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Why pressure induces an abrupt structural rearrangement in $PdTe_2$ but not in $PtTe_2$

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Abstract

High-pressure X-ray diffraction measurements were carried out for polymeric CdI_2-type compounds MTe_2 (M = Pt, Pd) to investigate if they undergo a structural phase transition under pressure as does $IrTe_2$. Up to 27 GPa at room temperature $PtTe_2$ does not undergo any structural phase transition. In contrast, however, an abrupt change in the inter-atomic distances occurs in $PdTe_2$ above 15.7 GPa at room temperature, and above 5 GPa at 300 °C, but the volume vs. pressure curve exhibits no discontinuity. To account for the differences between the isostructural compounds $PtTe_2$, $PdTe_2$ and $IrTe_2$, their electronic structures and bonding were analyzed on the basis of first principles electronic band structure calculations.

Keywords: $PdTe_2$; $PtTe_2$; X-ray diffraction

1. Introduction

The CdI_2-type transition metal dichalcogenides MQ_2 (M = transition metal, Q = chalcogen) consist of MQ_2 layers made up of edge-sharing MQ_6 octahedra, where adjacent MQ_2 layers are held together by van der Waals interactions. $IrTe_2$ adopts the polymeric CdI_2-type structure, i.e., a derivative of the CdI_2-type structure [1,2], in which adjacent MQ_2 layers have short $Q\ldots Q$ contacts thereby leading to a low c/a ratio, i.e., 1.38 instead of 1.67 expected on the basis of a classical hexagonal close stacking of the anions. From the viewpoint of the ionic electron counting leading to the charge balance $M^{4+}(Q^{2-})_2$, the occurrence of short interlayer $Q\ldots Q$ contacts is explained by considering the electron transfer from the p-block bands of Q to the d-block bands of M [3]. When the polymeric CdI_2-type $IrTe_2$ [2] (hereafter named h-$IrTe_2$) is subjected to pressure up to 32 GPa, it undergoes two structural phase transitions [4-6]. The hexagonal phase h-$IrTe_2$ is converted to a monoclinic-type structure (m-$IrTe_2$) at 5 GPa and at room temperature, and then to a pyrite structure (c-$IrTe_2$) at 32 GPa under laser heating.

$PtTe_2$ and $PdTe_2$ are similar to $IrTe_2$ in several structural and electronic properties under ambient conditions. They both adopt the polymeric CdI_2-type structure [7,8] with a low c/a ratio (i.e., 1.30 in $PtTe_2$ and 1.27 in $PdTe_2$). The three compounds $IrTe_2$, $PtTe_2$ and $PdTe_2$ have similar cell volumes per formula unit (i.e., 72.23(1) Å^3 for $IrTe_2$, 72.43(6) Å^3 for $PdTe_2$ and 73.35(4) Å^3 for $PtTe_2$), and their short Te…Te contacts are in the range of 3.44–3.56 Å. In addition, $IrTe_2$, $PtTe_2$ and $PdTe_2$ should be similar in electronic structure because the electronegativities of Ir, Pt and Pd are

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nearly the same (i.e., 2.20 for Ir and Pd, and 2.28 for Pt in Pauling scale), although MTe_2 (M = Pt, Pd) has one more valence electron per formula unit than does $IrTe_2$. Thus, one might suggest that the high-pressure behavior of MTe_2 (M = Pt, Pd) would be similar to that of $IrTe_2$. To test this speculation, we performed high-pressure X-ray diffraction experiments for MTe_2 (M = Pt, Pd) in both angle- and energy-dispersive configurations. MTe_2 (M = Pt, Pd) was not found to undergo a first-order structural phase transition up to 27 GPa. Only a sudden change in the pressure dependence of the interatomic distances was observed in $PdTe_2$ at about 19 and 6 GPa at room temperature and at 300 °C, respectively. To understand why $IrTe_2$, $PdTe_2$ and $PtTe_2$ behave differently under pressure, we compared their electronic structures on the basis of first principles electronic band structure calculations.

2. Synthesis and structure determination under pressure

2.1. Synthesis

A stoichiometric mixture of elemental powders (Pd sponge, 99.9% Aldrich; Pt powder, 325 mesh, 99.9 + %, Alfa Aesar; Te granules, 30 mesh, 99.99%, Aldrich) was ground and loaded into a quartz tube (~9 cm in length, 10 mm in diameter). The tubes were evacuated to 10^{-2} Torr, sealed and placed into a furnace whose temperature was raised to 850 °C at the rate of 5 °C per hour and kept there for 360 h, following the procedure of Lieth et al. [9] The powder sample was subsequently cooled to room temperature at the rate of 5 °C/h. X-ray powder diffraction data were collected on an INEL CPS 120 diffractometer (Debye–Scherrer geometry). The structure refinements were carried out using the JANA2000 software package [10]. The cell parameters obtained in the present work are in good agreement with those reported in the literature [7] (in italics and within parenthesis), i.e., $a = 4.027(1)$ (*4.026*) Å and $c = 5.223(2)$ (*5.221*) Å for $PtTe_2$, and $a = 4.037(2)$ (*4.037*) Å and $c = 5.132(2)$ (*5.126*) Å for $PdTe_2$. The corresponding volumes are 73.35(4) (*73.28*) $Å^3$ for $PtTe_2$ and 72.43(6) (*72.33*) $Å^3$ for $PdTe_2$.

2.2. Structure determination

Preliminary high-pressure energy-dispersive X-ray diffraction (EDX) measurements at 20 and 300 °C were carried out at the LURE (France). Experiments reported herein were performed in an angle-dispersive (ADX) mode on the ID30 beamline (ESRF, France) at room temperature (RT) for $PtTe_2$, and at RT and at 300 °C for $PdTe_2$. The experimental procedure has already been described elsewhere [11]. MTe_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 (DAC). The pressure-transmitting medium added to provide quasi-hydrostatic pressure conditions was N_2 for the experiments at RT, and LiF for those at 300 °C. The ruby fluorescence method [12] was used to measure the in situ pressure.

The diffraction patterns were recorded up to 27 GPa for 2θ angles ranging from 2° to 20° (Figs. 1 and 2). For the 300 °C experiments, the $PdTe_2$ powder placed in the DAC was resistively heated. The storage ring was operated at 6 GeV and 7–15 mA (single-bunch mode). A channel-cut monochromator was used to select the wavelength of 0.3738 Å. The energy calibration was carried out using the K-edge of an iodine foil. The beam was focused via two multilayer mirrors settled in the Kirkpatrick-Baetz (KB) configuration, and then collimated with slits, thus defining a spot of 20 μm in

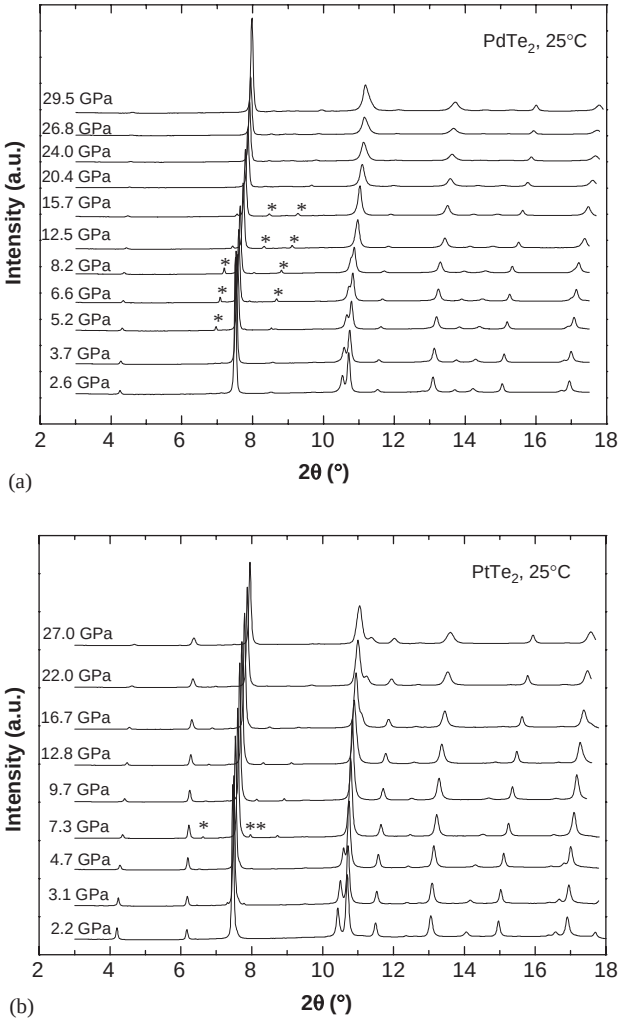

Fig. 1. Angle dispersive diffraction patterns of (a) $PdTe_2$ and (b) $PtTe_2$ under pressure during the decompression cycle at room temperature. The asterisks refer to the β-N_2 high-pressure phase.