1. Introduction

Gold, despite being very inert, can produce solids with quite remarkable properties. One of the most interesting are the materials containing Au and Te—metallic alloys [1, 2], and for certain compositions—real stoichiometric chemical compounds. Among those the main attention until now was attracted to AuTe₂—mineral calaverite (we recently predicted that also the compound with 1:1 ratio, AuTe could also exist [3]). For many years calaverite presented a puzzle for investigators. It is a rare case, of a solid having an incommensurate crystal structure [5–8]. Its puzzling behaviour was finally explained only recently [3], as a consequence of spontaneous charge disproportionation in situation with negative charge transfer gap. AuTe₂ is also interesting because it is one of very few materials containing Au which become superconducting when doped by Pd or Pt [8–10], and also under relative by small pressure of order of 2.6 GPa [12].

There exists in nature related materials, minerals muthmannite AuAgTe₂ [13, 14] and sylvanite AuAgTe₄. In sylvanite Au and Ag ions are ordered in stripes, and Te₆ octahedra around metals are distorted in such a way that Ag becomes linearly coordinated, what is typical for Ag¹⁺, whereas Au is square coordinated—it is typical for d⁸ configurations, i.e. one can assign to Au the valence 3⁺. Our theoretical study shows that at pressure Pₐ ≈ 5 GPa there should occur in it a structural transition such that above this critical pressure Te₆ octahedra around Au and Ag become regular and practically identical. Simultaneously Te–Te dimers, existing at P = 0 GPa, disappear, and material from a bad metal becomes a usual metal with predominantly Te 5p states at the Fermi energy. We expect that, similar to AuTe₂, AuAgTe₄ should become superconducting above Pₐ.

Keywords: sylvanite, structural transition, electronic structure, high-pressure phase

(Some figures may appear in colour only in the online journal)
states as it occurs e.g. in Cs₂Au₂Cl₆ [16]. Judging from the detailed crystal structure one can conclude that this is indeed what happens in AuAgTe₄. Apparently here the valencies of Au and Ag are different. Ag is surrounded by compressed Te₆ octahedra, so that Au becomes linearly coordinated (it has two short bond of 2.73 Å, two middle bonds of 2.92 Å and two long bonds of 3.22 Å). On the other hand, Te₆ octahedra around Au are strongly elongated, so that Au have four short bonds of 2.67 Å (2.69 Å) and two long bonds of 3.22 Å, and is practically square-coordinated, see figure 1. This coordination is common for Au²⁺ (d⁵) or for Au³⁺ (d⁶) states due to a strong Jahn–Teller effect on those (note that, as we just have mentioned, chemically Au³⁺ can hardly be stabilized; and Au²⁺ is a negative charge transfer ion, so that it’s real electronic configuration is in fact not d⁵, but rather d⁵L or even d⁶L², where L stands for a ligand hole [17–19]. Note right away that these distortions also lead to modification of Te sub-lattice, so that in it short Te–Te dimers are formed, with two Te’s in a dimer belonging to different MTe₂ planes (M = Ag, Au). Formation of such dimers may provide a rather strong coupling between these layers, so that AuAgTe₄ (and similarly AuTe₂) should not be treated as a van der Waals system.

In contrast to a relatively well studied AuTe₂, AuAgTe₄ attracted much less attention. Encouraged by extraordinary properties of calaverite AuTe₂, we undertook a theoretical investigation of sylvanite AuAgTe₄, using ab-initio calculations, in particular studying the behaviour of this material under pressure. Quite interestingly, we found that at a pressure of about Pₐ ≈ 5 GPa crystal structure of it should strongly change, so that, first of all, structural distortions disappear and MTe₆ octahedra around Au and Ag become regular, with equal Au–Te and Ag–Te distances; and second, despite different chemical elements, these AuTe₂ and AgTe₂ octahedra become practically identical, with the same M–Te bond lengths. Simultaneously with that Te–Te dimers disappear, so that in a sense this material under pressure becomes more two-dimensionaL. As to electronic structure, at ambient pressure due to Te–Te dimer formation the density of states at the Fermi energy develops a pseudogap, but at P > Pₐ this pseudogap disappears, and this material becomes a regular metal with Te 5p states at the Fermi level, so that the system turns out to be a so-called p-metal [12]. We believe that these changes may lead to the formation of superconductivity at the high-pressure phase of AuAgTe₄.

Figure 1. The crystal structure of AuAgTe₄ at room temperature and ambient pressure (left figure) and the structure obtained in GGA + SOC approximation at 5 GPa (right figure). The unit cell is marked by a dashed line. The crystal structure was drawn using VESTA [4] software.

2. Calculation details

The electronic structure calculations of AuAgTe₄ were carried out using the Vienna Ab-initio Simulation Package (VASP) [20, 21]. We utilized the projector augmented-wave (PAW) method [22] with the Perdew–Burke–Ernzerhof (PBE) type of exchange-correlation functional within the general gradient approximation (GGA) [23]. The energy cutoff was chosen to be E_cutoff = 500 eV and 4 × 4 × 2 Monkhorst–Pack grid of k-points was used during the calculations. The crystal structure was relaxed until forces falled behind 0.0005 eV Å⁻¹. The spin–orbit coupling (SOC) was included to the calculation scheme. The electron population numbers were obtained by integration within atomic spheres with radii 1.503 Å, 1.503 Å and 1.535 Å for Au, Ag, and Te correspondingly.

3. Results

The partial densities of states of AuAgTe₄ at normal conditions and at 10 GPa are presented in figure 2(a). At ambient pressure AuAgTe₄ has a pseudogap at the Fermi energy, which is due to presence of Te–Te dimers. This can be easily seen from figure 3, where the crystal orbital overlap population (COOP) function for Te 5p states is plotted (calculated in the local density approximation using the linearized muffin-tin approximation [24]). The COOP is a very useful tool to study chemical bonding. Positive COOP corresponds to bonding, while negative to antibonding states [25]. One may see from figure 3, that the Fermi level is almost exactly in the place where the COOP (corresponding to the p states of nearest neighbor Te ions) changes its sign. Thus, the pseudogap in AuAgTe₄ appears due to the bonding-antibonding splitting between Te p states in the Te–Te dimer.

The width of Au 5d band is about 4 eV and it is broader than Ag 4d one on ~1 eV. This is due to larger principal quantum number of covalent d orbitals and plaquette geometry of Au ions. Also the Au 5d band lies lower than Ag 4d band (on ~0.4 eV). The spin–orbit coupling shifts positions of both Au 5d and Ag 4d bands deeper in energy (compare figures 2(a) and (b)).

Another interesting feature of AuAgTe₄ electronic structure is that the Te 5p band lies higher than Ag 4d and Au 5d ones. This suggests that AuAgTe₄ is also (as AuTe₂) in the negative charge transfer energy regime [18, 19]. It means that
the 4d and 5d holes of transition metal ions will prefer to move to 5p shell of Te ions, and Au and Ag ions will have a much larger electronic occupation than one would expect from naive ionic consideration. Indeed there are 9.09 and 9.58 electrons on Au and Ag ions according to our GGA + SOC calculations. It also demonstrates a high level of hybridization between 4d (5d) TM and Te 5p states.

The results of structural optimization of AuAgTe₄ under pressure are summarized in figure 4 and in table 1. At 0 GPa the crystal structure of AuAgTe₄ is stable, the deviation of the calculated structure from the experimental one is negligible. But we see that with pressure a gradual decrease of distortions around Au and Ag takes place, and above critical pressure of $P_C \sim 5$ GPa the MTe₆ octahedra become practically ideal with all M–Te bond lengths equal (see figure 1). The elastic tensor was determined by calculation of six distorted lattice configurations and deriving the elastic constants from the strain-stress relationship [11]. Elastic moduli are presented in table 2. The positive values of elastic constants confirm the mechanical stability of calculated AuAgTe₄ structures at high-pressure phase.

More surprising, structural difference between Au and Ag is lost: all M–Te bonds at 10 GPa (above the transition) are $\sim 2.77$ Å (the average M–Te bond length differs by 0.01 Å

Table 1. The crystal structure of AuAgTe₄ at 5 GPa and at 10 GPa obtained from lattice optimization in the GGA + SOC approximation (see figure 1). The space group above 5 GPa was found to be $P2/m$.

|                | 5 GPa     | 10 GPa    |
|----------------|-----------|-----------|
| a, Å           | 5.1332    | 5.0451    |
| b, Å           | 4.1020    | 4.0378    |
| c, Å           | 7.1785    | 7.0377    |
| $\alpha$       | 90°       | 90°       |
| $\beta$        | 90.506°   | 90.24°    |
| $\gamma$       | 90°       | 90°       |

| Atomic positions | 5 GPa     | 10 GPa    |
|------------------|-----------|-----------|
| Au, 1b           | 0         | 0.5       |
|                 | 0         | 0.5       |
|                 | 0.5       | 0.5       |
| Ag, 1c           | 0         | 0.5       |
|                 | 0.5       | 0.5       |
|                 | 0.5       | 0.5       |
| Te1, 2n          | 0.299 13  | 0.330 67  |
|                 | 0.300 33  | 0.333 79  |
| Te2, 2m          | 0.289 64  | 0.835 86  |
|                 | 0.292 65  | 0.836 49  |

Figure 2. Partial densities of states (DOS) of AuAgTe₄ as obtained in the GGA (a) and GGA + SOC (b) approximations at ambient pressure and in GGA + SOC at 10 GPa (c). The Fermi energy is at zero.

Figure 3. The crystal orbital overlap population (COOP) function of AuAgTe₄ at 0 GPa. The Fermi energy is at zero.

Figure 4. The evolution of the Au–Te, Ag–Te ((a) and (b)) and Te–Te (c) bond lengths under the pressure after optimization of the crystal structure of AuAgTe₄ in the GGA + SOC approximation.

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in AgTe₂ and AuTe₂ octahedra). Nevertheless of course these remain different elements. The question is what could be the reason of this surprising behaviour. The electron occupation of Au 5d and Ag 4d states at 10 GPa are almost the same at normal conditions (9.11 and 9.54 electrons for Au and Ag). Thus the charge disproportionation in AuAgTe₄ does not disappear under pressure, and Ag and Au ions do not show the electron equivalency in the equivalent surrounding of Te ions.

Some clue can be found in the behaviour of the electronic density of states ρ(ε) with pressure, especially in the vicinity of the Fermi level. First of all, note that the main contribution to ρ(ε) close to EF is provided by the Te 5p states, contribution of d states of Au and Ag is being quite small, see figure 2. As we stressed above, at ambient pressure due to formation of Te–Te dimers there appears the dip, pseudogap at the Fermi energy, which makes AuAgTe₄ a bad metal. And indeed in this phase the usual notions of valence, in particular the usual rules of solid state chemistry connecting valence and electronic configuration of an ion with the structure of its surrounding work quite well (in our case it is linear coordination around TM, here Ag¹⁺, with d⁰ configuration, and square coordination for d⁰ configuration of Au⁵⁺).

Above Pₐ, however, the crystal structure changes in such a way that the bond lengths M–Te become equal. Simultaneously Te–Te dimerization disappears, see figure 4. In effect the electronic density of states changes significantly: the pseudogap at EF vanishes (at 10 GPa ρ(ε) ~ 3 states/(eV f.u.), and electronically AuAgTe₄ becomes similar to a regular metal. Here the main electron contribution close to the Fermi energy is provided by the Te 5p states. One can think that it is just the crossover to a regular metallic state which invalidates the usual notions applicable for localized electrons, such as the effectiveness of Jahn–Teller effect etc. Note in this respect the old idea of Goodenough that there exist two thermodynamically different states of electrons in matter: localized electrons, which in particular can make ions with orbitally-degenerate configurations Jahn–Teller active, and itinerant state, in which Jahn–Teller effect does not work (simply the conditions for its applicability—the presence of localized electrons, are not satisfied). We can think that the situation in AuAgTe₄ above this critical pressure is just that: the material becomes more similar to a regular metal, or rather to Au–Ag–Te alloy, in which Au and Ag d-bands lie relatively deep under the Fermi level and lose their localized character. Apparently the situation in calaverite AuTe₂ [12] above critical pressure may be described by the same picture.

One extra conclusion which we can draw from the obtained results and from this picture is that, similarly to AuTe₂ at P > Pₐ, also AuAgTe₄ at the high-pressure phase may become superconducting. Indeed, first of all, it becomes more two dimensional, which may help superconductivity. Second, it apparently becomes a good metal, and with Ag and Au ions becoming structurally identical, they would not induce strong scattering. Such regular metals or metallic alloys may indeed become superconducting if there appears an effective electron–electron attraction leading to Cooper pairing. For that the specific character of constituting atoms, Au and Ag, may be instrumental. In [3] we put forth some arguments that just the very well known tendency of Au (and Ag) to charge disproportionation of nominally Au₂⁺(d⁹) into Au¹⁺(d¹⁰) and Au¹⁺(d⁸) (or rather Au¹⁺(d¹⁰)L → Au¹⁺(d¹⁰) + Au¹⁺(d⁸)L²) can help superconductivity: this tendency actually means that there exist an ‘atomic’ tendency to form electron pairs (it is better to have not one d hole as in Au₂⁺(d⁹) but either no holes (d⁹) or two holes (d⁸ or d⁷L²). I.e. we can say that there acts in such valence skippers something like an effective electron attraction—effective negative U situation, using the terminology of the Hubbard model. We think that this mechanism can work in favour of making high-pressure phase of AuAgTe₄ superconducting.

4. Conclusion

Summarizing, we theoretically obtained that the AuAgTe₄, the mineral sylvanite, may strongly change its properties under pressure, from the bad metal with rather strongly distorted lattice, to the state similar to a regular metal, with much less distortions. We presented some arguments that this high-pressure phase of AuAgTe₄ may become superconducting. It might be very interesting to try to experimentally check this prediction, all the more so because the critical pressure needed for that is relatively low, of order of ~5 GPa.

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Table 2. Elastic constants (in GPa) of AuAgTe₄ at ambient pressure, 5 GPa and 10 GPa, calculated in the GGA+SOC approximation for monoclinic symmetry.

|      | c₁₁  | c₁₂  | c₁₃  | c₂₂  | c₂₃  | c₃₃  | c₄₄  | c₅₅  | c₆₆  |
|------|------|------|------|------|------|------|------|------|------|
| 0 GPa | 96.2 | 13.2 | 16.8 | 35.7 | 26.4 | 61.9 | 11.8 | 20.7 | 16.7 |
| 5 GPa | 192.3| 33.5 | 36.9 | 123.6| 90.9 | 117.3| 13.2 | 60.3 | 16.6 |
| 10 GPa| 235.8| 46.2 | 44.7 | 140.9| 116.4| 139.9| 13.4 | 75.3 | 15.6 |
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