Te...Te Interlayer Interactions, Te → Metal Electron Transfer and Electrical Conductivity in the MM′Te$_5$ Phases (M = Nb, M′ = Ni, Pd; M = Ta, M′ = Ni, Pt)

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The layered ternary tellurides NbNiTe$_5$, TaNiTe$_5$, TaPtTe$_5$ and NbPdTe$_5$ are all metallic, but the conductivity of the latter is between one and two orders of magnitude smaller. A tight binding study of the electronic structure of these phases suggests that the large conductivity difference results from the different Te···Te interlayer interactions and the Te → M (M = Nb, Ta) electron transfer that they induce.

Introduction

Several ternary transition metal tellurides are layered materials and exhibit metallic behavior.[1][2] Thus, one could expect that these materials may show the low temperature structural modulations and resistivity anomalies characteristic of many low-dimensional metals.[3][4] However this seems not to be the case.[5] The most likely reason for this unexpected behavior lies in the many short Te...Te interactions which these materials possess. As shown by several theoretical studies,[6−8] such interactions exert a strong control over the electronic structure in the region around the Fermi level. The mechanism by which the interlayer Te...Te interactions control the structural or transport properties of these materials is by raising the top of the tellurium bands which, as a consequence, overlap (or increase the overlap) with the transition metal d-block bands. This has two consequences. First, there is a Te → metal electron transfer so that the transition metal atom is really in an oxidation state somewhat lower than that expected from the stoichiometric formula and usual ideas concerning transition metal and chalcogen oxidation states. For instance, the layered binary telluride NbTe$_2$, in which the Nb atoms are formally d^1, exhibits a structure with double zigzag chains which would be expected if Nb was really d$^{4/3}$.[9] Theoretical calculations have shown that the Te → Nb electron transfer does indeed occur.[6b,9] Second, the density of states at the Fermi level, which has a strong control over the conductivity of these metallic systems, can be significantly affected. We have recently suggested that the large difference in the metallic conductivity (one order of magnitude) of the two structurally related tellurides Ta$_3$Pd$_3$Te$_{14}$ and Ta$_4$Pd$_3$Te$_{16}$, can be rationalized on the basis of the different density of states at the Fermi level for the two phases, and that such a difference is largely imposed by the interlayer Te...Te interactions.[7]

A series of ternary layered tellurides exhibiting interesting conducting properties is that of the MM′Te$_5$ (M = Nb, M′ = Ni, Pd; M = Ta, M′ = Ni, Pt) phases.[1] All of these systems are metallic but one of them, NbPdTe$_5$, is between one and two orders of magnitude less conducting than the other three. The NbNiTe$_5$, TaNiTe$_5$ and TaPtTe$_5$ phases have similar conductivities. The layers of the four salts are of the same type but, interestingly, the interlayer stacking is the same for the three phases with similar conductivity and differs from that of the less conducting phase.[1] This immediately suggests that the Te...Te interlayer interactions must exert a strong control over the conductivity of these phases also.[1d] Thus, we felt it would be interesting to study the possible relationship between the interlayer Te...Te interactions and the conductivity of the four MM′Te$_5$ phases.

The calculations reported here are of the extended Hückel type[10] with the exponents and parameters summarized in Table 1. The electronic structure of NbNiTe$_5$ and NbPdTe$_5$ was studied by Halet et al[8] some years ago. However, as briefly discussed above, the understanding of the role of the Te...Te interactions in determining the electronic structure of ternary tellurides has considerably progressed in recent years so that we thought it was of interest to reexamine some aspects of the electronic structure of these phases. Here we will concentrate on the possible relationship between the Te...Te interlayer interactions, Te → metal electron transfer and conductivity for this interesting family of solids and refer the reader to the work of Halet et al[8] for a more complete discussion of the relationship between the geometrical and electronic structure of the MM′Te$_5$ layers.

Results and Discussion

Crystal Structure and Te···Te Short Contacts

The electronic structure of these materials is very complex[8] so that it is very important to clearly understand

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Table 1. Exponents and parameters used in the calculations.[a]

atom	orbital	H_{ii} (eV)[b]	ζ_1	ζ_2	c_1[c]	c_2[c]
Nb	5s	−6.71	1.89			
	5p	−3.88	1.85			
	4d	−8.14	4.08	1.64	0.6401	0.5516
Ta	6s	−6.89	2.28			
	6p	−3.94	2.24			
	5d	−8.03	4.76	1.94	0.6597	0.5589
Ni	4s	−8.13	2.10			
	4p	−4.18	2.10			
	3d	−12.40	5.75	2.30	0.5683	0.6292
Pd	5s	−7.55	2.19			
	5p	−4.06	2.15			
	4d	−13.76	5.98	2.613	0.5264	0.6372
Pt	6s	−7.69	2.55			
	6p	−4.13	2.55			
	5d	−13.53	6.01	2.696	0.6334	0.5513
Te	5s	−18.78	2.51			
	5p	−10.16	2.16			

[a] A modified Wolfsberg-Helmholz formula (J. Ammeter, H.-B. Bürgi, J. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 3686) was used to calculate the off-diagonal H_{ij} values. – [b] A. Vela, J. L. Gázquez, *J. Phys. Chem.* **1988**, *92*, 5688. – [c] Contraction coefficients used in the double-ζ expansion.

what are the key aspects of the crystal structure on which we must concentrate when trying to understand the band structure calculations to be reported in the next sections. There are different ways to describe the crystal structure of a solid depending on the particular aspect one wishes to examine. Since the conductivity of a metal is dominated by the levels near the Fermi level, the appropriate structural description should be that leading to a qualitative feeling of the nature and structural dependency of such levels. As shown in Figure 1a, the $MM'Te_5$ layers present in the $MM'Te_5$ phases can be considered to result from the condensation of MTe_3 face sharing trigonal prismatic chains and $M'Te_3$ edge sharing octahedral chains. Because of the condensation, the M atoms form two additional bonds with the Te atoms of the adjacent octahedral chains so that they are really in a bicapped trigonal prismatic environment. Consequently, the $MM'Te_5$ layers can be simply described as a series of bicapped trigonal prismatic MTe_5 chains glued by the M′ atoms which reside in the octahedral holes in between them.

The previous description has an important implication. As already discussed,[7] these bicapped trigonal prismatic (btp) chains lead to five chains of direct Te...Te short contacts (see Figure 1a) as well as to four zigzag chains of Te...Te short contacts formed by the capping Te atoms and those of the triangular basis of the prisms (i.e., the four zigzag chains, two of *n* contacts and two of *o* contacts, shown in Figure 1b). The Te p orbitals parallel to these chains (both along the zigzag and direct chains) are very well oriented to make very strong overlaps and lead to very strongly dispersive Te-based bands which cross the Fermi level and are responsible for the above mentioned Te → metal electron transfer. Thus, it is tempting to consider the pentagonal shaped columns of Te atoms glued together by the M and M′ atoms as the essential building blocks that we should use in order to try to understand what happens near the Fermi level.

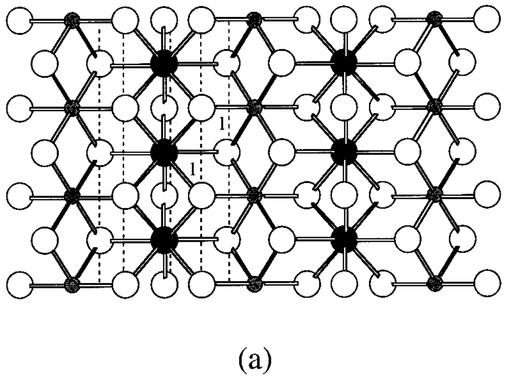


Figure 1a. View of a $MM'Te_5$ layer along a direction perpendicular to the slab.

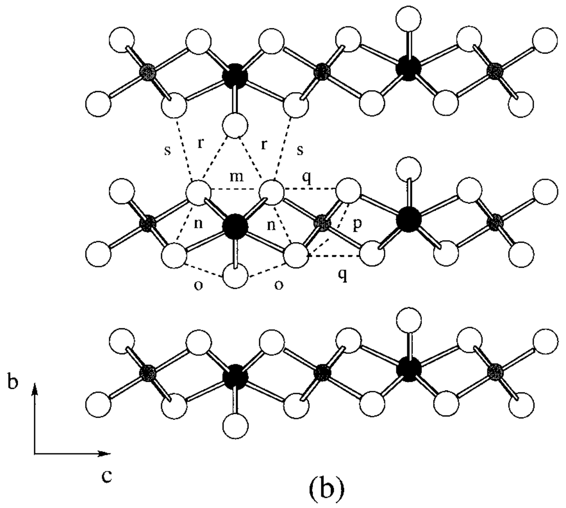


Figure 1b. Projection view of the crystal structure of $NbNiTe_5$, $TaNiTe_5$ and $TaPtTe_5$ along the *a* axis.

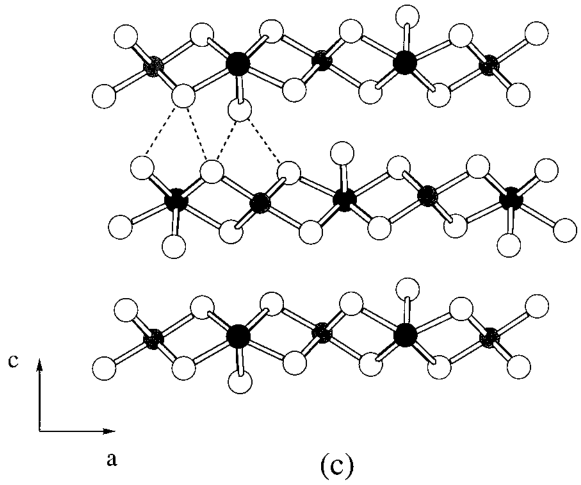


Figure 1c. Projection view of the crystal structure of $NbPdTe_5$ along the *b* axis. Large black circles represent the M atoms (Nb, Ta), large open circles the Te atoms and smaller grey circles the M′ atoms (Ni, Pd, Pt). The Te···Te contacts discussed in the text have been shown as dotted lines.

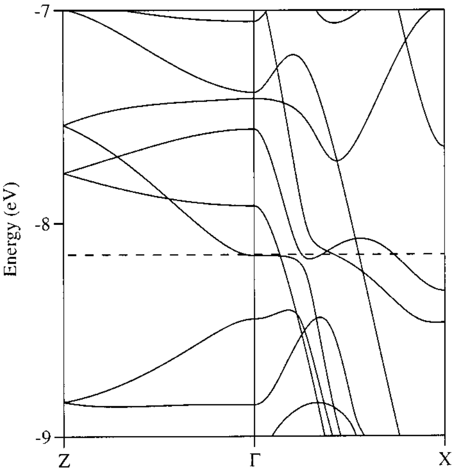
If we proceed along this line, we should next consider how these Te columnar units interact. Obviously, they interact along the intralayer intercolumn direction through the M′−Te bonds. However, the bonding and antibonding M′−Te levels are far from the Fermi level. The levels of the columnar units crossing the Fermi level must be Te-based so that the intercolumn interactions along the layer must be dominated by the direct Te...Te intercolumn contacts. There are five Te...Te short contacts of this type per formula unit. If for instance we look at the $NbNiTe_5$ structure these contacts are 3.623 Å and 3.788 Å(×4) (see contacts *p* and *q* in Figure 1b, respectively). Of course, these contacts should have a non-negligible but comparatively smaller influence than the intracolumn ones on the dispersion of the above mentioned Te very wide bands. Not only the orbital orientation is much better along the columns but there are more and considerably shorter intracolumn Te...Te contacts: 3.331 Å (×4), 3.460 Å (×4), 3.656 Å (×5) for $NbNiTe_5$ (see contacts *o*, *n* in Figure 1b and *l* in Figure 1a, respectively). There is another very short intracolumn Te...Te contact (3.196 Å in $NbNiTe_5$, see *m* in Figure 1b) which is perpendicular to the chain direction and is going to play an important role in our discussion (see later).

The way in which the layers order relative to each other for $NbNiTe_5$/$TaNiTe_5$/$TaPtTe_5$ and $NbPdTe_5$ is shown in Figures 1b and 1c, respectively. The btp chains in one layer are aligned with those in the next layer in Figure 1b ($NbNiTe_5$/$TaNiTe_5$/$TaPtTe_5$) whereas this is not the case in Figure 1c ($NbPdTe_5$). Of course, this leads to somewhat different Te...Te contacts, those in $NbPdTe_5$ being shorter. However, at this point, the important aspect we would like to scrutinize is the possible strength of these Te...Te contacts with respect to the intercolumn intralayer ones. In $NbNiTe_5$ there are six interlayer contacts: 3.789 Å (×4) and 3.931 Å (×2) (see contacts *r* and *s* in Figure 1b, respectively). Thus, for the time being, and just on the basis of the crystal structure information, we may suggest that the influence of the Te...Te intralayer and interlayer intercolumn contacts on the dispersion of the Te levels near the Fermi level should not be that different. We conclude that around the Fermi level there should be Te bands with very large dispersion along the direction of the Te columns and only a moderate one along *both* the intralayer and interlayer intercolumn directions.

Can the M and M′ levels be completely neglected as seems to be suggested by the previous discussion? As already mentioned, the M′-based bands (M′ being a very electronegative metal atom) will be far from the Fermi level and thus we can ignore them in our qualitative scheme. However this is not the case for the low-lying M-based ones. The very wide Te-based bands will cross some of the low-lying M-based bands, which would be empty if it were not for the existence of such wide Te bands, and lead to the Te → metal electron transfer. Thus, some of the low-lying *d* levels of the M atoms can play a very important role in understanding the electronic structure of the $MM'Te_5$ phases near the Fermi level and this is why, coming back to the beginning of this section, we propose that the MTe_5 btp chains are the more convenient building blocks to be used in discussing the relationship between the electronic structure and electrical conductivity of the $MM'Te_5$ phases.

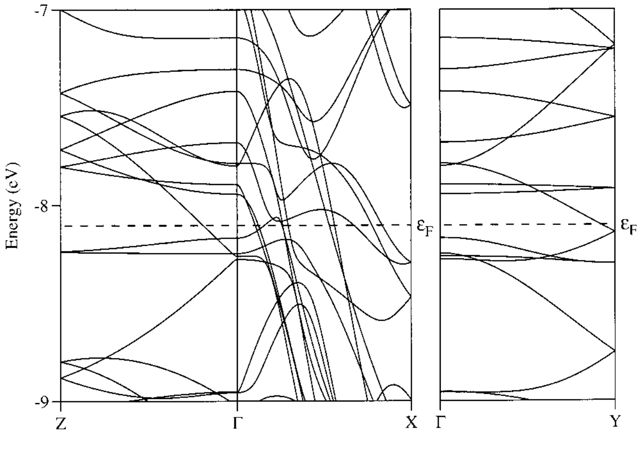
Band Structure of the $MM'Te_5$ Phases

The calculated band structures for a single layer and the three dimensional structure of $TaNiTe_5$ are shown in Figures 2a and 2b, respectively. It should be remembered that the unit cell of $TaNiTe_5$ contains two $TaNiTe_5$ layers. Because of the overall similarity of the results we will only discuss here those concerning $TaNiTe_5$, although a similar study has been carried out for all the phases of this family.



(a)

Figure 2a. Calculated dispersion relations for a single layer of $TaNiTe_5$.The Γ, X and Z labels in refer to the wave vector points (0, 0), (*a**/2, 0) and (0, *c**/2), respectively. The dashed line refers to the Fermi level.



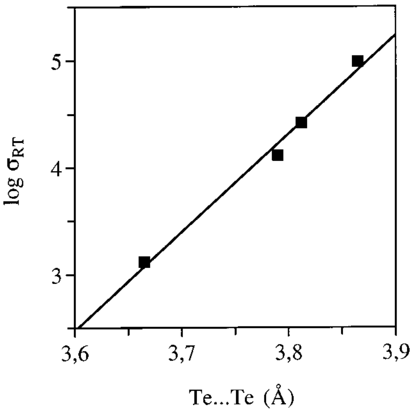
(b)

Figure 2b. Calculated dispersion relations for the 3D structure of $TaNiTe_5$, where the dashed lines refer to the Fermi level. The labels Γ, X, Y and Z refer to the wave vector points (0, 0, 0), (*a**/2, 0, 0), (0, *b**/2, 0) and (0, 0, *c**/2), respectively.

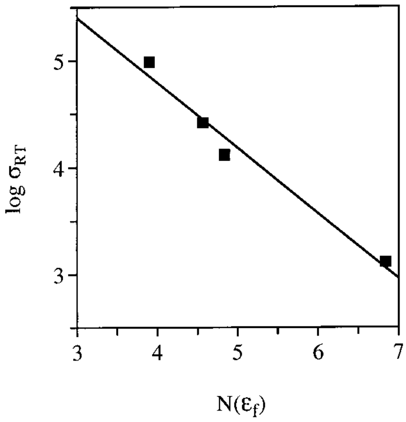
The most important observations based on the calculated band structures are the following. First, the 3D band structure is not just the superposition of twice that of a single layer. Indeed, some bands split considerably when introducing the interlayer interactions (compare for instance the two band structures along the Γ → Z direction). This is also clear when looking at the Γ → Y direction in Figure 2b (i.e., along the *b**-direction, *b* being the interlayer direction): some bands which cross or lie near the Fermi level have a quite sizeable dispersion. Thus, it is clear that the interlayer Te...Te interactions cannot be neglected. Second, there are several extremely wide bands along the Γ → X direction (i.e., along the *a**-direction, *a* being the propagation direction of the btp chains) which are mainly Te in character and which cross the Fermi level, as expected from the presence in these phases of Te-based btp chains. Third, in the region around the Fermi level these wide bands cross two bands per layer which are much less dispersive and are mainly Ta (or Nb in the $MNbTe_5$ phases) in character. Fourth, the dispersion of most of the bands along the Γ → X direction is very large but those along the Γ → Y and Γ → Z directions (i.e., the interlayer and intralayer interchains directions, respectively) are smaller but non-negligible and of the same order of magnitude along both directions.

The first and fourth observations make the importance of the interlayer Te...Te interactions clear and, maybe more surprisingly, the fact that the interlayer interactions are as strong as the intralayer interchain interactions. The second and third observations clearly show that there is an important electron transfer from Te to Ta (or Nb in the $MNbTe_5$ phases). Of course, this transfer is something inherent to the $MM'Te_5$ layers (see Figure 2a) but it is importantly affected by the interlayer Te...Te interactions. These conclusions are common to the four $MM'Te_5$ phases and completely validate the qualitative discussion of the previous section. From the viewpoint of the electrical conductivity our study suggests that these phases must be 3D metals although with a strong anisotropy, i.e., the conductivity should be much higher along the btp chain direction. The only difference between the $NbPdTe_5$ and the $NbNiTe_5$/$TaNiTe_5$/$TaPtTe_5$ phases is that the Fermi level does not cut bands along the interlayer Γ → Y direction for $NbPdTe_5$; there is a relatively small band gap along this direction. This fact is probably inherent to the different interlayer stacking and is not a parameter dependent feature because it was also noted by Halet et al[8] who used a different set of parameters in their calculations. Thus, $NbPdTe_5$ should have a weaker 3D metallic character than the other three $MM'Te_5$ phases. However, we should not conclude that the smaller conductivity of $NbPdTe_5$ originates from this fact because the conductivity of these phases is largely dominated by the Te...Te interactions along the btp chain direction. We must look in more detail at the electronic structure before discussing this point.

Our previous work[7] on the ternary tellurides $Ta_3Pd_3Te_{14}$ and $Ta_4Pd_3Te_{16}$ showed how the interlayer Te...Te interactions are responsible for the large difference in the density of states at the Fermi level [$N(\varepsilon_f)$] between the two phases and we proposed that this fact was at the heart of the large difference in conductivity between the two phases. Both the qualitative discussion of section 2 and the band structure calculations, suggest that the interlayer Te...Te interactions must also be very important in determining the conductivity of the $MM'Te_5$ phases whereas the nature of the M′ transition metal atom should not play a major role. That the conductivity and the strength of the Te...Te interlayer interactions should be correlated can be seen in Figure 3a where we have plotted the room temperature conductivity of the four $MM'Te_5$ phases vs the shortest Te...Te interlayer contact (such a correlation has already been noted previously[1a]). The four $MM'Te_5$ phases appear perfectly aligned in this plot and $NbPdTe_5$ is clearly separated from the other three phases, the shorter interlayer Te...Te contacts being associated with the smaller conductivities.



(a)



(b)

Figure 3. (a) Plot of the log σ_{RT} (σ_{RT}: room temperature conductivity) vs the shortest Te···Te interlayer contact for the $MM'Te_5$ phases. (b) Plot of the log σ_{RT} vs the calculated density of states at the Fermi level $N(\varepsilon_f)$ for the $MM'Te_5$ phases.

Figure 3b shows a plot of the room temperature conductivity versus the calculated $N(\varepsilon_f)$ for the $MM'Te_5$ phases. Contrary to intuitive expectations, the conductivity increases as $N(\varepsilon_f)$ decreases. This result is also obtained when the N(ε_f) calculated for a single layer is used. Thus, it is clear that the situation in the MM′Te_5 series is very different from that in the $Ta_3Pd_3Te_{14}$ and $Ta_4Pd_3Te_{16}$ phases: the N(ε_f) cannot be taken as a basis for understanding the conductivity differences in the MM′Te_5 phases. In fact, these results should not be that surprising given that there are many bands crossing the Fermi level and that some of them are quite flat for large zones of the Brillouin zone. In other words, with such a complex situation, an increase in N(ε_f) does not necessarily mean that the conductivity must increase because the mobility of the different types of electrons can be rather different. A fraction of the electrons may be very mobile and delocalized making a strong contribution to the electrical conductivity of the phase and another fraction can behave as localized electrons having a very weak contribution to the electrical conductivity. As a matter of fact, the magnetic susceptibility of the metallic phases $NbNiTe_5$ and $TaNiTe_5$ is temperature dependent[1d] as if there were localized electrons as well as delocalized electrons in these phases. For $TaPtTe_5$ and $NbPdTe_5$ the magnetic susceptibility is temperature independent as expected for a normal metal.[1d] Thus, there seems to be a strong competition between a localized vs delocalized behavior for some of the electrons near the Fermi level in the MM′Te_5 phases so that it is not really surprising that there is no correlation between the calculated values of the N(ε_f) and the conductivity.

Te...Te Interlayer Interactions, Te → M (M = Nb, Ta) Electron Transfer and Conductivity of the MM′Te_5 Phases

At this point we would like to have a closer look at the Te → metal electron transfer induced by the Te...Te interlayer interactions mentioned above. As expected, the Te → M′ electron transfer (M′ = Ni, Pd, Pt) is very small (0.014, 0.017, 0.021 and 0.041 electrons per M′ atom for $TaPtTe_5$, $TaNiTe_5$, $NbNiTe_5$ and $NbPdTe_5$, respectively). The Te → M electron transfer (M = Nb, Ta) is quite strong (0.129, 0.157, 0.189 and 0.267 electrons per M atom for $TaPtTe_5$, $TaNiTe_5$, $NbNiTe_5$ and $NbPdTe_5$, respectively). As shown in Figure 4a, there is a clear correlation between the strength of this Te → M electron transfer and the shorter Te...Te interlayer contacts. The transfer increases when the Te...Te interlayer contacts become shorter, i.e., the interlayer Te...Te interactions become stronger. Interestingly, the four MM′Te_5 phases appear perfectly aligned in this plot and $NbPdTe_5$ is clearly separated from the other three phases. These results make clear the relationship between the Te...Te interlayer interactions and the very important electron transfer that they induce. Since we noted the excellent correlation between the conductivity and the Te...Te interlayer interactions (see Figure 3a) it is not surprising to find also an excellent correlation between the conductivity and the strength of the Te → M electron transfer (see Figure 4b).

In order to analyze the nature of this electron transfer we carried out calculations in which the Te...Te interlayer overlaps were deleted and we compared the results with those for the full calculations. The electrons are mainly transferred from the two Te atoms forming the shorter side (3.196 Å in $NbNiTe_5$) of the triangular faces of the prisms (see contact *m* in Figure 1b). In fact they are transferred from the bonding combination of the two p orbitals of these atoms perpendicular to the layer, i.e., from a bonding π-type orbital. These Te p orbitals interact very well with the p orbital of the two capping Te atoms which is parallel to the direction of the btp chain. They are also those pointing towards the next layer and implicated in the shorter interlayer Te...Te short contacts. Of course, the overlap population of the shorter Te−Te triangular side decreases when the Te...Te interlayer interactions are switched on. Assuming that the local x, y and z coordinates point approximately towards the *a*, *b* and *c* directions of Figure 1b, the electrons are transferred towards an M orbital which can be described as x^2-y^2 which mixes in some z^2 character, in

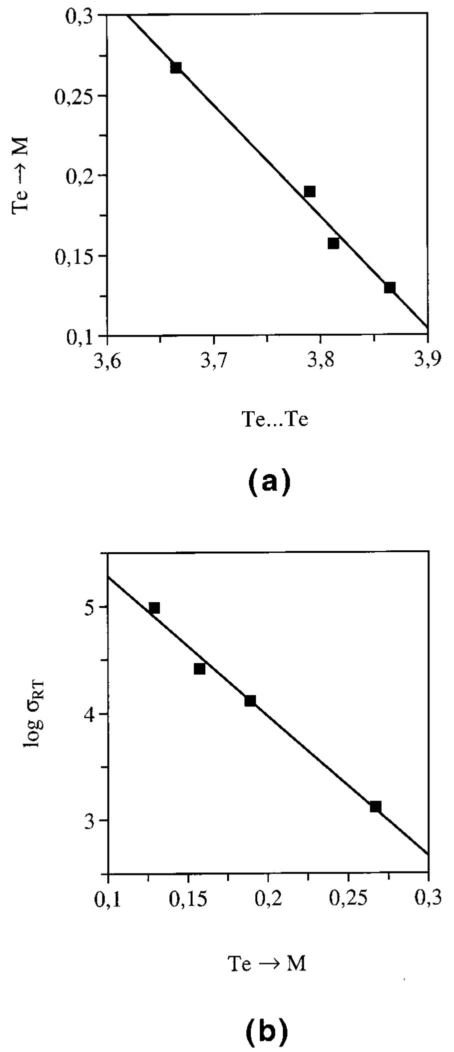


Figure 4. (a) Plot of the Te → M (M = Nb, Ta) electron transfer due to the interlayer Te···Te interactions vs the shortest Te···Te interlayer contact for the MM′Te_5 phases. (b) Plot of the log σ_{RT} vs the Te → M (M = Nb, Ta) electron transfer induced by the interlayer Te···Te interactions for the MM′Te_5 phases.

other words, an orbital which is in between an x^2-y^2 orbital and a z^2 orbital.

Coming back to our main purpose, we suggest that it is the Te → M electron transfer induced by the interlayer interactions which lies behind the conductivity differences for the $MM'Te_5$ phases. The reason is the following: because of the Te → M electron transfer, the electrons dominating the conductivity of the $MM'Te_5$ phases, i.e., the Te-based electrons near the Fermi level, are less screened from the core attractive forces of the Te atoms engaged in the Te → M electron transfer. Consequently, they are more tightly bound and their contribution to the conductivity is reduced.[11] In chemical terms, the Te atoms engaged in the electron transfer behave as 'more electronegative' because of the electron transfer and attract more strongly their electrons. This effect will increase with the strength of the Te...Te interlayer interactions making less metallic the $MM'Te_5$ phases with stronger interlayer Te...Te interactions.

Let us remember that the electrons transferred leave a Te−Te bonding orbital located in the shorter side of the triangular faces of the prisms. Thus, the conductivity of the $MM'Te_5$ phases and the length of this Te...Te short contact should be correlated: as the Te → M electron transfer increases, the Te...Te short contact should increase and the conductivity decrease. In fact, this is the case. According to the presently available crystal structures[1] this Te...Te short contact is 3.153 Å for $TaPtTe_5$, 3.183 Å for $TaNiTe_5$, 3.196 Å for $NbNiTe_5$ and 3.242 Å for $NbPdTe_5$. This is in excellent agreement with the conductivity of these phases which decreases in the same order. Thus, we believe that even if our argument is very simple and naive, it grasps the essential feature underlying the conductivity behavior of these phases.

Finally, concerning the two structurally related $Ta_3Pd_3Te_{14}$ and $Ta_4Pd_3Te_{16}$ phases, we would like to point out that the former, which has a conductivity one order of magnitude smaller than the latter, also has a larger Te → M electron transfer and the shortest interlayer Te...Te contacts. Thus, the argument developed here should also work for these phases. However, $Ta_3Pd_3Te_{14}$ also has a considerably smaller density of states at the Fermi level so that it is not clear which of the two effects really leads to the difference in conductivity. Magnetic susceptibility measurements could be helpful in scrutinizing this point.

Conclusions

In summary, we believe that the present work provides a simple explanation for the long standing problem of the conductivity differences in the $MM'Te_5$ phases. It also provides additional evidence for the important role that interlayer Te...Te interactions can play in modulating the conductivity of metallic layered tellurides.

Acknowledgments

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