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Communication

Electronic structure and possible electronic instability of the novel alkali metal telluride Cs_3Te_{22}

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Summary — The recently reported Cs_3Te_{22} phase contains infinite $[Te_4Te_{4/2}]^{3-}$ layers of tellurium atoms with an average charge of $-1/2$. Tight-binding band structure calculations show that this layer is best described as a series of $(Te_4)^-$ square units coupled through Te^- spacers. This study also suggests that Cs_3Te_{22} might be a new low-dimensional metal and that the infinite tellurium layers may exhibit a density wave instability.

tellurium compound / low-dimensional system / Fermi surface instability

Résumé — **Structure électronique et possible instabilité électronique du nouveau tellurure Cs_3Te_{22}.** *La phase* Cs_3Te_{22} *récemment rapportée, contient des feuillets infinis* $[Te_4Te_{4/2}]^{3-}$ *où les atomes de tellure ont une charge moyenne de* $-1/2$. *Des calculs de structure de bandes par la méthode des liaisons fortes montrent que ces feuillets peuvent être décrits comme une série d'unités carrées* $(Te_4)^-$ *couplées par des* Te^-. *Cette étude suggère aussi que la phase* Cs_3Te_{22} *peut être un nouveau métal de basse dimensionalité et que les feuillets infinis de tellure pourraient être le siège d'une instabilité du type onde de densité de charge (ou de spin).*

tellurure / système à basse dimensionalité / instabilité électronique

Introduction

Alkali metal tellurides exhibit a remarkable diversity of crystal structures [1]. The tellurium sublattices of such phases have been found to possess not only different discrete $(Te_n)^{n-}$ units (for instance $(Te_2)^{2-}$ in K_2Te_2 [2], $(Te_3)^{2-}$ in K_2Te_3 [3], $(Te_6)^{2-}$ in $NaTe_3$ [4] or $(Te_8)^{2-}$ in $CsTe_4$ [5] to name just a few) but also infinite chains [6] and layers [7]. Recently, the novel alkali metal telluride Cs_3Te_{22} has been reported [8]. This new phase is interesting for several reasons. First, its crystal structure contains both discrete and infinite tellurium units. Second, it contains the long-awaited discrete crown-shaped Te_8 rings [9]. Third, the existence of both an infinite layer and an odd number of electrons per unit cell suggests that Cs_3Te_{22} could well be a new low-dimensional metal and thus exhibit unusual physical properties. In order to explore this possibility we have studied the electronic structure of Cs_3Te_{22} by means of extended Hückel tight-binding band structure calculations [10]. Recently, this type of calculation has proved to be very useful in understanding the electronic structure of many low-dimensional chalcogenides [11].

The crystal structure of Cs_3Te_{22} can be described as containing two types of layers alternating along the *c* direction [8]. The first is a double layer containing the crown-shaped Te_8 rings in between which there are Cs^+ cations. The second contains the planar infinite tellurium layer shown in figure 1, in each hole of which resides one Cs^+ cation. There are no short contacts between the crown-shaped Te_8 rings, so they can be considered as isolated from each other. Our calculations for these Te_8 rings show that there is a large energy gap for an electron count of 48 electrons, confirming that they should be viewed as Te_8^0 units. This leads to a total of 39 electrons per unit cell of the infinite layer.

There are two different types of Te atoms in the layer (denoted Te_1 and Te_2 in figure 1) and two types of Te–Te bonds with quite similar bond lengths: 3.003 (Te_1–Te_1) and 3.077 Å (Te_1–Te_2). So the question arises of how the three extra electrons are distributed between the two different types of Te atoms, and how similar are the two Te–Te bonds; in other words, how

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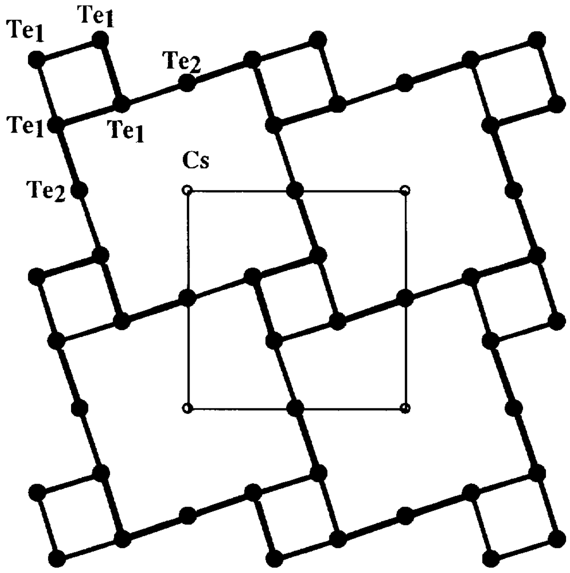

Fig 1. Planar infinite layers in Cs_3Te_{22} (•: Te, ○: Cs).

should the Te layer be described? as a defective square net of Te atoms [12] or as a series of Te_4 squares connected through the extra Te atoms. As will be seen later, this question is not just of academic interest. The calculated overlap populations for the Te_1–Te_1 and Te_1–Te_2 bonds are 0.2838 and 0.1631 respectively. Thus, despite the not-so-different bond lengths, the intrasquare bonds are clearly stronger. The calculated charges are −0.22 (Te_1) and −1.06 (Te_2). These results suggest that the $[Te_4Te_{4/2}]^{3-}$ layer should be described as a series of $(Te_4)^-$ square units coupled through Te^- spacers. Why the Te_1–Te_2 bonds are weaker than the intrasquare Te_1–Te_1 ones is easy to understand. The σ bonds between the squares and the spacers implicate orbitals of the square mainly directed diagonally outwards from the Te_4 units (according to an approximate sp^2 scheme). The spacer Te atoms are situated out of these diagonal directions, so that the overlap between the square and spacer orbitals is far from optimum. Thus, the bond strength is only moderate. In contrast, the intrasquare bonding can be described with the usual cyclobutane-type orbitals [13] so that the bond strength is normal for a four-center ring and stronger than for the outer Te_1–Te_2 bonds.

The band structure near the Fermi level for the $[Te_6]^{3-}$ layer is shown in figure 2. The highest band is half-filled and exhibits a sizable dispersion (1.3 eV) so that Cs_3Te_{22} is very likely to be a metallic system. The main aspects of the band structure, which for the purpose of electron counting can be understood in a very simple way, are the following. To begin with there is a block of eight filled σ-bonding bands essentially associated with the eight Te–Te σ bonds per unit cell of the layer. Since the Te–Te distances are relatively long, the six π-type bands are found in a fairly narrow energy range and are completely filled. In addition, because of the local coordination of the Te_2 atoms, one of the in-plane p orbitals, ie, that perpendicular to the Te_1–Te_2–Te_1 direction, formally acts as an in-plane lone pair (which of course becomes somewhat delocalized through interaction with the nearest-neighbor squares) and leads to two additional bands. In total these bands account for 32 electrons per unit cell. The extra seven electrons must be housed in the block of eight σ^*-antibonding bands, thus explaining the relatively long Te–Te distances of this layer. The important point is that, as a consequence of the different strength of the Te_1–Te_1 and Te_1–Te_2 bonds, the eight σ^*-antibonding bands split into two blocks of four bands each, the lowest one being more heavily associated with the weaker Te_1–Te_2 bonds and the upper one with the stronger Te_1–Te_1 bonds (these bands lie at energies higher than −9.5 eV and are not shown in figure 2). There are seven electrons to fill the four bands of the lower block so that the upper band is only half-filled. Because of the very different strength of the Te–Te bonds the two blocks are quite well separated and as a consequence the upper band of the lower block acquires a sizable dispersion through square–spacer interactions. Since this band is half-filled Cs_3Te_{22} may show metallic properties. Thus the topology of the lattice seems to have a very important role in controlling the dispersion of the partially-filled band, and hence the transport properties of the lattice.

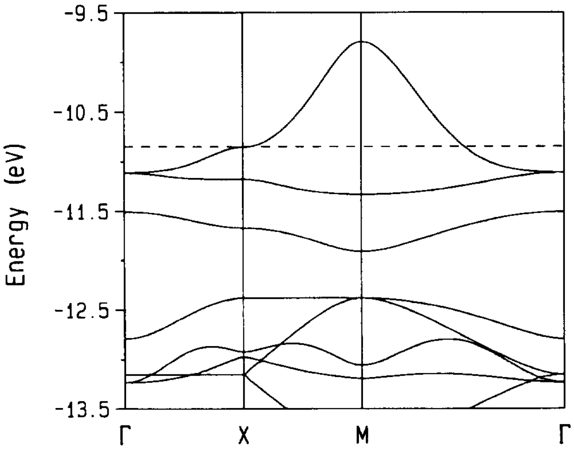

Fig 2. Calculated dispersion relations for the $[Te_4Te_{4/2}]^{3-}$ layers of Cs_3Te_{22}, where the dotted line refers to the Fermi level. Γ, X and M refer to the wave vectors (0, 0), ($a^*/2$, 0) and ($a^*/2$, $b^*/2$), respectively.

The calculated Fermi surface for the planar tellurium layer is shown in figure 3. A metallic state predicted by the one-electron band theory is not stable when its Fermi surface is nested and becomes susceptible to a metal-to-insulator transition [14]. As shown in figure 3, the Fermi surface of the $[Te_4Te_{4/2}]^{3-}$ layer is almost perfectly nested by the wave vector $q = (a^* + b^*)/2$ (and thus also by $q' = (-a^* + b^*)/2$). Consequently, if the metallic character of Cs_3Te_{22} is experimentally confirmed, we suggest that there may be a charge-density wave instability associated with these nesting vectors, which would be responsible for a metal-to-insulator transition. The new unit cell would be twice as big and have its principal axes along the $(a^*+b^*)/2$ and $(-a^*+b^*)/2)$ diagonal directions. Such a charge density wave would most probably involve the Te_2 atoms, which are implicated in the weaker bonds, and would lead to the appearance of satellite reflections in the X-ray diffraction patterns. Alternatively, if the lattice is too stiff to sustain the formation of a charge density wave, the nesting mechanism could also lead to a metal-to-insulator transition as a result of a spin density wave. However, in view of the nature of the lattice we believe that the charge density wave mechanism is more likely. Transport measurements, as well as partial substitution of the alkali metal sites by a divalent cation in order to change the band filling and the Fermi surface of the system, would thus be very interesting.

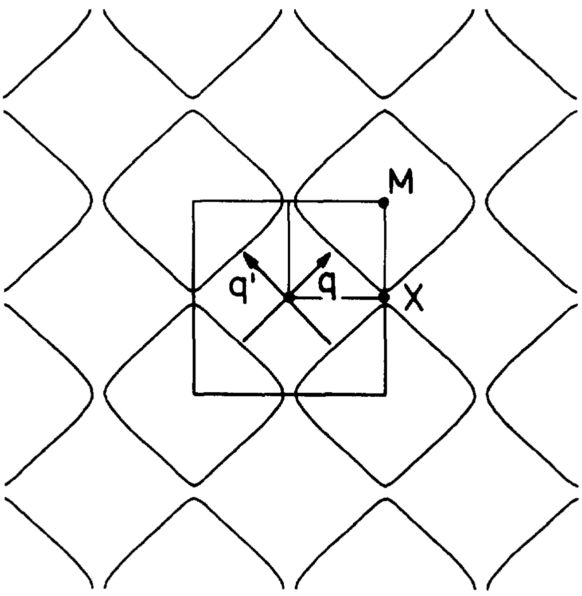

Fig 3. Calculated Fermi surface for the $[Te_4Te_{4/2}]^{3-}$ layers of Cs_3Te_{22}.

Although charge density wave instabilities have often been invoked to explain structural modulations of transition metal chalcogenides, only very recently has it been shown that they can also occur in a purely tellurium-containing network, ie, the square tellurium layers of $K_{0.33}Ba_{0.67}AgTe_2$ [15]. However, in that case, the charge density wave has already developed at room temperature and the system is a room-temperature semiconductor. According to our study, Cs_3Te_{22} could well be the second example of a phase containing a purely tellurium network exhibiting the typical instabilities of low-dimensional metals and hence an interesting physics. It will be very interesting to see if Cs_3Te_{22}, in contrast with $K_{0.33}Ba_{0.67}AgTe_2$, is a room-temperature metal. Certainly, telluride systems, and more specially those corresponding to defective square lattices, hold real promise in the search for new low-dimensional materials with unusual properties.

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