PRESSURE INDUCED PHASE TRANSITION IN $MnTe_2$

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Energy dispersive high-pressure powder X-ray experiments have been performed for $MnTe_2$ up to a pressure of 20 GPa. $MnTe_2$ undergoes a discontinuous transformation from the cubic pyrite type structure to the orthorhombic marcasite type structure at 7.0±0.5 GPa upon increasing pressure. The transformation is accompanied by a large reduction in the specific volume ($\Delta V/V = 0.18$) which probably reflects different magnetic properties of the two modifications of $MnTe_2$.

The TX_2 (T = Cr, Mn, Fe, Co, Ni; X = P, As, Sb, S, Se, Te) compounds often crystallize in one of several related structure types [1,2]. Among these, the pyrites (FeS_2-p), marcasites (FeS_2-m) and arsenopyrites (FeAsS-ap) have the largest number of representatives. As a function of temperature and composition (e.g. in ternary solid solution phases) conversions m → p are well established [3,4] and continuous second-order transitions are found between m- and p-type phases [2]. The MnX_2 (X = S, Se, Te) compounds [1,5,6] crystallize in the p type structure over their entire temperature range of stability. However, recently a structural transformation (probably associated with a change in spin state) was found in MnS_2-p, when hydrostatic pressure was applied [7,8]. The high pressure modification (not stable at ambient conditions) is of the m-type structure and is characterized relative to the p-type structure by taking a much lower unit cell volume per formula unit. Such relatively large variations in unit cell volume between different modifications most likely represent differences in physical (magnetic) properties [9]. A similar situation to that of MnS_2 may possibly exist for the isostructural phases $MnSe_2$ and $MnTe_2$. In this work we report on a high pressure energy dispersive X-ray diffraction study on $MnTe_2$.

Powder samples of $MnTe_2$ were synthesized from the elements (Mn, crushed flakes, 99.99%, Johnson, Matthey & Co.; Te, powder, 99.999%, Koch Light Laboratories) using the sealed silica capsule technique. After the first heat treatment at 650°C for 5 d the samples were cooled to room temperature and crushed before being subjected to two further similar annealing cycles (500°C, 10 d). The product obtained by this procedure contained only minor traces of free Te.

Powder X-ray diffraction data were collected at ambient conditions with a Guinier camera (Cu $K\alpha_1$ radiation, Si as internal standard). The cubic lattice constant for $MnTe_2$-p (space group $Pa\bar{3}$) a = 695.32(12) pm agrees with already reported values [1,10]. High-pressure powder X-ray diffraction data were obtained by the energy dispersive technique, using a tungsten tube. Pressures up to 20 GPa were generated in a gasketed diamond anvil cell [11], and the pressure was determined using the ruby fluorescence technique [12]. The spectra were partly masked by the presence of Te characteristic radiation peaks and reflections resulting from the inconel gasket material. The positions of the Bragg reflections of $MnTe_2$ were obtained through a curve fitting procedure. Calculated powder X-ray intensities with the LAZY-PULVERIX programme [13] were used as guide in the indexing of the X-ray diagrams.

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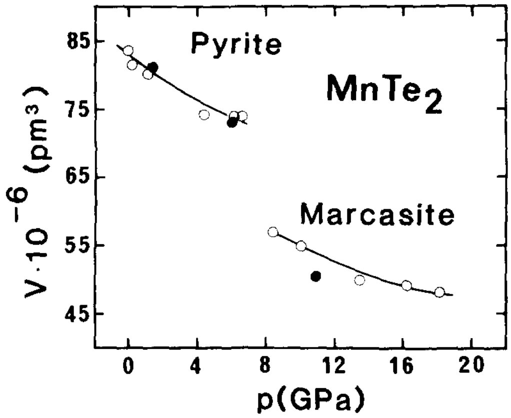

Fig. 1. Variation of the specific volume of $MnTe_2$ for pressures up to 18 GPa. Open and filled symbols refer to increasing and decreasing pressures, respectively. The full lines represent a fit of the Birch equation of state to the data points.

The p-type modification of $MnTe_2$ was found to exist at pressures up to 7.0 ± 0.5 GPa. The variation in specific volume with pressure is shown in fig. 1. At pressures $p > 7.0$ GPa the reflections characteristic for the p-type structure disappeared and a new set of reflections appeared. A meaningful interpretation of the pattern consisting of only 4–5 reflections requires input of some structural informations. As the high pressure modification of MnS_2 is unambiguously of the m type [7,8], we assume this to hold also for $MnTe_2$. The intensity of the observed reflections were in good agreement with those calculated for $MnTe_2$-m, using positional parameters for $FeTe_2$ [14] (space group Pnnm). The variation of the specific volume of $MnTe_2$-m with pressure is shown in fig. 1. The p → m transformation is accompanied by a volume decrease of about 18%. This volume collapse is somewhat larger than that found for MnS_2 (15%) [7]. However, the pressure required for triggering the transformation is lowered from 14 GPa for MnS_2 to 7 GPa for $MnTe_2$.

A fit of the Birch equation of state [15] to the data points yield the parameters B_0 = 14.9 GPa, B_0' = 16.3 GPa, and B_0 = 9.2 GPa, B_0' = 4.4 GPa for the p- and m-type modifications, respectively. Attempts to fit the data points to a zeroth-order Birch equation of state (B_0' = 4, fixed value; $B_0 \sim 40$ GPa) were not satisfactory, indicating that the unusual large value of B_0' in the pyrite type structure may be real. Due to the large scattering of the data points which results from overlapping characteristic lines, mentioned before, the values of B_0 and B_0' may have errors of about 20% to 30%. Ultrasonic measurements should be made to improve the accuracy of B_0 resulting in an improvement of the error of B_0'. The B_0 and B_0' values in the marcasite type high pressure structure have been determined for completeness. However, they cannot be compared with the values in the pyrite type structure, as the marcasite structure is only hypothetical at low pressures.

Some TX_2 compounds (e.g. FeS_2 [4], $OsTe_2$ [4]) are known to crystallize with both the m- and the p-type structures, and transformations m → p are established as a function of temperature. For FeS_2 and $OsTe_2$ the pyrite modifications take the smallest specific volume ($\Delta V = -2.9 \times 10^6$ pm^3 for $OsTe_2$). This shows, that only small differences in the specific volume are connected with the different packings of the X_2 dumbbells in the p-, m-, and ap-type structures. Therefore, the huge ΔV of the p → m transformations in MnS_2 and $MnTe_2$ can probably not be attributed to the structural rearrangement (reorientation of the X_2^{2-} pair).

A main distinction between the MnX_2-p and other TX_2 compounds is the magnetic state of the metal atom. The MnX_2 compounds exhibit paramagnetic and long range antiferromagnetic properties associated with ~5 unpaired electrons [1,16,17] (d^5 high spin state) contrary to the diamagnetic properties found in e.g. FeX_2 [1]. This difference in the magnetic properties is probably responsible for the observed reduction of the specific volume on going from MnX_2 to the corresponding FeX_2 compounds. Therefore we are tempted to conclude that the volume collapse accompanying the p → m transformation in MnS_2 and $MnTe_2$ reflects mainly a change of the magnetic state. However, for verification, measurements of spin dependent properties at high pressures are required. The Mössbauer data for ^{57}Fe substitution in MnX_2 [18,19] demonstrate a high to low spin transition for the iron atoms upon increasing pressure (i.e. going from the p- to the m-type structure) and thus lend support to the assumption of coupled magnetic and structural transformations in MnX_2. A similar high pressure X-ray diffraction study of $MnSe_2$ is in progress.

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