



	Experiment title: Electronic transfer induced by high pressure in dichalcogenides	Experiment number: HS-1909
Beamline: ID30	Date of experiment: from: 23/05/03 to: 26/05/03	Date of report: 05/05/04
Shifts: 9	Local contact(s): Mohamed Mezouar, Anne-Claire Dhaussy	<i>Received at ESRF:</i>
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Report:

1. Introduction

IrTe₂ adopts a polymeric CdI₂-type structure which is a derivative of CdI₂-type structures. When polymeric CdI₂- type IrTe₂ (named therein h-IrTe₂) is subjected to pressure up to 32 GPa, the p(Te) bands are destabilized and the electronic transfer is enhanced, giving rise to two new forms of IrTe₂. The hexagonal structure (h-IrTe₂) exhibits a first phase transition to a monoclinic type (m-IrTe₂) at 5 GPa and at room temperature. A second transition occurs at 32 GPa (after laser heating) and leads to the cubic form (c-IrTe₂). The charge balance of h-IrTe₂ can be written (Ir³⁺)(Te^{-1.5})₂. In m-IrTe₂, an analysis of the interatomic distances and band structure calculations leads to the charge balance (Ir³⁺)₃(Te₂)²⁻(Te^{-1.75})₄. This is the proof of the high reactivity of Te-Te bonding contacts which, when destabilized, give rise to (Te)_n entities and original structural arrangements. Our goal is therefore, thanks to high pressure, to shorten the Te-Te distances to destabilize antibonding levels, to modulate the electronic transfers, and to better understand the redox mechanisms of the structural rearrangements.

On the basis of IrTe₂ example, we wanted to extrapolate the high pressure behavior of MTe₂ family compounds. We chose to investigate the high pressure behavior of MTe₂ (M = Pt, Pd) which have very similar structural properties to IrTe₂. Indeed they also adopt polymeric CdI₂- type structures with low c/a ratio (1.30 for PtTe₂ and 1.27 for PdTe₂) indicating, as in h-IrTe₂, an electronic transfer. The volumes per formula unit are of the same range (72.23 Å³ for IrTe₂, 72.33 Å³ for PdTe₂ and 73.28 Å³ for PtTe₂). The Te-Te short bonding contacts are all ranging between the small interval 3.441 and 3.558 Å. On the basis of the below structural and electronic considerations, the charge balance of MTe₂ should then be much more closer to M³⁺(Te^{-1.5})₂ than to the usual one M⁴⁺(Te²⁻)₂. We then expect all the three MTe₂ compounds to have the same high pressure behavior.

In the present work, we performed high pressure experiments realized by X-ray diffraction in both angular- and energy-dispersive configuration at ambient and high temperature. We showed that, surprisingly, no phase transition was observed up to 30 GPa. We investigate here the reasons why IrTe₂ and MTe₂ (M =Pt, Pd) do not behave similarly under pressure. On the basis of electronic band structure calculations, we discuss the charge balance of MTe₂ (usually given as M⁴⁺(Te²⁻)₂) and the oxidation state of the metal (corresponding to a d-electron count of d⁶) in these compounds.

2. Experimental section

Pure $M\text{Te}_2$ powder samples were ground to a fine powder in an agate mortar and loaded in the pressure chamber of a membrane-type diamond anvil cell. A pressure transmitting medium (a mixture of water/ethanol/methanol for ambient temperature and LiF for high temperature experiments) was added to provide quasi-hydrostatic pressure conditions. The ruby fluorescence methodⁱ was used to measure the pressure by mixing ruby chips in the powder sample. A first set of experiments was carried out in an energy-dispersive (EDX) mode on the DW11 beamline (LURE, Orsay) on both PdTe_2 and PtTe_2 at room temperature and at 300°C. A second set of experiments was performed in an angular-dispersive (ADX) one on the ID30 beamline (ESRF, Grenoble) only on PdTe_2 at 300°C up to 30 GPa. The x-ray wavelength was 0.3738 Å. The experimental, calculated, and difference plots obtained at 30 GPa for PdTe_2 are represented in **Figure 1**.

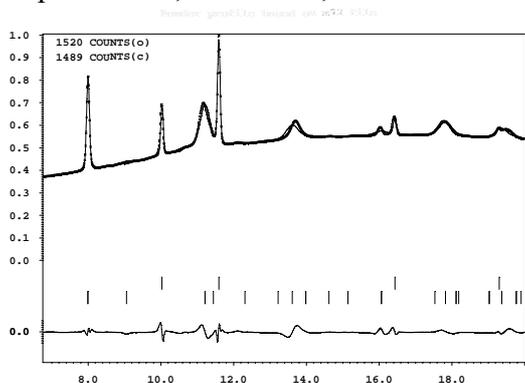


Figure 1

For each value of pressure it was possible to assign all the diffraction peaks to the CdI_2 -type structure, so we conclude that neither PdTe_2 nor PtTe_2 undergoes a phase transition under the pressure and temperature conditions realized during our experiments. The similarity of volume under pressure (for example for PdTe_2 : 58.2(1) Å³ for 20°C and 57.3(1) Å³ for 300°C) indicates that no phase transition has to be expected as there is no difference between the room and high temperature phases.ⁱⁱ This is an unexpected result regarding the behavior of IrTe_2 .

3. Discussion : Structure evolution of PdTe_2 and PtTe_2 under pressure

In order to explain the behavior of $M\text{Te}_2$ under pressure, we performed both VASPⁱⁱⁱ calculations (to obtain an evaluation of the distances when Rietveld refinements were not possible to carry out) and FP-LAPW^{iv} calculations to obtain the density of state (DOS) curves.

The plots of the electronic DOS calculated for PtTe_2 , PdTe_2 and IrTe_2 are represented in **Figure 2**. The solid lines refer to the total DOS curves, the dotted lines to the partial d orbitals of M (M = Ir, Pt, Pd) and the vertical lines to the Fermi levels. In capturing the essential features of the DOS curves, it is convenient to consider the oxidation state of the metal atoms. With the oxidation state of Ir^{3+} for Ir (corresponding to a d^6 count), the ionic electronic counting scheme predicts that the t_{2g} bands are completely filled but e_g -block bands are empty in IrTe_2 .

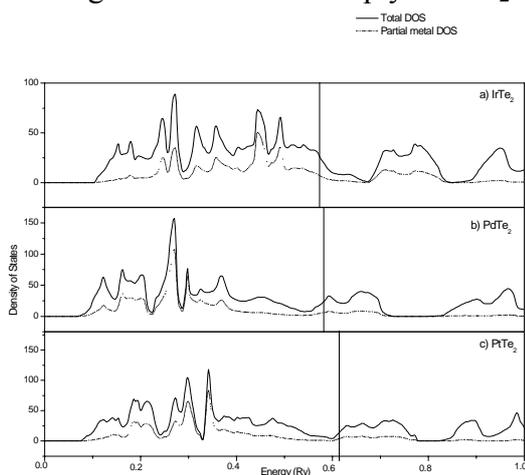


Figure 2

Another study had already mentioned a different charge balance for these compounds and had assumed that a more realistic charge balance should be written $M^{3+}(\text{Te}^{-1.5})_2$.^v Indeed, on the basis of Te-Te distances, we note that the shortest interlayer $\text{Te}\cdots\text{Te}$ distance in $M\text{Te}_2$ (3.464 Å for M = Pt and 3.333 Å for M = Pd) is comparable to the shortest non-bonding interchain $\text{Te}\cdots\text{Te}$ distance (3.472 Å) in trigonal tellurium^{vi}, and to the shortest interlayer $\text{Te}\cdots\text{Te}$ distance (3.469 Å) in monoclinic tellurium^{vii}. Moreover, in the arsenic-type tellurium^{viii}, the anionic hexagonal net is identical to the $M\text{Te}_2$ one with quite similar interlayer $\text{Te}\cdots\text{Te}$ distances (3.477 Å). This suggests that the charge distribution on tellurium in $M\text{Te}_2$ is

These predictions are consistent with the total and partial DOS plots shown in **Figure 2a** and allow us to assign the e_g bands to the energy region between 0.675 and 0.854 Ry. The same assignment for the e_g -band can be done for PdTe_2 (e_g -block bands to the energy region between 0.546 and 0.725 Ry) and PtTe_2 (e_g -block bands to the energy region between 0.600 and 0.793 Ry). Assuming that Pt and Pd have an oxidation state of +4 (like it is usually done in the literature), the electronic counting is d^6 , as in IrTe_2 , and the e_g -block bands should be empty. But, as we can see on **Figure 2b** and **c**, this is not the case: the e_g -block bands are partially filled. As a consequence, the real oxidation state of Pt and Pd is lower than +4.

similar to that in elemental tellurium. Thus, it would be appropriate to consider that the tellurium of $M\text{Te}_2$ has the oxidation state close to 0 rather than to -2 . Nevertheless, the state oxidation of tellurium can not be strictly equal to 0 as all the distances in elemental tellurium and $M\text{Te}_2$ are not the same: Te may have an oxidation state between 0 and -1. Then the oxidation state of Pt and Pd in $M\text{Te}_2$ would be much closer to 0 - +2 rather than to +4, and the d-electron count of Pd and Pt in $M\text{Te}_2$ would be close to d^8 - d^{10} . This is confirmed by the rough approximation of the number of electrons on the d orbitals which can be obtained by means of FP-LAPW calculations. We find that the d levels are occupied by $6.7 e^-$ for IrTe_2 (which is in good agreement with the oxidation state +3 for Ir) and $8.2 e^-$ for both PtTe_2 and PdTe_2 . We can then assign the charge balance $M^{+2}(\text{Te}^-)^2$ ($M = \text{Pt}, \text{Pd}$) corresponding to a d electron counting of d^8 under ambient conditions. Thus the d levels are almost filled. As a consequence, even if the top portion of Te p bands are raised in energy when destabilized under pressure, the electron transfer is difficult because the d levels are almost full and can hardly accept more electrons. The electron depletion at the top of the anionic band is not important enough to reach the threshold hole concentration leading to a structural rearrangement.

Nevertheless, the electron transfer induced by pressure is a reality as probed by the evolution of experimental Te-Te distances with pressure. Indeed, we observe a Te-Te interlayer distances decreasing corresponding to an electronic transfer $sp(\text{Te}) \rightarrow d(\text{M})$ (vide supra). So the decrease of experimental distances obtained for PdTe_2 show that the electronic transfer is existing up to 5 GPa. However, when pressure is increased above 5 GPa, Te-Te distances are equal within the uncertainties (**Figure 3**). That is to say no more electronic transfer can be achieved under pressure: the d levels are full. This was confirmed by Huckel DOS calculations^{ix} performed using the atomic parameters of PdTe_2 at 30 GPa and 300°C obtained by Rietveld refinements (**figure 4**). Under pressure we have then generated extra-electronic transfers leading to the complete reduction of telluride in Te^0 in the $M\text{Te}_2$ compounds. The charge balance is $M^0(\text{Te}^0)_2$. This is consistent with the fact that the anionic subnetwork is very similar to the one found in a high pressure form of elementary tellurium (As-type), i.e. $\sim 2.87 \text{ \AA}$, the same value as in PdTe_2 within uncertainties.

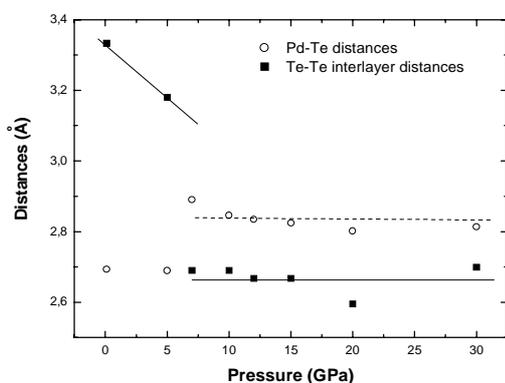


Figure 3

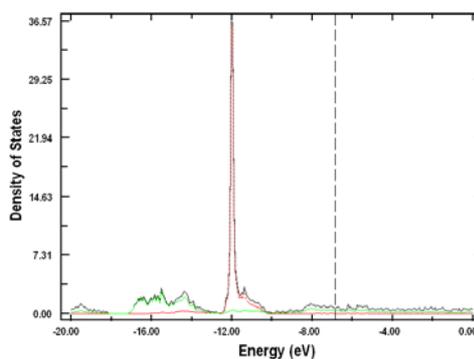


Figure 4

4. Conclusion

By means of high pressure and high temperature experiments we were able to better describe the charge balance of PdTe_2 and PtTe_2 , which can be written $M^{+2}(\text{Te}^-)_2$. This new charge balance accounts for the lack of phase transition observed under high pressure because the d levels are almost full and so the electronic transfer is less important than in IrTe_2 : the threshold concentration in holes can not be reached for the holes to condense and to give a structural rearrangement. We also evidenced an electronic transfer leading to the oxidation state of 0 for Pd and Te.

Work to be published under the title : « PdTe_2 and PtTe_2 answer to pressure », C. Soulard, P.-E. Petit, S. Jobic, M.H. Whangbo and A.-C. Dhaussy.

ii Sikka

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ix Our calculations were carried out employing the CAESAR program package (Ren, J.; Liang, W.; Whangbo, M.-H., *Crystal And Electronic Structure Analysis Using CAESAR*, 1998; Free download from <http://chvamw.chem.ncsu.edu/>).