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High Pressure Phases of Some Compounds of Groups II–VI

Abstract. *The high pressure phases of the mercury and cadmium sulfides, selenides, and tellurides have been determined by means of x-ray diffraction patterns obtained while the materials are under pressure.*

The effect of high pressure on the properties of many of the Group II–VI compounds has been the subject of many recent discussions (*1, 2*). The most pronounced effects of pressure have been the drastic changes in the electrical resistances of the materials, and these changes are again attributed to crystallographic transformations (*3*). In some cases, direct evidence of the transformation has been obtained from x-ray diffraction patterns taken while the material is under pressure (*4*). However, the new structures are usually based on the appearance of a rather limited number of x-ray reflections.

Table 1. Lattice parameters of atmospheric and transformed phases crystal. Structure: B_1 cubic NaCl type; B_3, cubic zinc-blende type; B_4, hexagonal wurtzite type; B_9, hexagonal cinnabar type.

Compound	Atmospheric phase		High pressure phase		Applied pressure* (kb)
	Crystal structure	Lattice parameters a_0 – – – c_0 (A)	Crystal structure	Lattice parameters a_0 – – – c_0 (A)	
HgS	B_3	5.85	B_9	4.15–9.50	—
HgSe	B_3	6.09	B_9	4.32–9.68	15
HgTe	B_3	6.44	B_9	4.46–9.17	20
CdS	B_4	4.14–6.72	B_1	5.32	33
CdSe	B_4	4.30–7.01	B_1	5.49	32
CdTe	B_3	6.46	B_1	5.81	36

* As calculated from gas pressure applied to piston.

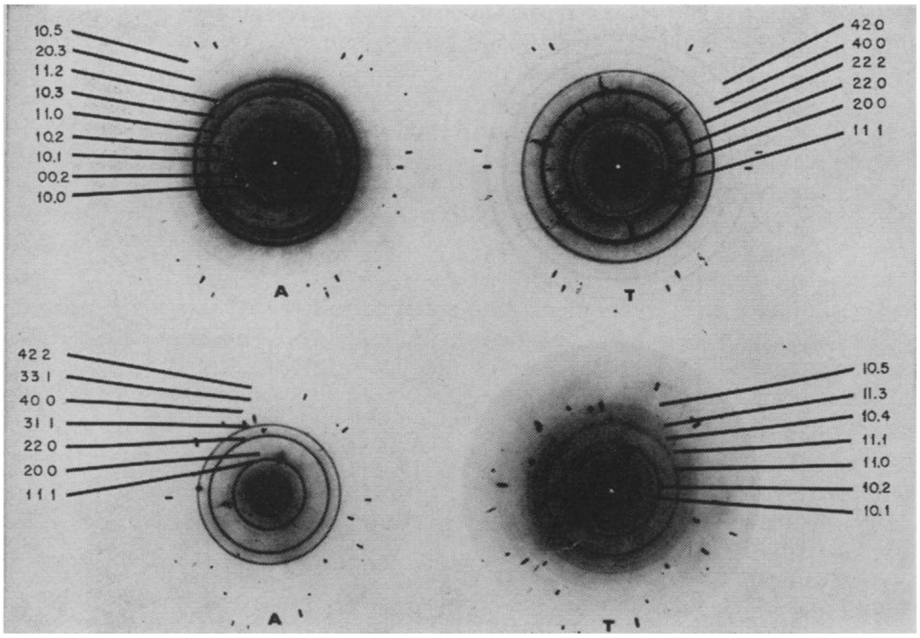

Fig. 1. X-ray diffraction patterns. Top *A*, CdSe at atmospheric pressure; Top *T*, CdSe at 32 kb; Bottom *A*, HgTe at atmospheric pressure; Bottom *T*, HgTe at 20 kb.

This report presents a series of x-ray parameters for some Group II–VI compounds that were obtained on an x-ray pressure camera similar to that described by Piermarini (*5*). However, the camera was modified by the addition of a film cassette whereby higher resolution patterns can be obtained over a larger angular range. With molybdenum radiation and the modified cassette, 2θ angles of about 40 degrees were recorded on films about 10 cm in diameter. The camera constant was calculated by using the untransformed x-ray diffraction pattern as a standard. Typical x-ray diffraction patterns with (*hkl*) indices, superimposed on the Laue pattern from the diamond anvils, are shown in Fig. 1.

The pressure was applied to the samples, held between two diamond anvils, by means of a gas-activated piston arrangement. The applied pressures were calculated from the known radii of the piston and diamond-bearing surfaces. The calculated values and comparisons with known transformation points from electrical data indicated ranges of 40 to 50 kb could be obtained with standard compressed gas cylinders. No attempt was made to measure the actual pressures in the camera except to apply sufficient pressures to cause the transformation.

The x-ray parameters and type of crystal structure obtained for a series of Group II–VI compounds are presented in Table 1.

These data are in fair agreement with parameters published for CdS and CdSe, 5.30 Å and 5.54 Å, respectively (*4*). It is difficult to ascribe any significance to the slight discrepancies because of inherent errors in attempting to measure pressure gradients over such small areas. No attempts have been made to correct the lattice parameters for compressibility effects of the transformed phase. The apparent inconsistency of the C_0 parameter of mercury telluride compared to the parameters of other mercury compounds does, however, indicate that compressibility could be responsible for the smaller C_0 parameter.

The cadmium compounds, representing both zinc-blende and wurtzite structures at atmospheric pressure, transformed into cubic NaCl-type structures. The mercury compounds, all zincblende structures at atmospheric pressure, transformed into the distorted NaCl-type or cinnabar structure. The effect of electronegativity and ion radii as discussed by Jayaraman (*1*) could account for the two different types of high-pressure phases obtained for the structurally similar CdTe and HgTe.

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Cosmic-Ray Exposure Age of the Farmington Meteorite from Radioactive Isotopes

Abstract. *The cosmic-ray exposure age of the Farmington meteorite was found to be greater than 7000 years from the ratio of the carbon-14 and argon-39 present and less than 25,000 years from the ratio of the aluminum-26 and argon-39 present. This exposure age is about an order of magnitude smaller than was estimated previously.*

Cosmic-ray exposure ages of meteorites have been determined from the ratio of the amount of a cosmic-ray-produced stable isotope to a cosmic-ray-produced radioactive isotope. Exposure ages of meteorites have also been estimated from the amount of a cosmic-ray-produced stable isotope alone. Schaeffer (*1*), Anders (*2*), and Arnold (*3*) have recently reviewed this topic. For the Farmington meteorite we determined the exposure age from the radioactive isotopes alone.

Kirsten, Krankowsky, and Zähringer (*4*) measured an unusually low content of the spallation rare-gas isotopes He^3 and Ne^{21} in the Farmington meteorite. Anders (*5*) found the Al^{26} content of Farmington also to be low, 3.6 ± 2.5 disintegrations per minute per kilogram, consistent with He^3 and Ne^{21} values. He interpreted these results to indicate an exposure age of less than 1 to 2 × 10^5 years. It is also possible to interpret the low He^3, Ne^{21}, and Al^{26} contents on the basis of shielding from cosmic-rays while the meteoroid was in space. The shielding interpretation requires the mass of the meteoroid to be more than 5 tons (metric); this mass is certainly possible. In order to rule out the shielding interpretation it is necessary to measure a cosmic-ray-produced radioactive isotope of a comparatively short half-life. We measured Ar^{39}, H^3, C^{14}, and Al^{26}. From the contents of these radioactive isotopes it is not only possible to rule out the shielding interpretation for the low He^3, Ne^{21}, and Al^{26} contents but also possible to determine the exposure age.

For measuring H^3 and Ar^{39} and for extracting the carbon in the form of CO_2 (*6*), the sample is melted with carrier gas by a radio-frequency heater and the gas is removed from the sample. The hydrogen and argon, after purification, are put into Geiger counters with volumes of 80 cm^3 and 0.7 cm^3. The CO_2, after purification, is put into a proportional counter of 35 cm^3 volume. The Geiger and proportional counters are operated in our low-level counting system (*6*). Since the Farmington meteorite fell in 1890 (*7*), there is a large uncertainty in the H^3 content, 550 ± 150 disintegrations per minute per kilogram. We found that the Ar^{39} content of a 35.3-gram sample obtained from C. Frondel was 7.3 ± 0.4 disintegrations per minute per kilogram, and a 35.7-gram sample obtained from B. Mason was 7.3 ± 0.3 disintegrations per minute per kilogram. This value of 7.3 disintegrations per minute per kilogram for Farmington is approximately the same as the content of Ar^{39} in ten other recently fallen meteorites that we have measured. We have measured the C^{14} content of only two meteorites, Farmington and Bruderheim; we obtained 47 ± 10 disintegrations per minute per kilogram for Farmington and 60 ± 10 disintegrations per minute per kilogram for Bruderheim. We determined the Al^{26} concentrations in two different samples of the Farmington meteorite by the nondestructive γ-γ coincidence method. This method is identical to that used by Anders (*5*). One sample was a 880-gram slice, 13 mm thick, obtained from C. Frondel. The other sample was 200 grams of powder from which the metal was removed; this powder was from a sample obtained from E. Olsen. We counted the 880-gram sample with a pair of crystal NaI(Tl) detectors of 6-inch diameter and 4-inch thickness; we counted the 200-gram sample with a pair of cylindrical 3 by 3 inch NaI (Tl) detectors. We prepared two calibration standards from a powdered mixture of NaCl and Fe with a known amount of Na^{22}. These standards contained 2.05 and 3.15 disintegrations per minute per gram and had the identical mass densities and electron densities as the meteorite samples. To duplicate the configuration of the slice we made an epoxy mold of the slice and poured the calibration powder in the mold. Background standards were prepared in the same way as the calibration standards. We measured 0.4 ± 0.4 disintegrations per minute per kilogram of Al^{26} in the 880-gram slice and 1.6 ± 1.6 disintegrations per minute per kilogram in the 200-gram powder. The errors given are one standard deviation in the counting statistics. These values are to be compared with an average value of about 54 disintegrations per minute per kilogram for chondrites (*8*). We have measured the Al^{26} content in nine chondrites and have found approximately the same average value. The chemical composition of the Farmington meteorite is similar to that of an average chondrite (*7*). Table 1 summarizes our measurements for Farmington.

Table 1. Radioactivity in the Farmington meteorite corrected to the date of fall. The half-life (in years) is given in parentheses.

Wt. of sample (g)	Isotope			
	H^3 (12.4)	Ar^{39} (320)	C^{14} (5770)	Al^{26} (7.5 × 10^5)
	(disintegration min^{-1} kg^{-1})			
35.3	550±150	7.3±0.4	47±10	
35.7		7.3±0.3		
880				0.4±0.4
200				1.6±1.6

The Ar^{39} activity shows that the Al^{26} and C^{14} production rates in the Farmington meteoroid for approximately 1000 years prior to its fall were similar to other chondrites. If the production rates were constant for time, t, then t is the cosmic-ray exposure age. The Al^{26} and C^{14} activities are related to t in years by the equations

$$\mathrm{Al}^{26} = 54\,[1 - \exp(-t/1.06 \times 10^6)]$$

$$\mathrm{C}^{14} = 60\,[1 - \exp(-t/8.33 \times 10^3)]$$

In the Farmington meteorite the Al^{26} is less than 1 disintegration per minute per kilogram and the C^{14} is within 10 disintegrations per minute of the value