Pressure-induced structural transitions in PbI$_2$: A high-pressure Raman and optical absorption study

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Abstract. The effect of pressure on the 2H and 4H polytype of PbI$_2$ has been investigated by Raman and optical absorption spectroscopy, using the diamond anvil cell. The 2H-polytype undergoes pressure-induced phase transitions at 5 kbar and near 30 kbar. The 4H-polytype exhibits phase transitions near 8 kbar and above 30 kbar. The Raman modes abruptly change at these pressures. The optical absorption edge shifts red at the rate of 15 ± 1 MeV/kbar in the 2H-PbI$_2$ and at the rate of 7 MeV/kbar in phase II. The latter phase is most likely to possess a 3d-structure and not a layer type. The possible structures for the high pressure phases are discussed.

1. Introduction

Lead iodide (PbI$_2$) crystallizes in the CdI$_2$ layer-type structure and is known to exist in several polytypes (Hanoka and Vand 1968). In this structure, each layer consists of a plane of Pb atoms sandwiched between two extended iodine layers, I-Pb-I. The simplest of the polytype is the so-called 2H which has one composite layer of I-Pb-I, and the crystal has the trigonal point group symmetry D_{3d}. The polytypes represent different stacking sequences of the I-Pb-I unit and can be obtained by varying the growth conditions (Prasad 1976) and techniques (Hanoka et al 1967).

Our interest in PbI$_2$ was stimulated mainly by the finding of two pressure-induced phase transitions by Bridgman (1937, 1948) near 4 kbar and 25 kbar. These transitions were accompanied by volume changes of 4% and 2% respectively. These rather large volume discontinuities suggest that the transitions cannot be due to interpolytype conversion, but must involve a change in the dimensionality of the structure, from the layered lattice to a three-dimensional lattice structure. In this connection it occurred to us that a high pressure Raman study of PbI$_2$ would be of interest.

Two high pressure Raman studies (Belyi et al 1982; Khilji et al 1982) on PbI$_2$ have already been reported in the literature and in these the 4H and 6H polytypes were studied up to 8 kbar and 14 kbar respectively. In another study Zallen and Slade (unpublished) investigated the 2H and 4H polytypes by Raman spectroscopy at high pressures. Optical transmission measurements (Carillon and Martinez 1977; Powell 1978) have also been reported up to 8 kbar. However, these studies have not established

the nature of pressure-induced phase transitions and further there are some discrepancies between them.

We have carried out Raman and optical absorption studies on $2H$-PbI_2 up to 60 kbar hydrostatic pressure in a gasketed diamond anvil cell and have also studied the 4H polytype. The results of these investigations will be presented and discussed in this paper.

2. Experiments and results

Vapour grown crystals of PbI_2 were available to us. These were a few millimeters in thickness and 5 or 6 mm in linear dimensions. The crystals were deep orange in colour and in thin layers exhibited an orange yellow transmission. For optical absorption and Raman studies very thin slices (20–30 μm thick) were peeled off and shaped to the appropriate size for mounting inside the gasket hole. The material is so soft that its shaping to the desired size presented no problems.

Hydrostatic pressure was generated in a gasketed diamond anvil cell (Piermarini and Block 1975) and the pressure was measured using the ruby fluorescence technique (Barnett *et al* 1973). For pressure medium the standard 4 : 1 methanol-ethanol mixture was used.

All Raman measurements were carried out using a Spex double monochromator equipped with a conventional photon-counting system. For excitation the 647·1 nm line of a krypton laser was used, at a power level of 20–30 mW. The absorption spectra were taken using a microoptic set-up similar to the one used in our study of lead tungstates (Jayaraman *et al* 1985). The Raman as well as the absorption spectra in the diamond cell were taken at room temperature.

2.1 $2H$-PbI_2

The Raman spectrum of the 2H-polytype is shown in figure 1 for 1 bar, 5·5 kbar and 22 kbar. The 1 bar spectrum exhibits three peaks at 73 cm^{-1}, 95 cm^{-1} and 110 cm^{-1}. For the 2H-polytype, group theory predicts two Raman active eigenfrequencies, due to the iodine intralayer symmetric stretching vibrations of E_g symmetry (doubly degenerate shear deformation modes) and A_{1g} symmetry (nondegenerate breathing mode). Polarization studies (Zallen and Slade 1975) have established that the 73 cm^{-1} peak corresponds to E_g symmetry and the 95 cm^{-1} peak to the A_{1g} symmetry mode. The feature at 110 cm^{-1} is believed to be due to a combination band.

At a pressure just above 5 kbar the crystal undergoes a phase transition abruptly. The initially transparent crystal is criss-crossed by a triangular pattern and appears brownish in colour. The Raman spectrum of this high pressure phase is shown in figure 1(b) recorded at 5·5 kbar pressure. The spectrum is very different and in particular has new sharp peaks at lower frequencies. The 22 kbar spectrum is basically the same except for a companion peak to the 70 cm^{-1} and 115 cm^{-1} peaks. At a pressure just above 35 kbar the spectrum is very complex and we attribute this to the second pressure-induced phase transition. Bridgman reported the second phase transition in PbI_2 at about 25 kbar and this lower value is probably due to the presence of shear stresses in Bridgman's compression studies. In the present experiments the samples were surrounded by a hydrostatic pressure medium. The pressure dependence of the Raman
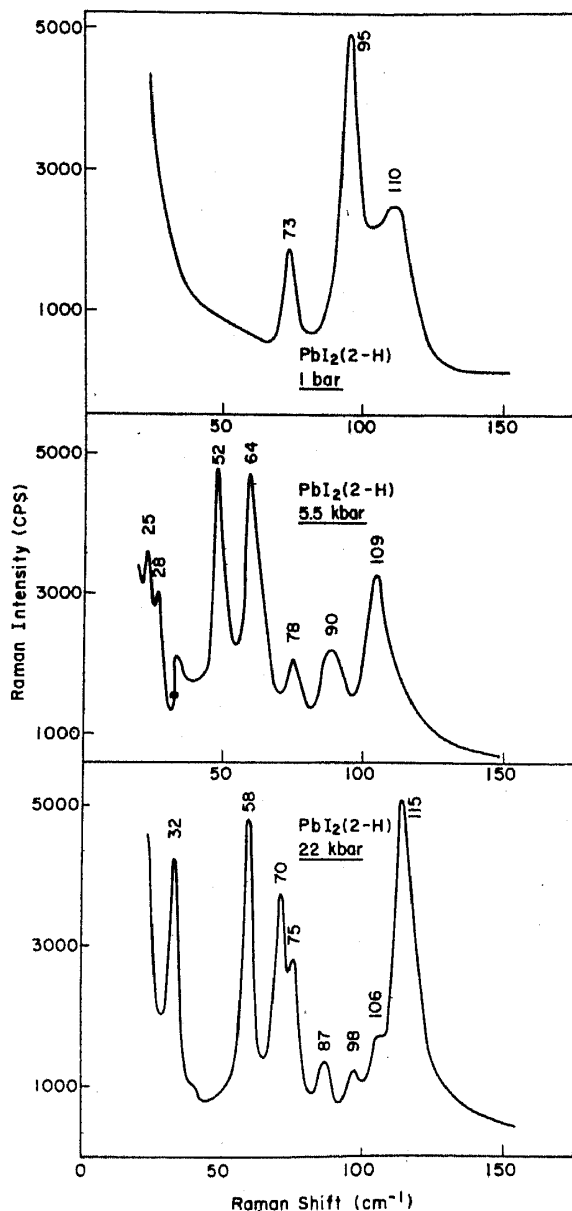
Figure 1. Raman spectra of 2H-PbI$_2$ at different pressures.

frequencies is plotted in figure 2, which clearly shows the pressure-induced phase transitions. Above 45 kbar pressure only one Raman peak near 60 cm^{-1} was observed. It is not clear if this is due to yet another phase transition to a simpler structure. The transitions are reversible and as judged by the Raman peaks the sample goes back to the 2H-polytype. However, a large hysteresis is observed. The reverse transition to 2H occurs near 0·5 kbar.

PbI$_2$ showed striking changes in optical transmission when pressurized in the diamond cell and viewed under the microscope; the substance changed colour from yellow to black. Therefore, we investigated the changes in the optical absorption with pressure up to 60 kbar. In figure 3 the optical absorption curves for the 2H-polytype is shown for several pressures. The sample thickness was of the order of 20–30 μm and
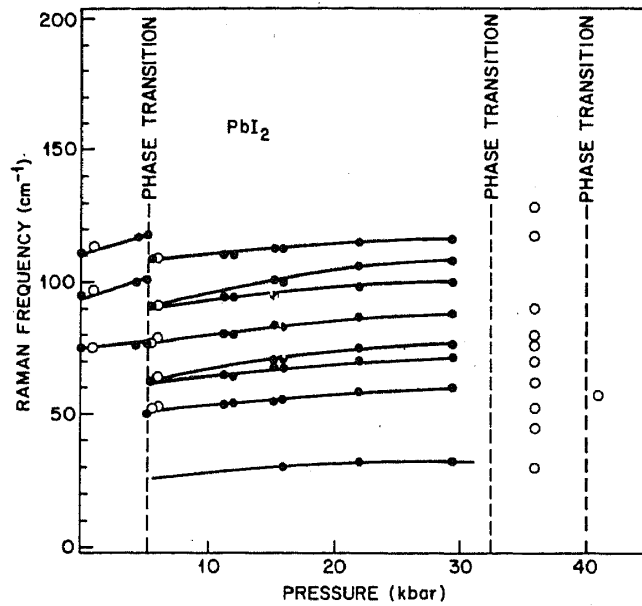
Figure 2. Pressure dependence of the Raman peaks in 2H-PbI$_2$. Phase transition shown near 40 kbar is tentative.
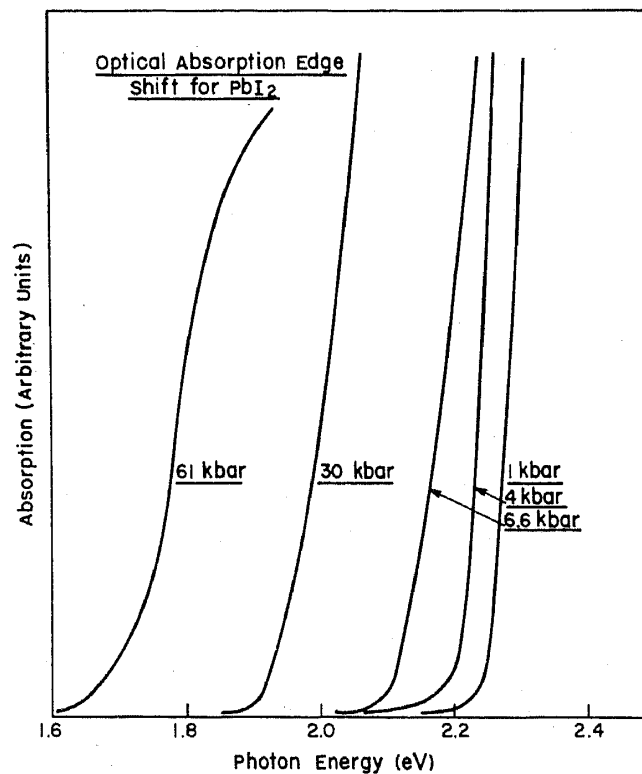

Figure 3. Shift in the optical absorption edge of 2H-PbI$_2$ at different pressures. Above 4 kbar it is phase II and above 30 kbar it is phase III.

hence these are really thick sample absorption curves. The absorption edge is well defined and the shifts are parallel up to 5 kbar for phase I. The curve for 6·6 kbar very definitely belongs to the high pressure phase PbI$_2$ (II) and this is qualitatively different from the curve for phase (I). Although the crystal broke up in some areas and traversed

by a triangular pattern, for taking the absorption data in phase II the light spot was focussed on a portion of the crystal which did not show any direct light coming through. The absorption curve for the 30 kbar also belongs to phase II and it is parallel to that of the 6·6 kbar edge. At 61 kbar the transmission becomes much weaker and the crystal appears dark red in colour. The absorption curve also looks qualitatively different. In this region the PbI_2 (II) phase would have transformed to another high pressure phase. The qualitative feature of this absorption edge suggests that it may be associated with an indirect edge. The absorption edge shift with pressure for the 2H-PbI_2 is plotted in figure 4. A clear break in slope at the I to II transition is seen.

2.2 $4H$-PbI_2

Zallen and Slade (1975) have shown by high temperature Raman studies that the 2H-polytype transforms to the 4H-type when heated above 145°C and the phase is quenchable on cooling to room temperature. The 4H-polytype samples for our study were obtained by heating the 2H-type to 180°C and cooling to RT. The spectrum of the heat-treated sample is shown in figure 5a and this is consistent with that of the 4H-polytype. In particular the rigid layer mode at $15\ cm^{-1}$ is characteristic of the 4H-polytype. This polytype undergoes the first pressure-induced phase transition near 8 kbar and the phase transition appears qualitatively similar to that of the 2H polytype near 5 kbar. However the Raman spectrum of this high pressure phase is different. These spectra taken at 10 kbar, 19 kbar and 33 kbar are shown in figures 5 and 6. The 48 kbar spectrum shown in figure 6 is quite different and evidently is due to another phase transitions. On releasing the pressures the transitions are reversible, but the phase obtained at 1 bar is found to be not the 4H-polytype but the 2H-polytype. This is confirmed by recompression, when the first-phase transition occurs near 5 kbar and has an identical Raman spectrum with that of the phase II of the 2H-polytype.

3. Discussion

Zallen and Slade (unpublished) first investigated the 2H-PbI_2 under hydrostatic pressure by Raman spectroscopy and found the I-II phase transition to occur near
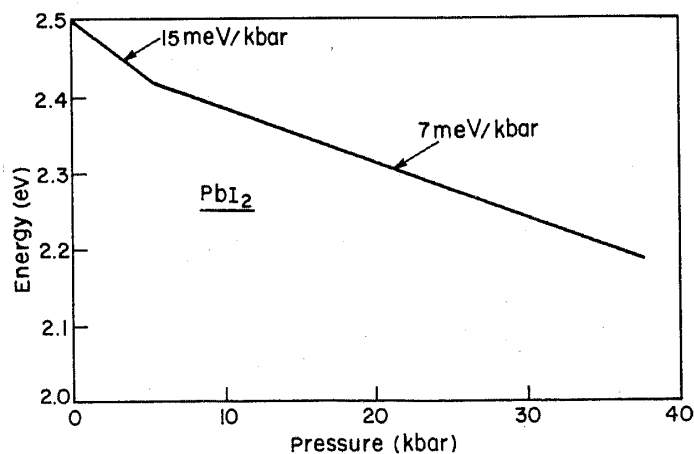

Figure 4. A plot of the energy gap shift with pressure. The break in slope is due to the 5 kbar phase transition.
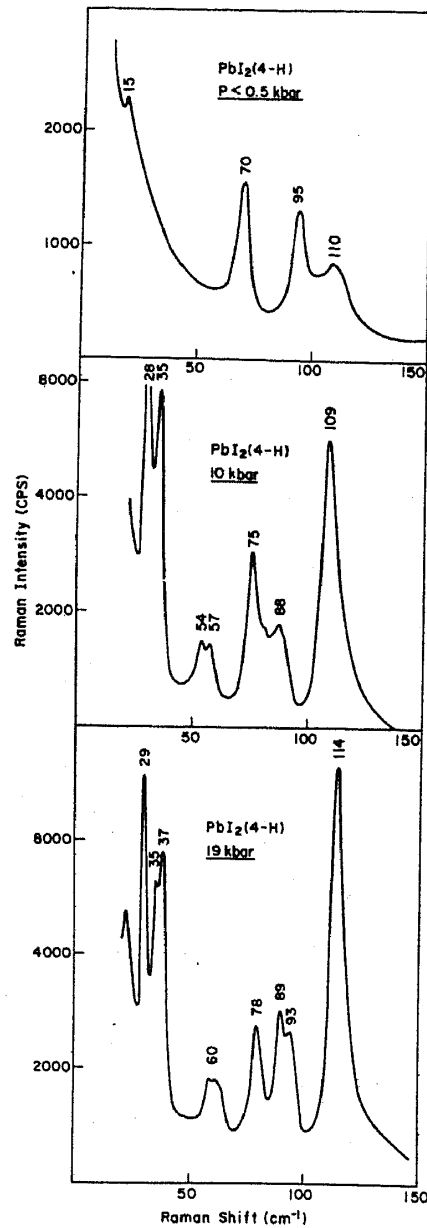
Figure 5. Raman spectra of 4H-PbI$_2$ at different pressures.

4 kbar. Further, Zallen (unpublished) noted that the 4H-polytype failed to transform even at 6 kbar, the limit of pressure in that experiment. Our observations and the spectrum of the high pressure phase are in very good agreement with the results of the above studies.

Belyi *et al* (1982) investigated PbI$_2$ under hydrostatic pressure up to 7 kbar, by Raman spectroscopy. In this study the I-II phase transition was found to occur near 5 kbar, as evidenced by the abrupt change in the Raman spectrum, and the starting material is stated to be the 4H-PbI$_2$. On the other hand we find that the 4H-polytype undergoes the first pressure-induced phase transition near 8 kbar, and it is only the 2H-polytype that shows this transition near 5 kbar. Further, the spectrum obtained by Belyi *et al* for the high pressure phase is exactly the same as our spectrum for phase II
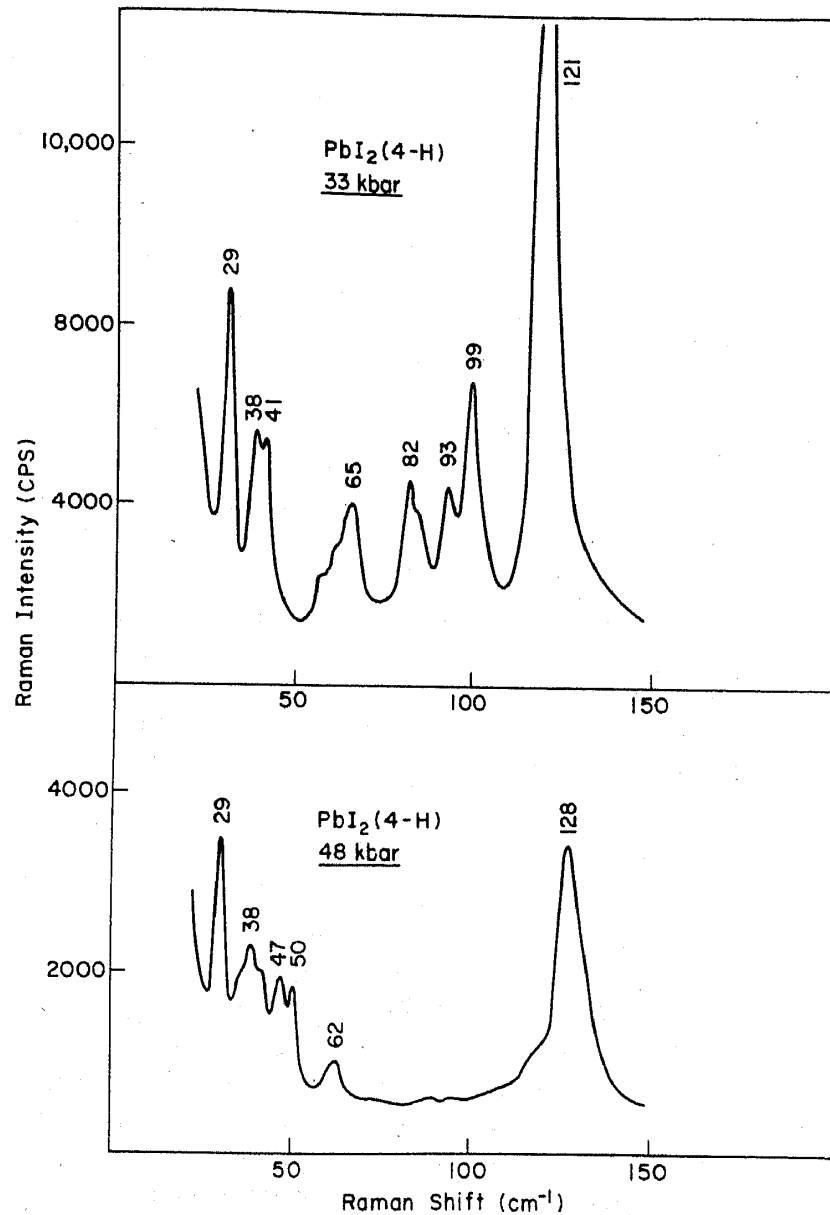
Figure 6. Raman spectra of 4H-PbI₂ at two different pressures.

obtained with the 2H-polytype as the starting material. Therefore we believe that the starting material in Belyi *et al* study must have been the 2H-PbI₂ and not the 4H-PbI₂.

Khilji *et al* (1982) investigated the 6H-PbI₂ up to 14 kbar hydrostatic pressure by Raman spectroscopy and found the first pressure-induced phase transition at 8·2 kbar. The Raman spectrum of this phase is not the same as our spectrum for phase II. However Khilji *et al* (1982) found that the spectrum changed on recompression and the pressure of transition moved downwards. After two recyclings a consistent spectrum was obtained. This final spectrum is exactly the same as our spectrum for phase II. In our experiments on the 4H-polytype a similar behaviour was noticed. After one cycling the transition pressure came down to 5 kbar and the Raman spectrum became identical with that of the spectrum of phase II obtained with the 2H-polytype as the starting

material. Our interpretation of Khilji *et al*'s results is that the high pressure phase reverts to the 2H-polytype and once the seeds of other polytypes are removed by repeated cycling, the reversion is all to the 2H-polytype.

Band structure calculations (Schluter and Schluter 1974) indicate that PbI_2 has a direct gap at the A point in the Brillouin zone, which is the lowest. The pressure coefficient for this gap is expected to be negative, as in the case of Pb monochalcogenides (Martinez 1980). There are three excitonic transitions associated with this edge, but at room temperature and with thick samples these are not resolved. Therefore we can obtain only the pressure coefficient of the lowest edge and we find that this has a value of -15 ± 1 MeV/kbar. This value is in good agreement with the pressure coefficients obtained by Powell (1978) (-15.5 MeV/kbar) and by Carillon and Martinez (1977) (-14.5 ± 0.5 MeV/kbar). The large value of the pressure coefficient, roughly a factor of two larger than in Pb mono-chalcogenide semiconductors, is attributed to the layered character of the lattice (Martinez 1980) of PbI_2.

In phase II the absorption appears to be due to a direct gap and the pressure coefficient has a value -7 MeV/kbar. This value is more in line with the coefficients of Pb mono-chalcogenides which have the NaCl-type structure. Therefore we attribute the change in the pressure coefficient to the lower value, to a transition from the layer structure to a 3d lattice structure.

At the present time very little can be said about the nature of the absorption edge in phase III. The absorption curve at 61 kbar is suggestive of an indirect gap for the material.

3.1 *Structure of the high pressure phase*

The large volume change noted by Bridgman at the I to II phase transition and the Raman spectrum of phase II strongly suggest that the above transition is not an interpolytype one. Richter and Clark (1979) investigated the P-T diagram of PbI_2 and speculated that phase II might have a defect NiAs-type structure. However this would be a semiconductor-to-metallic transition. This can be ruled out in the light of the present and previous optical absorption and Raman studies. Belyi *et al* (1982) proposed the β-HgI_2 (yellow modification) structure for the phase II of PbI_2. But the Raman spectrum of phase II bears no resemblance whatever to the spectrum of five phases of HgI_2 reported by Khilji *et al* (1981).

For AX_2 compounds crystallizing in the CdI_2 layer-type structure increasing coordination leads to the following structure types (Seifert 1968): ZrO_2 (monocl.) (Arashi and Ishigame 1982) with 7-fold coordination, ZrO_2(tet) or fluorite type with 8-fold coordination and finally the $PbCl_2$ type with approximately 9-fold coordination. Of these, the $PbCl_2$ structure is the densest for AX_2 oxides and halides. No pressure-induced phase transition is known for compounds with $PbCl_2$ structure (Pistorius 1976). Fluorite structure compounds are known to transform under pressure to the $PbCl_2$ type structure (Pistorius 1976). Thus the possible sequence for CdI_2-type structure is ZrO_2(monocl.) $\rightarrow$ ZrO_2(tet) $\rightarrow$ fluorite $\rightarrow$ $PbCl_2$-type. Of these, the tetragonal ZrO_2 structure is more likely for PbI_2-phase II, and fluorite or $PbCl_2$-structure for phase III. Only an *in situ* high pressure x-ray diffraction study can settle this question.

Finally it is interesting to note that CdI_2, which has the same layer structure does not exhibit any phase transition up to 90 kbar, the limit of pressure reached in a high

pressure Raman study on 4H-CdI$_2$ by Katahama *et al* (1983). Therefore it is possible that the phase instability in PbI$_2$ at such a low pressure as 5 kbar is connected with the electronic structure of lead.

Acknowledgements

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