

Pressure-Induced Disproportionation of Cesium Iodide

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X-ray diffraction and electrical conductivity measurements demonstrate that CsI undergoes pressure-induced, high-temperature decomposition to its constituent elements at pressures exceeding 45 GPa. Our results provide a natural explanation for the apparent discrepancy between previous shock-wave and static compression measurements performed on CsI. Also, our observations imply that the metallic phase of CsI is metastable and that changes in the electronic properties of the heavy alkali metals at high pressures strongly decrease the tendency of these elements to form ionic compounds.

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The properties of CsI at high pressures have been a matter of considerable recent interest. As the most compressible of the alkali halides, its behavior at moderate pressures is widely regarded as indicative of the properties of other alkali halides at still higher pressures. Therefore, the structural transitions,¹⁻⁴ equation of state,¹⁻⁴ band-gap closure,^{2,5,6} and reflectivity⁷ of CsI have all been documented to pressures of approximately 100 GPa under the static conditions of the diamond-anvil cell. In fact, CsI is the first alkali halide to have been experimentally metallized, at a pressure of 110 GPa.⁷ Additionally, dynamic experiments have been conducted on the electrical conductivity,⁸ Hugoniot equation of state,^{9,10} temperature,¹⁰ and sound velocity¹¹ of CsI under shock loading. From the two sets of static and dynamic data, an apparent discrepancy has arisen: Most static 300-K determinations of the CsI equation of state¹⁻³ produce volumes essentially identical to those measured at comparable pressures under the high-temperature shock-loading regime. Two possible explanations have been suggested for this phenomenon: (1) a negligible thermal expansion of CsI at high temperatures and high pressures, possibly induced by electronic effects¹²; or (2) systematic errors in one set of measurements.¹¹ In order to resolve this issue, we have performed diamond-cell experiments on CsI at pressures and temperatures comparable to those occurring under dynamic loading. Our results document a new physical process: high-temperature, high-pressure decomposition of an alkali halide to its constituent elements. Although such a phenomenon has been previously suggested to explain both the high-pressure behavior of CuCl¹³ and the high-pressure, high-temperature properties of AgI,¹⁴ this study represents the first direct observation of such a result for any alkali halide.

That CsI is unstable at high pressures is suggested by Fig. 1, which compares the experimentally measured volume of the compound relative to that of the combined elements as a function of pressure. Above 5.5 GPa, the volume of the elements becomes significantly less than that of the ionic compound. This dramatic crossover in

the volume curves is predominantly due to changes in the electronic properties of Cs with pressure: The relative volume at the transition to the Cs(V) structure at 10 GPa is $V/V_0 \approx 0.27$.¹⁶ The thermodynamic consequence of the volume collapses of cesium and iodine with pressure is shown in Fig. 2. On the basis of a room-temperature calculation, we find that the reaction $\text{CsI} = \text{Cs} + \text{I}$ is expected to proceed forward above about 65 GPa. If we consider the volume change of the reaction to be constant with temperature, higher temperatures (such as those that occur under shock loading) should lower the pressure at which the elements are stable relative to CsI, as the entropy of Cs+I is expected to be higher than that of CsI.¹⁹

To confirm our expectation that CsI disproportionates under pressure, we carried out experiments using a Mao-Bell-type diamond cell,²⁰ with pressures calibrated by the ruby-fluorescence technique.²¹ A spring-steel gas-

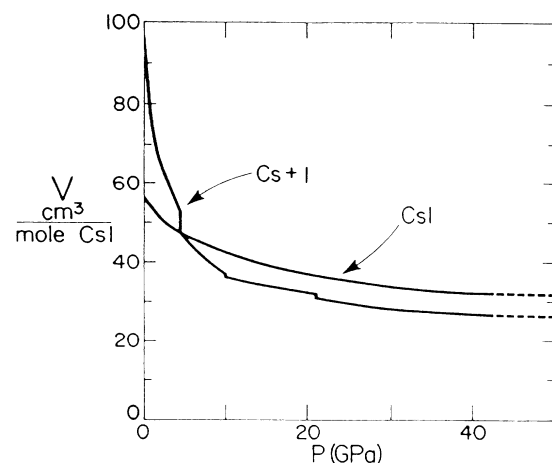


FIG. 1. Molar volume of CsI and of Cs+I as functions of pressure. Volume data for CsI are from Ref. 1, while those for I are from Ref. 15. Cesium compression data from 20 to 43 GPa are derived from this study, while below 20 GPa the data of Takemura and co-workers (Refs. 16 and 17) are used.

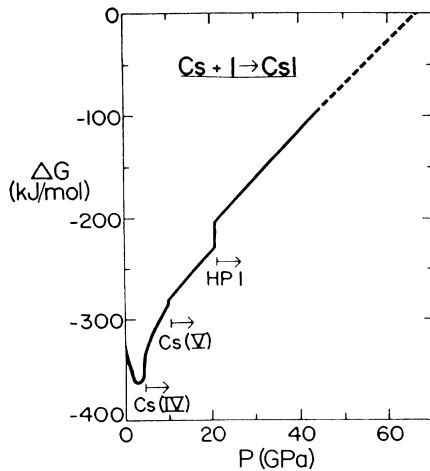


FIG. 2. Gibbs free energy of formation of CsI from its constituent elements at 300 K. Compression and crystallographic modifications of Cs and I are from the same sources as for Fig. 1. The values of Ref. 18 are used for entropies and heats of formation.

ket is used to contain the sample, which was heated with a 20-W cw Nd-doped yttrium-aluminum-garnet laser tuned in TEM₀₀ mode and operating at 1.16 eV. Notably, our thermal quench rates are extremely rapid ($\geq 10^6$ K/sec) as a result of the high thermal conductivity of the diamond anvils and the thinness of our samples (estimated to be ≈ 10 μm at high pressures). As CsI undergoes continuous, pressure-induced band-gap closure (with a band gap of about 2.0 eV at 50 GPa⁶), we rely on absorption of the laser by the low-energy tail of the absorption edge to heat our samples. We find that in this manner, temperatures in excess of 6000 K can be produced in molten CsI under pressure. Our temperatures are measured spectroradiometrically, by means of a system described elsewhere.²² X-ray Debye-Scherrer patterns were collected from the samples at high pressure and room temperature; we use collimated and monochromated Mo- $K\alpha$ radiation from a rotating-anode x-ray generator, with the diffraction pattern being recorded on film.

Consistent with our thermodynamic calculations, visual observations on decompressed samples that have been laser heated document that the normally transparent CsI has become pale bluish in transmitted light. This is reminiscent of the color of alkali-metal colloids in alkali halides.²³ Highly localized dark purple regions (about 20- μm in diameter) are also observed, similar in appearance to that expected for dilute iodine. In addition, samples held at high pressure (≈ 50 GPa) following laser heating exhibit an approximately three order of magnitude drop in electrical resistivity²⁴ compared with that of CsI at similar pressures. This implies that the initially semiconducting CsI has partially reacted to a more highly conductive assemblage of phases, such as a mixture of

TABLE I. X-ray pattern, post heating; $P=42.5(\pm 1.0)$ GPa. For Cs, $V=54.86$ cm³/mole ($Z=8$), $a=585$ pm, $b=517.8$ pm, $c=300.7$ pm. Prior to heating, the 101, 110, 112, 211, 202, and 220 lines of CsI were observed: These yielded a V/V_0 for CsI of $0.548(\pm 0.015)$, in excellent agreement with the values of Ref. 1.

Observed d spacings (pm)	Assignment	Calculated	I/I_0 ^a
292.5 (± 0.7)	(200)Cs	292.5	15
	(101)Cs	267.4	32
	(101)CsI ^b	266.4	50
261.9 (± 0.5)	(110)CsI ^b	260.2	100
	(011)Cs ^b	260.0	
258.2 (± 0.8)	(020)Cs ^b	258.9	100
	(210)Cs ^b	254.7	
237.6 (± 0.3)	(111)Cs	237.6	24
	(201)Cs	209.7	31
196.1 (± 0.3)	(211)Cs	194.3	6
	(220)Cs	193.9	
186.0 (± 0.2)	(121)Cs	186.0	29
	(200)CsI	184.0	20
154.3 (± 0.2)	(221)Cs	162.9	11
	(211)CsI ^c	151.4	33
148.4 (± 0.3)	(400)Cs	146.3	7
	(230)Cs	148.6	
128.4 (± 0.3)	(031)Cs	149.7	23
	(102)Cs	145.6	
	(131)Cs	145.0	
	(410)Cs	140.7	
	(112)Cs	140.2	
	(321)Cs	138.3	
	(231)Cs	133.2	
117.2 (± 0.2)	(401)Cs	131.5	16
	(220)CsI [?]	130.1	18
128.4 (± 0.3)	(411)Cs	127.5	18
	(420)Cs	127.3	
	(302)Cs	119.1	
117.2 (± 0.2)	(331)Cs	118.7	8
	(240)Cs	118.4	
117.2 (± 0.2)	(421)Cs	117.3	

^aFrom Reference 16 for Cs; from Ref. 1 for CsI.

^bMutual interference between 101, 011, 210, 020 lines of Cs, 110, 101 lines of CsI, and possibly 110, 011 lines of iodine.

^cPossibly interfered with by 121 line of iodine.

metallic cesium and iodine together with unreacted CsI.

Definitive evidence for dissociation comes from our x-ray patterns taken at high pressure. These demonstrate the appearance of cesium upon laser heating of CsI at 48 GPa (Table I). Our patterns are indexed by use of the orthorhombic (*B*) structure of Cs(V) proposed by Takemura and Syassen.¹⁶ We find that the x-ray lines of Cs in our samples show substantial spottiness, probably indicating the presence of nonrandomly oriented crystallites of Cs. The volume of Cs(V) at 42.5 GPa is calculated only from the lines which can be unambiguously assigned to single sets of lattice planes of the structure. Thus, our results at 42.5 GPa document the stability of

the Cs(V) phase to a substantially higher pressure than previously observed.

We note that there is still a substantial amount of CsI in our quenched samples (Table I). Energy-dispersive x-ray analysis using a scanning electron microscope also demonstrates the presence of regions containing both Cs and I as well as regions of pure cesium in the quenched samples. This indicates that the decomposition reaction has not proceeded to completion, perhaps as a result of unreacted CsI being retained in cooler regions of the sample next to the highly thermally conductive diamond anvils. Similarly, the apparent lack of diffraction lines from crystalline iodine may be caused by iodine being present in any amorphous or poorly crystalline phase in our samples (Table I).

Although both our experiments and thermodynamic calculations indicate that CsI is unstable at high pressures (above 65 GPa at 300 K), observations of the optical properties and lattice parameters of this compound have been made to pressures in excess of 90 GPa^{6,7} and to 95 GPa,³ respectively. Thus the decomposition reaction must be kinetically prohibited at ambient temperature. Additionally, unless there is a substantial volume change associated with metallization of CsI (which calculations indicate is probably not the case¹⁸), metallic CsI must also be metastable. The physical reason for this metastability is largely due to a change in electronic properties of Cs: Between 0 and 10 GPa, electron density is shifted from the 6*s* band to the more localized 5*d* bands of Cs,^{16,25} producing an anomalously large compression ($V/V_0 \approx 0.27$ at 10 GPa). Our results thus are probably applicable to other ionic compounds involving Cs⁺: Effectively, the outermost electron lying in the 6*s* orbital is much more easily ionized than when it lies in the 5*d* manifold, and it is not volumetrically advantageous for Cs to ionize at high pressures. Additionally, iodine undergoes a net volume change comparable to that of CsI over a similar pressure range. A 4% change in V/V_0 at the first-order transition of iodine at 21 GPa (which has been attributed by some^{15,26} to a change in bonding character from diatomic I₂ to monatomic I²⁷) and a change in the slope of the pressure-volume relation of iodine at 32 GPa¹⁵ also contribute to the small volume of the elements relative to CsI.

Our observations provide a simple explanation for the apparent discrepancy between the volume of CsI measured by static and by shock techniques: CsI disproportionates to a mixture of elements under the high-temperature, high-pressure conditions of shock loading.²⁸ Whereas the room-temperature static-compression data reflect the properties of CsI (at both stable and metastable conditions), the shock-wave measurements are no longer being made on CsI beyond about 30 GPa, but are rather on a molten, dissociated mixture of cesium and iodine. Thus, the two sets of measurements are not directly comparable. Also, the anomalously large heat

capacity observed under the shock loading^{10,11} is now interpretable as being due to a combination of the heat of the decomposition reaction and electronic contributions from the presence of metallic cesium and iodine. Indeed, our observations provide strong support for the inference that electronic excitation and structural changes occurring in molten CsI at pressures in excess of 30 GPa contribute significantly to the shock-wave measurements.¹⁰

Extending our results, we find that other alkali halides could also become unstable with respect to their constituent elements under pressure. Both rubidium and potassium show anomalously large compressions associated with changes in electronic properties at pressures of up to at least 12 and 18 GPa, respectively.^{25,29,30} Thus RbI, in particular, should become metastable at ≈ 90 GPa (at 300 K) if the volume decrease across the decomposition reaction determined at 28 GPa (the highest pressure for which x-ray diffraction data are available on Rb) is constant to higher pressures.^{15,29,31} The equation of state of K is unknown above 18 GPa, where it transforms to an unknown structure.³⁰ Below this pressure, the volumes of the elements do not favor the decomposition of KI,³¹ but it is possible that the phase transitions in both K and I eventually drive the compound to instability (particularly at elevated temperatures). Among the bromides, CsBr is expected to disproportionate at the lowest pressure.^{26,32,33} If the volume change on decomposition of CsBr is constant above 42 GPa, CsBr becomes unstable at pressures in excess of 100 GPa. However, if bromine undergoes a transition at pressures above 42 GPa comparable to that occurring in iodine at 21 GPa,³² the pressure at which CsBr decomposes could be substantially lower. As RbI, ScBr, and KI undergo a greater degree of band-gap closure at lower pressure than any of the other alkali halides,^{31,33} they are the most likely candidates for experimental metallization among the alkali halides. Thus, we conclude that the metallic phases of these compounds are likely to be thermodynamically metastable, as is the case for metallic CsI.

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