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bcc lead at 109 GPa: Diffraction studies to 208 GPa

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Energy-dispersive x-ray diffraction studies have been made on lead to 208 GPa with platinum as a pressure marker material using a synchrotron source. A new phase transition from hcp Pb(II) to Pb(III) begins at 111 GPa on compression and the reverse transition begins at 107 GPa on decompression. It is shown that Pb(III) has the body-centered-cubic crystal structure. The hcp-to-bcc phase transformation in Pb is sluggish at room temperature and an unusually large hysteresis is associated with the completion of this transformation on compression as well as on decompression.

Lead belongs to the group-IV elements and crystallizes in the fcc phase at room temperature and room pressure. Balchan and Drickamer[1] first detected the Pb(I), fcc, to Pb(II) transition based on resistance measurements at a pressure of 16 GPa based on a force versus pressure curve and earlier electrical resistance calibrations of transitions on other materials by Bridgman. Kennedy and La Mori[2] showed that "(Bridgman's) values, determined by electrical resistance, are probably too high by approximately 30% for all the transitions above 2.5 GPa." This would reduce the transition pressure to the 12–13-GPa range. Klement,[3] on the basis of measured transitions in Pb-Bi alloys, suggested that Pb(II) should be the hcp structure. Takahashi, Mao, and Bassett[4] showed that the transformation is to the hcp structure at 13 GPa. The volume change at the transition subsequently was found to be very small (on the order of -0.01 cm^3/mole) by Mao and Bell.[5] Moriarty, on the basis of GPT calculations using *ad hoc* corrections for spin-orbit effects, predicted that lead would transform from the hcp, Pb(II), structure to a bct structure ($c/a=0.94$, nearly cubic) at a pressure of 63 GPa.[6]

One-third carat, sixteen-sided natural diamond anvils with a birefringence of less than 10^{-4} were used in the diamond-anvil cell.[7] The first set of studies during loading to 124 GPa were made at the National Synchrotron Light Source (NSLS) using diamonds with 100-μm-diam flats and 5° bevels to a diameter of 300 μm and ended in fracture on the next loading. The second set of studies which included loading studies from 109 to 208 GPa and unloading studies from 208 to 0 GPa were made at the Cornell High Energy Synchrotron Source (CHESS) using diamonds with 50-μm-diam flats and bevels of 7° to a diameter of 300 μm. This experiment was not carried to higher pressures to ensure that the reverse transitions could be studied. A spring steel gasket (1% C), initially 250 μm thick, was preindented to a thickness of 20 μm. A 50-μm-diam sample hole was drilled at the center of the indentation. A mixture of fine lead and platinum powder (7 wt% Pt) was placed in the hole. Platinum was used as the x-ray marker material to obtain the pressure; recent careful shock studies on this material provide an equation of state[8] which can be used for pressure measurement. Further, the diffraction peaks of platinum do not interfere with the hcp peaks of lead or the expected bcc peaks of lead in the pressure ranges under study (based on the equation of state of lead known from shock studies[9]).

The techniques used for the x-ray studies are described elsewhere[7,10,11] and are based on previous experiences of studying diffraction to 245 GPa in rhenium, 255 GPa in iron,[12] and 282 GPa in iron and platinum.[13] The sample of 99.9999% lead was studied with a 25-μm-diam collimated x-ray beam. The Pb sample was preloaded to a pressure of 20 GPa and was found to be in the hcp phase consistent with previous measurements.[1–5] At 111 GPa on loading the (110) peak of bcc lead appeared as a shoulder on the low-energy side of the (101) peak of hcp lead. As the pressure was increased this new bcc peak increased in intensity and the (200) and (211) peaks of the bcc structure appeared while the hcp peaks decreased in intensity, but with the surprising result that the (101) hcp peak (the strongest hcp peak) did not completely vanish until a pressure of 200 GPa was reached. The c/a ratio is essentially constant for the hcp phase on the range of 26 to 200 GPa at a value of 1.63, close to the ideal 1.633 ratio of rigid spheres. No diffraction peaks from the iron of the gasket were present. At the highest pressure (208 GPa) a "circle" of transmitted light was observed at the circumference of the flat, suggesting that the diamonds had either pushed through the lead or that the thickness of the lead was less than the skin depth for visible radiation. Of course, the sample at the center would be thicker than this, probably 5 μm at the thickest position. Only bcc peaks were present in the range from 208 to 125 GPa during decompression from 208 GPa. Figure 1 (upper panel) shows the diffraction pattern of the new bcc phase of lead [Pb(III)] at 164 GPa obtained during decompression. Also present are the Pt peaks used to calibrate the pressure. The summary of the data is shown in Table I. The relative peak intensities are in good agreement with the theoretically calculated relative intensities despite the thinness of the sample. The diffraction pattern for the hcp phase of lead at 68 GPa (during decompression) is shown in Fig. 1 (lower panel). The errors shown are based on an error analysis given elsewhere.[14] When the pressure was lowered from 208 to 107 GPa, the (101) hcp peak of lead

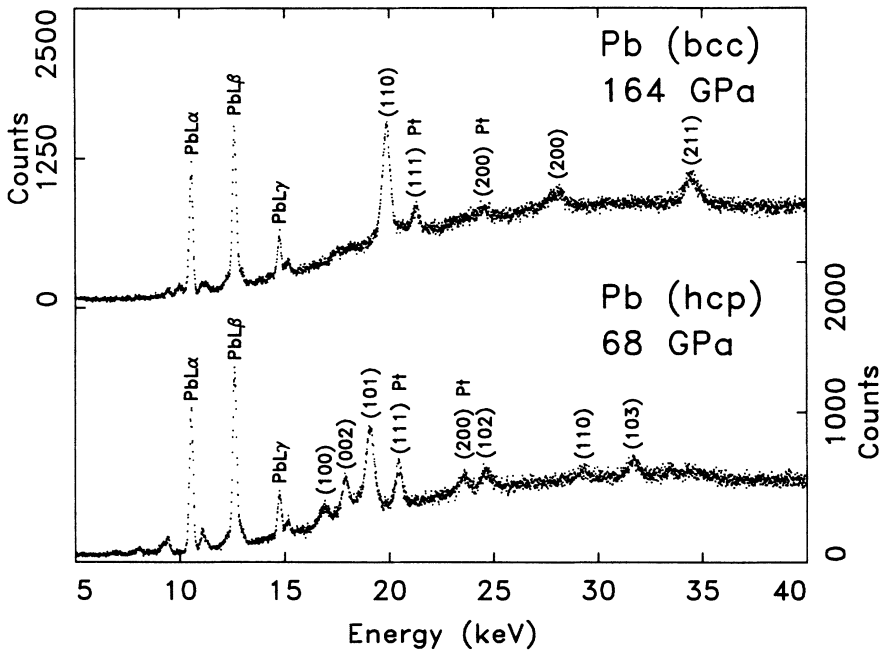

FIG. 1. Energy dispersive x-ray diffraction spectrum of bcc lead and fcc platinum at 164 GPa (upper panel) and hcp lead and fcc Pt at 68 GPa (lower panel). There are several platinum and lead fluorescence peaks at low energies. The data are from CHESS. The energy-interplanar spacing product Ed was 43.886 ± 0.006 keV Å in both cases.

reappeared as a shoulder on the high-energy side of the (110) peak of bcc lead. [See Fig. 2 (upper panel).] The intensities of the hcp peaks increased while the bcc peak intensities decreased as pressure was decreased below 107 GPa. See Fig. 2 (lower panel) for a representative spectrum of a mixture. When the pressure reached 68 GPa, the bcc peaks were absent.

Inasmuch as the hcp to bcc transition was observed at 111 GPa on loading and the reverse transition at 107 GPa on unloading, we estimate the transition pressure to be at 109 GPa. The reduced volume at the transition in the hcp phase is $V/V_0 = 0.568$. The fractional volume change

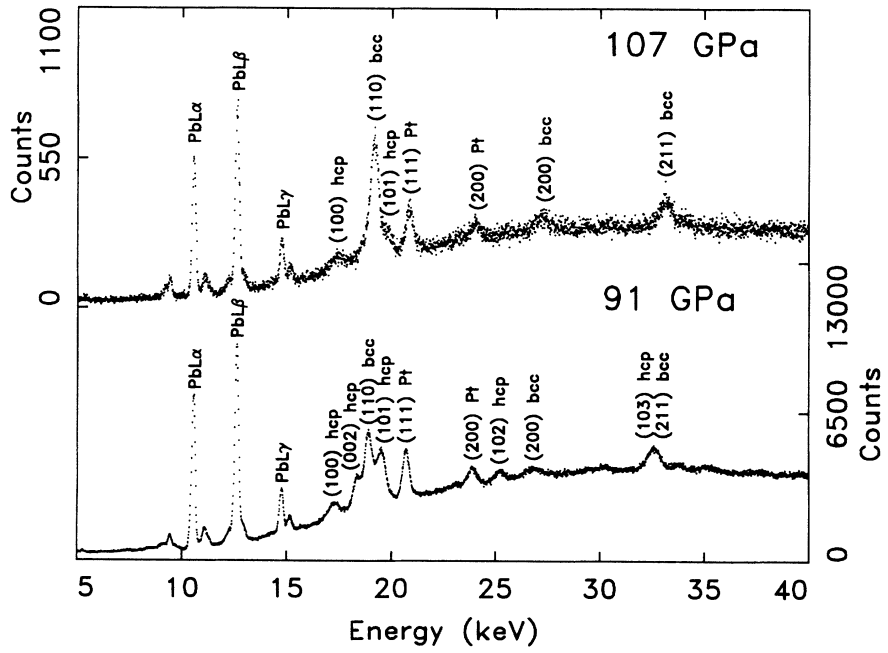

FIG. 2. Energy dispersive spectrum at the onset of the bcc to hcp transition in Pb during decompression at 107 GPa (upper panel) and with a mixture of both phases upon further decompression to 91 GPa. The data is from CHESS. The product of the energy-interplanar spacing Ed was 43.886 ± 0.006 keV Å in both cases.

TABLE I. Comparison of observed and calculated interplanar spacings d and relative intensities I for the bcc phase of lead at 164 GPa and the hcp phase of lead at 68 GPa.

Pressure and structure	(hkl)	d_{obs}	d_{calc}	I_{obs} (%)	I_{calc} (%)
164 GPa	(110)	2.208	2.208 [a]	100	100
(bcc Pb)	(200)	1.563	1.561	34	27
	(211)	1.272	1.275	47	52
(fcc Pt)	(111)	2.062	2.063 [b]		
	(200)	1.789	1.786		
68 GPa	(100)	2.602	2.603 [c]	22	16
	(002)	2.541	2.542	31	22
	(101)	2.300	2.300	100	100
	(110)	1.498	1.502	11	70
	(103)	1.384	1.384	34	40
(fcc Pt)	(111)	2.146	2.147 [d]		
	(200)	1.863	1.860		

[a]Based on $a = 3.124 \pm 0.01$ Å
[b]Based on $a = 3.572 \pm 0.01$ Å.
[c]Based on $a = 3.007 \pm 0.01$ Å; $c = 4.906 \pm 0.01$ Å.
[d]Based on $a = 3.719 \pm 0.01$ Å.

$\delta V/V_0$ at 127 GPa (where both phases were present) is -0.006 ± 0.006. We note that the error in $(\delta V/V_0)$ involves random errors only. At 208 GPa, $V/V_0 = 0.486$.

We carefully examined the intermediate range (109–208 GPa) for the presence of another phase because of the unusually large hysteresis in the hcp-to-bcc transformation. For example, could the hcp phase be transforming to dhcp, thcp, the nine-layer samarium structure, or to a tetragonal structure rather than transforming slowly to the bcc structure? We found that none of these were consistent with the data. Although we do not see the hcp to bct transition ($c/a = 0.94$) as predicted by Moriarty,[6] we do see the hcp-to-bcc transition (bct with $c/a = 1$). Perhaps a more exact fully relativistic calculation would remove this small discrepancy as Moriarty has noted.[6] We note that the group-IV elements tin and zirconium transform finally to the bcc structure, Sn at 41 GPa (Ref. 15) and Zr at 30 GPa (Ref. 16), with the bcc phase of tin known to be stable at 120 GPa (Ref. 17) and of zirconium to 32 GPa.[16] Approximate first-principles methods have been used to predict that another group-IV element, silicon,[18] will also transform at multimegabar pressures to the bcc structure.

In summary, lead transforms from the hcp structure to the bcc structure at 109 GPa. There is large hysteresis associated with the completion of this transformation in both directions.

Note added in proof. Recently Marvin Cohen provided us with an unpublished work "Theory of high-pressure phases of Pb" by A. Garcia, A. Y. Liu, M. L. Cohen, B. K. Godwal, and Raymond Jeanloz, in which calculations favor a bcc structure.

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