from linearity at $T \approx 600$ K, iii) the ADPs become more anisotropic at high temperature. At variance with SnSe, in GeSe d_2 and d_3 do not approach significantly with increasing temperature, but the sample partially undergoes a reconstructive phase transition to cubic at 907 K. The orthorhombic and cubic phases co-exist up to the melting point at 940 K.

Analysis of the chemical bonding within the Quantum Theory of Atoms in Molecules shows that the intra-layer framework in GeSe is ionic with minor covalent contributions. The isolated Ge atom is not expected to exhibit charge concentration relative to the 4s4p shell, however, upon bonding, the formation of a (3,-3) critical point in $-\nabla^2\rho(r)$ 1.14 Å from Ge, and almost collinear with the charge concentration maximum

relative to the M-shell, G_3 , is a clear sign of the presence of the lone pair in crystalline GeSe. The present analysis could be in principle applied to experimental multipole model electron density distributions to locate the presence of the lone pair in similar systems. The local charge concentration is also corroborated by the ELF analysis. NCI analysis shows Van der Waals interlayer interactions.

Experimental Section

Synthesis

1 g of GeSe was synthesized by placing stoichiometric amounts of Ge and Se in a ~20 cm quartz tube (inner diameter: 11.4 mm). The quartz tube was evacuated to 10^{-5} mbar and subsequently sealed and heated in a tube furnace with the following temperature profile: heating from 300 K to 723 K (rate: 10 K / hour), kept for 36 hours at 723 K and subsequently cooled to room temperature (rate: 25 K / hour). The powder was crushed and resealed in a quartz tube, evacuated to 10^{-5} mbar and heated in a tube furnace with the following temperature profile: heating 300 K to 873 K (rate: 75 K / hour), kept for 12 hours, cooled to room temperature (rate: 100 K / hour).

Synchrotron X-ray powder diffraction

The GeSe sample was prepared by floating the crushed powder in ethanol, and then placed in a 0.2 mm diameter quartz capillary. The capillary was sealed under argon to prevent oxidation. Data were collected at BL44B2^[33] at SPring-8, Japan. The wavelength was refined to 0.50030 Å using CeO_2 as standard ($a = 5.411651$ Å). An image plate detector was used. Data were measured from 120 K to 940 K (see supporting information). The temperature was calibrated with a thermocouple.

Refinements were carried out with JANA2006.^[34] Data were corrected for anomalous dispersion ($f'_{\text{Ge}} = 0.315$, $f''_{\text{Ge}} = 0.978$, $f'_{\text{Se}} = 0.290$, $f''_{\text{Se}} = 1.222$). The Berar's correction^[35] was applied to obtain reliable standard uncertainties from the Rietveld refinement. Initially, a profile fitting was performed including 5 background terms (Chebyshev polynomials), Gaussian GW and Lorentzian LY parameters of the Thomson-Cox-Hastings pseudo-Voigt function,^[36] anisotropic strain parameters $S202$, $S040$, $S022$, $S004$ in the modified version of Stephens formalism^[15] as implemented in JANA2006,^[37] and specimen displacement, sycos . In the Rietveld refinement scale, $x(\text{Ge})$, $z(\text{Ge})$, $x(\text{Se})$, $z(\text{Se})$, and ADPs were refined. $y(\text{Ge})$ and $y(\text{Se})$ were fixed to 0.25. At $T > 841$ K the R-factors increase despite the maximal resolution decreases and the difference between the observed and the calculated powder pattern shows marked discrepancies. The scale parameter decreases significantly. For well packed capillaries, the packing ratio is around 30 %.^[38] Given that sublimation occurs already at 843 K^[39] it is likely that vapors of GeSe move from the hot side of the

capillary, i.e. the one that is under the N₂ flow, to the cold one, i.e. the part of the capillary which is on the sample holder. Particle sintering and decrease of scale result in a worsening of particle statistics, which leads to a worsening of the Rietveld fit. Therefore Rietveld refinements were carried out at data collected up to 841 K, whereas only profile fitting was performed at higher temperatures.

Theoretical calculations

Periodic quantum mechanical calculations were performed with CRYSTAL14.^[25a] The functionals PBE,^[26b] PBE-D2, i.e. PBE corrected with Grimme's dispersion correction^[26a,40] and PBE0^[26c] were used with the basis-set pob-TPVZ.^[26d] The reciprocal space was sampled with a 8 × 8 × 8 grid in the irreducible Brillouin zone. Frequencies at the experimental geometry of each temperature and corresponding anisotropic ADPs were computed.^[25b]

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Keywords: Germanium selenide • GeSe • Crystal structure • Thermoelectric • Chemical bonding

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The crystal structure of GeSe is studied up to the melting point with high resolution synchrotron X-ray diffraction and compared with SnSe. Analysis of the chemical bonding within the Quantum Theory of Atoms in Molecules shows that GeSe is mainly ionic with Van der Waals inter-layer interactions.

Mattia Sist, Carlo Gatti, Peter Nørby, Simone Cenedese, Hidetaka Kasai, Kenichi Kato, and Bo B. Iversen***

Page No. – Page No.

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Page No. – Page No.

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Text for Table of Contents