



Old puzzle of incommensurate crystal structure of calaverite AuTe₂ and predicted stability of novel AuTe compound

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Gold is a very inert element, which forms relatively few compounds. Among them is a unique material—mineral calaverite, AuTe₂. Besides being the only compound in nature from which one can extract gold on an industrial scale, it is a rare example of a natural mineral with incommensurate crystal structure. Moreover, it is one of few systems based on Au, which become superconducting (at elevated pressure or doped by Pd and Pt). Using ab initio calculations we theoretically explain these unusual phenomena in the picture of negative charge-transfer energy and self-doping, with holes being largely in the Te 5p bands. This scenario naturally explains incommensurate crystal structure of AuTe₂, and it also suggests a possible mechanism of superconductivity. An ab initio evolutionary search for stable compounds in the Au–Te system confirms stability of AuTe₂ and AuTe₃ and leads to a prediction of an as yet unknown stable compound AuTe, which until now has not been synthesized.

incommensurate crystal structure | calaverite | superconductivity

It is very well known that gold is one of the least reactive chemical elements and it is typically mined as a pure native element. It also occurs in alloys but very rarely it can be found in the form of compounds. The only compound existing in nature from which one can extract gold on an industrial scale is gold telluride—AuTe₂, calaverite. This material is extremely interesting in many aspects. It even influenced the gold rush in Australia, where miners in gold mines first discarded calaverite as an “empty” waste and used it for paving the roads, but, after discovering that it contains real gold which can be extracted, very carefully scrapped all these roads.

Another, very specific feature of AuTe₂ is that it is one of very few materials having in natural form an incommensurate crystal structure. This at one time was of much concern to mineralogists and crystallographers: They could not understand the peculiar faceting of calaverite crystals, contradicting Haüy’s law. Usually the stable natural facets of a crystal are those with small Miller indexes, and in calaverite everything looked odd, until it was realized that the very crystal structure is incommensurate (1). But the origin of the incommensurability is still obscure. Last but not least, AuTe₂ was found to be a superconductor at a relatively low pressure of 2.3 GPa or upon Pt or Pd doping (2–5), with critical temperature ~4 K.

In the present paper, we show that all these properties of AuTe₂ can be naturally explained, if one takes into account that it is in a negative charge-transfer energy regime, which drives a charge disproportionation resulting in an incommensurate crystal structure at normal conditions or a superconducting state at higher pressures. Moreover, an extensive structural study of different gold tellurides allowed us to predict the existence of a hitherto unknown compound: AuTe. We report the predicted crystal structure and properties of this material.

Old Puzzle of Calaverite’s Crystal Structure

AuTe₂ has a distorted layered CdI₂-type structure [the average structure has space group *C*2/*m* (6)], with triangular layers of Au with Te atoms in between. However, there is a periodic displacive modulation along the [010] direction, which makes overall crystal structure incommensurate (7). The mechanism of incommensurability is unclear. One may argue that it can be due to a specific electronic structure, which results in a charge density wave (CDW) instability, but accurate band structure calculations have not found nesting of the Fermi surface at corresponding wave vectors (8, 9). Schutte and de Boer (10) proposed another explanation based on the formal assignment of valencies in Au²⁺(Te₂)²⁻ [in analogy with another mineral—the “fool’s gold” Fe²⁺(S₂)²⁻]. However, whereas Fe²⁺ is a stable ionic state, every chemist knows that Au²⁺ is extremely difficult to stabilize: It exists as Au¹⁺(*d*¹⁰) or Au³⁺ (nominally low-spin *d*⁸). If one could manage to really stabilize Au²⁺(*d*⁹), it would be a realization of an old dream—a “magnetic gold.” [It was actually indeed made, however not in oxides, but in systems with more ionic bonds—in Au(AuF₄)₂ and Au(SbF₆)₂ (11).]

The phenomenon of skipped valence (12) of Au²⁺ can lead to the possibility of charge disproportionation into Au¹⁺ and Au³⁺, and it seems to naturally explain the ground-state properties of AuTe₂, as it works for example in Cs₂Au₂Cl₆ (13).

Significance

It is shown that the long-standing puzzle of incommensurate crystal structure of AuTe₂ can be solved, if this material is considered as a negative charge-transfer system. Using modern computational methods, we demonstrate that charge redistribution associated with incommensurate modulations of crystal structure occurs not so much on Au, but predominantly on Te sites. This substantially reduces Coulomb energy costs for creating such a unique crystal structure. The same mechanism also explains superconductivity of doped AuTe₂. Exploring different Au–Te compositions, we also discovered a previously unknown compound AuTe, which theoretically is very stable, and we predict its crystal structure.

Author contributions: S.V.S. and D.I.K. designed research; S.V.S., V.V.R., and A.V.U. performed calculations; S.V.S., A.R.O., and D.I.K. analyzed data; and S.V.S. and D.I.K. wrote the paper.

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The high-pressure phase of AuTe_2 is also very interesting due to another aspect—the superconductivity, which appears in it below $T_c = 2.3$ K (2). One may stabilize this phase not only by pressure, but also by Pt doping (3), which also results in the stabilization of the same $P3m1$ structure. The superconductivity was proposed to be induced by breaking of Te–Te dimers, which exist in the $C2/m$ phase, but disappear in the high-pressure superconducting $P3m1$ phase (3). In particular, it was speculated that the formation of Te–Te dimers modifies the electronic structure of AuTe_2 through formation of bonding (σ) and antibonding (σ^*) Te 5p bands (3). We have seen that the bands at the Fermi level indeed have a very large contribution of the Te 5p states, but they are strongly hybridized with Au 5d and have the symmetry of Au 5d orbitals (Fig. 1), while the σ -bonded Te 5p states are far away from the Fermi level (~ 5.2 eV below and ~ 3.2 eV above E_F). Thus, it seems that the Te–Te dimerization is not directly related to the suppression of the superconductivity. In fact, this is just one of the consequences of the formation of the CDW. In Fig. 3 the directions of Te atom displacements due to the CDW are indicated. One may see that the formation of AuTe_4 plaquettes and AuTe_2 dumbbells naturally results in dimerization of the Te atoms, which, however, is not a driving force but rather a consequence of the CDW formation in AuTe_2 .

One can argue that the physics disclosed in our calculations, specifically the origin of the incommensurability—the tendency to the skipped valence and charge disproportionation of “ Au^{2+} ,” occurring in the situation with negative CT energy with the self-doping—is also instrumental in providing a mechanism of superconductivity in AuTe_2 under pressure or with doping. This tendency, both on the d levels (reaction Eq. 1) and more realistically on ligand states (reaction Eq. 2), means that there exists a tendency for holes to form pairs; that is, there exists an effective attraction of these holes.

The idea that the tendency to charge disproportionation (which actually means the local “chemical” tendency to form pairs of electrons or holes) can be instrumental in providing the mechanism of Cooper pairing was first suggested by Rice and Sneddon (32) in connection with the superconductivity of doped BaBiO_3 . This material is also known to experience charge disproportionation of the type $2\text{Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}$ (and again with a lot of action on ligands, e.g., ref. 17). For high- T_c cuprates a similar idea was proposed in ref. 33. It is also closely related to some theoretical studies of superconductivity in systems with coexisting ordinary electrons and bipolarons (e.g., refs. 34 and 35). We suppose, by analogy with the abovementioned papers,

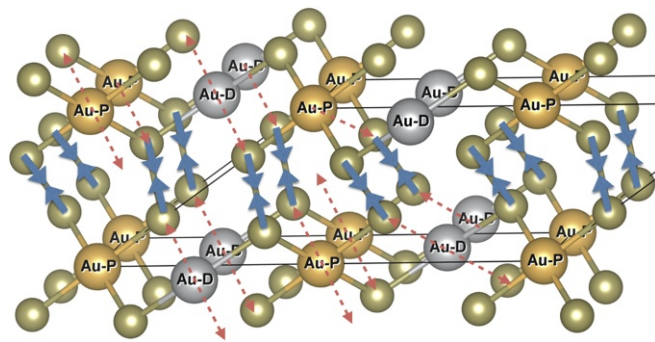


Fig. 3. Formation of the Te–Te dimers due to charge disproportionation on Au sites. The “strength” of distortions in AuTe_6 octahedra is not the same for all Au–Te bonds. There are “strongly” distorted with respect to undistorted $P3m1$ ($\delta_{\text{Au–Te}} \sim 0.45 - 0.55$ Å) and “weakly” distorted Au–Te bonds ($\delta_{\text{Au–Te}} \sim 0.15$ Å). Plotting (for simplicity) only strongly distorted Au–Te bonds (red lines; arrows show direction of distortions), one immediately obtains Te–Te dimers (shown by blue arrows).

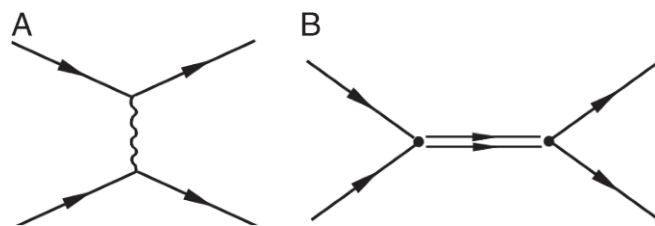


Fig. 4. (A and B) Diagrams illustrating (A) conventional Bardin–Cooper–Schrieffer “t-channel” pairing and (B) “s-channel” pairing proposed for AuTe_2 .

that the chemical tendency of Au^{2+} to charge disproportionate into, nominally, Au^{1+} and Au^{3+} , which is the main ingredient of our theory and which, as we argued above, plays a crucial role in explaining the main properties of AuTe_2 , may be also instrumental in providing the mechanism, or at least helping the realization, of superconductivity in AuTe_2 when doped or under pressure.

One can phenomenologically describe this situation by an effective Hamiltonian like the Anderson lattice model (where 5p electrons of Te play the role of conduction electrons, while 5d electrons of Au are localized), but with an effective attraction—with negative U on localized levels. After excluding d electrons, we get in effect also an attraction of conduction electrons, which, on one hand, can provide the mechanism of CDW formation (not even requiring nesting of the Fermi surface, although nesting would help). And, on the other hand, in this model we have a natural mechanism of formation of Cooper pairs leading to superconductivity. In diagrammatic language, this mechanism of pairing is described in Fig. 4B [two electrons (or holes) of a conduction band “drop” into the Au 5d levels, where they experience attraction and form pairs, before decaying again into conduction electrons.] This situation is reminiscent of a model with bipolarons (36) and is different from the usual electron–phonon exchange in Fig. 4A (although the standard electron–phonon coupling could also contribute). Thus, AuTe_2 may be the long-sought second example of the same physics as proposed for BaBiO_3 (32), with the same mechanism of both charge disproportionation and superconductivity.

As Yet Unknown Compound AuTe

Since USPEX has shown its efficiency in determining the AuTe_2 crystal structure, we extended these calculations to a whole $\text{Au}_{1-x}\text{Te}_x$ series with arbitrary x . Fig. 5 shows thermodynamic convex hulls and a phase diagram of the Au–Te system in the GGA and GGA + SOC approximations. A compound is thermodynamically stable if its thermodynamic potential (e.g., the Gibbs free energy) is lower than that of any other phase or phase assemblage of the same composition. On a graph showing the enthalpy of formation of all compounds of a given system (e.g., Au–Te system) from the elements, all points corresponding to stable compounds can be connected to form a convex hull. Height above the convex hull is a measure of thermodynamic instability of a compound. One may note that in addition to experimentally observed structures such as AuTe_2 and AuTe_3 (37) there appears another one: AuTe.

AuTe has never been synthesized so far, but there exists mineral muthmannite, AuAgTe_2 , found in Western Romania (38), where Au and Ag ions are in a 1:1 ratio. Muthmannite has a distorted NiAs-type structure with space group $P2/m$. Our calculations have shown that the $C2/c$ structure predicted for AuTe by USPEX is significantly more stable (by 0.164 eV per atom with SOC) than the muthmannite structure. The predicted $C2/c$ structure of AuTe, shown in Fig. 6, can be considered a distorted NaCl-type structure (NiAs and NaCl structures are relatives).

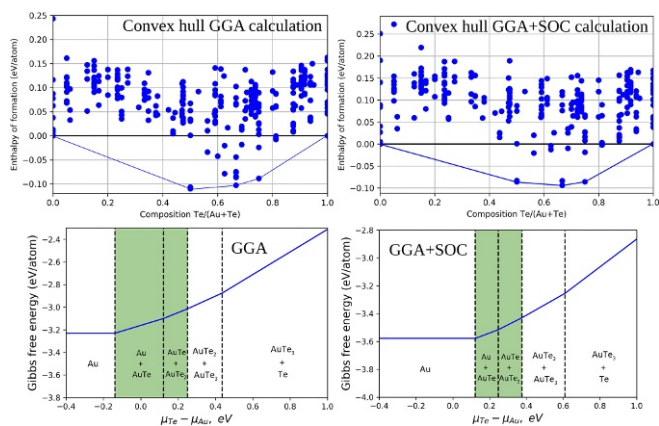


Fig. 5. Thermodynamic convex hulls and Gibbs free energy G vs. chemical potential μ for the Au–Te system with different Te concentrations.

The Au ions are in the strongly distorted plaquettes with two short (2.68 Å) and two long (2.90 Å) Au–Te bonds.

It is worthwhile mentioning that the SOC additionally lowers the position of the Au 5*d* band and thus affects stability of different phases in the Au–Te system. One can see from Fig. 5 that while both GGA and GGA + SOC calculations show stability of the same phases and crystal structures, there are large changes in stability fields. The plot of Gibbs free energy vs. chemical potential demonstrates that inclusion of the SOC expands the stability field of Au (in effect making it more inert) and AuTe₂, at the expense of shrinking the stability fields of AuTe and AuTe₃. The relatively narrow stability field may explain why AuTe is not yet known.

AuTe was found to be a nonmagnetic metal in the GGA + SOC calculations. Analysis of the charge density, $\rho(\vec{r})$, corresponding to the bands at the Fermi level, shows that there are nearly equal contributions to $\rho(\vec{r})$ from Au 5*d* and Te 5*p* states. This may explain why USPEX did not find the solution corresponding to charge disproportionation, as it did for calaverite (two inequivalent Au ions: in dumbbells and plaquettes): The energy costs due to the on-site Coulomb repulsion are too large in AuTe. Thus, in effect AuTe should resemble the high-pressure phase of AuTe₂, with all Au equivalent, and one could expect that it could also be superconducting.

Conclusions

The Au–Te system presents an interesting example of compounds of a very inert element, gold, with nontrivial properties. We found that there exist in the Au–Te system three stable stoichiometric compounds: AuTe, AuTe₂, and AuTe₃. [There exists also Au₃Te₇ with a simple cubic structure and statistical distribution of Au and Te atoms (39), but it is likely a solid solution. We have not found a stable compound with such stoichiometry in calculations at $T = 0$ K, which indicates that it is probably entirely entropy stabilized.] The second and the less “popular” third compound are known and studied. AuTe has not been synthesized, however, although a similar material, mineral muthmannite AuAgTe₂, is known. It would be very interesting to check our predictions and try to synthesize and study AuTe.

Much better studied, but still presenting several, until now unresolved puzzles, is calaverite, AuTe₂. This is the system whose properties we now explain on the basis of ab initio calculations. The picture emerging from our calculations is the following: The nominal average valence of gold in AuTe₂ is 2+, similar to many pyrites like FeS₂ and MnS₂ (40). But this state is, first of all, chemically unstable (only Au¹⁺ and Au³⁺ are known to exist, with very few exceptions). And, most importantly, both Au²⁺

and Au³⁺ in AuTe₂ correspond to the situation with negative CT energy, that is, practically Au²⁺ → Au¹⁺ \underline{L} and Au³⁺ → Au¹⁺ \underline{L}^2 . This means that in fact all of the holes go to ligand (here Te) bands (but still with significant hybridization with *d* states of Au). This is actually the situation of self-doping (17, 19). In this case there occurs a phenomenon met also in several other systems: the valence, or charge disproportionation, which, however, again occurs not so much on the *d* shells themselves, but on ligands; that is, corresponding disproportionation is described not as in Eq. 1, but instead as in Eq. 2. This transition is accompanied (and is largely driven) by the change of the Au–Te bond lengths (and local coordination—linear for Au¹⁺ and square for Au³⁺ = Au¹⁺ \underline{L}^2); that is, it should be better called not charge, but bond disproportionation (17). But the outcome is very similar: There occurs in this case a structural transition with the formation of corresponding superstructures, commensurate as in, e.g., nickelates RNiO₃ (17, 22, 23) or incommensurate as in the case of a frustrated triangular lattice of AuTe₂. This picture naturally explains both the structural characteristics of AuTe₂ and the spectroscopic data, showing apparently constant occupation of *d* shells of Au. Despite this equivalence, the tendency to this charge or bond disproportionation is intrinsically connected with the “atomic” property of, here, Au (skipped valence Au²⁺). Suppression of this superstructure by pressure or doping leads to the formation of a homogeneous metallic state with all Au (or Ni in RNiO₃) becoming equivalent, and in AuTe₂ this state becomes superconducting. The situation with negative CT gap and with a lot of ligand holes existing in particular in AuTe₂ is the solid state analogue of dative bonding known in coordination chemistry.

We argue that the same mechanism—the tendency to charge disproportionation, which is in fact the tendency to form electron or hole pairs—may be instrumental for the appearance of superconductivity in doped AuTe₂ or AuTe₂ under pressure. Thus, this exciting material, gold telluride, indeed is extremely interesting, both because of its rich history and, more important for us, as an example of very interesting physics.

Methods

The DFT calculations were performed within the Perdew–Burke–Ernzerhof functional (41) using the all-electron PAW method (42) as realized in the VASP code (43). We took into account the SOC and used scalar-relativistic GW PAW potentials with an [Xe] core (radius 2.1 a.u.) and [Kr] core (radius 2.2 a.u.) for Au and Te atoms, respectively, and plane wave cutoff of 400 eV. The evolutionary structure prediction algorithm USPEX (27) was applied in the search for stable phases. Structure relaxations used *k*-mesh with a resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$ and electronic smearing of 0.1 eV. The USPEX simulation included 80 structures per generation for a

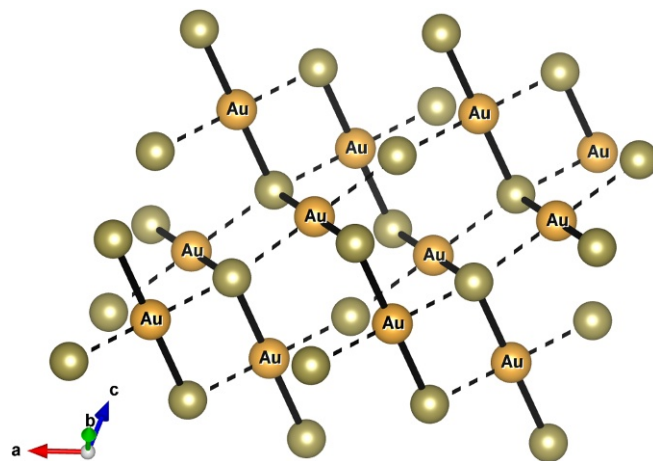


Fig. 6. The crystal structure of AuTe. Thick solid and dashed lines correspond to short and long Au–Te bonds, respectively.

variable-composition run. Also all known Au–Ag–Te compounds (with silver atoms substituted by gold) were included in the calculation (6, 37, 39, 44, 45). Phonon calculations were performed using Phonopy (31) with a $4 \times 4 \times 2$ supercell.

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