

Transitions to Metallic States in Ionic Crystals, with Particular Reference to Cesium Iodide

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Shock-wave experiments by Alder and Christian have indicated that metallic transitions might occur in certain ionic crystals. Therefore, one heavy ionic crystal, CsI, has been studied by the cellular method of band theory, both for the normal lattice parameter and for a reduced spacing corresponding to an estimated pressure of $\sim 250\,000$ atmospheres. Our principal conclusion is that the energy gap between valence and conduction bands varies little with pressure in the range we consider. A gap of 6 or 7 eV is obtained with our relatively crude potential. The width of the valence band is estimated at 3–4 eV, and with our potential, and neglect of spin-orbit effects, a state at the zone edge along [100] appears to be the highest in this band, while the conduction band minimum is at $\mathbf{k}=0$. The results under normal conditions are in good agreement with the photoemission experiments of Philipp, Taft, and Apker, both for the gap and the valence bandwidth, but the shock-wave experiments of Alder and Christian cannot be understood along the present lines. Later static pressure experiments by Griggs *et al.*, are not, however, in conflict with our findings.

1. INTRODUCTION

ALDER and Christian¹ have recently reported investigations which they have carried out using shock-wave techniques on some molecular and ionic crystals. As a result of attaining pressures up to $\sim 250\,000$ atmospheres they claimed that transitions from the normal insulating states to metallic states had occurred in certain cases. It seemed to us initially to be of especial interest that the two alkali halide crystals which, they claimed, showed a tendency to become conducting (CsI and CsBr) have the cesium chloride structure, which is also taken up at sufficiently high pressures by other alkali halides normally having the sodium chloride structure.²

In view of the interest thus aroused in the high-pressure behavior of ionic crystals, theoretical studies have been undertaken independently by Behringer³ and the present writers.⁴ As we remarked earlier, in reporting our group-theoretical investigations,⁴ for the reasons given above we have been primarily concerned with the CsCl structure, in which like atoms are found at the sites of two simple cubic lattices, whereas Behringer considered the NaCl structure.

We report here our final results on the heavy ionic crystal CsI. However, since we embarked on our theoretical investigation, some static pressure experiments have been reported by Griggs *et al.*⁵ which leave the experimental position somewhat confused. Our findings throw some light on these matters and also allow us to make a comparison with photoemission experiments of Philipp, Taft and Apker⁶ on CsI under normal conditions.

2. THE CELLULAR METHOD APPLIED TO THE CsCl STRUCTURE

Of the now numerous methods of solving the one-electron problem for a periodic potential, it seemed to us that the cellular method should be particularly favorable for a crystal involving the heavy atoms Cs and I. Unfortunately, the cellular method is only practicable if the potential is assumed spherically symmetrical within each cell, and this may constitute an objection to the procedure. More work will undoubtedly be required eventually on the refinement of the crystal potential we have used here.

The CsCl structure can be thought of as consisting of two interpenetrating simple cubic lattices, one based on the point (0,0,0) and the other on $(a/2, a/2, a/2)$, a being the lattice constant. The crystal is divided up into identical polyhedra around each nucleus, filling the whole volume of the crystal. The basic direct cell is thus simply that of the body-centered-cubic lattice, and is of volume $a^3/2$, while the first Brillouin zone of the CsCl lattice is a simple cube of side $2\pi/a$.

With the assumption that the potential in each cell is spherically symmetrical about the central nucleus, the wave function may be expanded in spherical harmonics $Y_{lm}(\theta, \phi)$ in the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{lm} A_{lm} R_l(r) Y_{lm}(\theta, \phi),$$

where the functions $R_l(r)$ are to be determined by integrating the radial Schrödinger equation and the A_{lm} are to be obtained by applying suitable boundary conditions. As is well known, by choosing only points of high symmetry in the Brillouin zone, it is possible to reduce the number of terms in the expansion by group theory.^{4,7}

The matching methods we have used in the present problem are similar to those suggested by Howarth and Jones,⁸ and we have made extensive use of the empty

¹ B. J. Alder and R. H. Christian, *Phys. Rev.* **104**, 550 (1956).

² R. B. Jacobs, *Phys. Rev.* **54**, 468 (1938).

³ R. E. Behringer, *Phys. Rev.* **113**, 787 (1959).

⁴ M. Flower, N. H. March, and A. M. Murray, *Phys. Rev.* **119**, 1885 (1960).

⁵ D. T. Griggs, W. G. McMillan, E. D. Michael, and C. P. Nash, *Phys. Rev.* **109**, 1858 (1958).

⁶ H. Philipp, E. A. Taft, and L. Apker, *Phys. Rev.* **120**, 49 (1960).

⁷ D. G. Bell, *Revs. Modern Phys.* **26**, 311 (1954).

⁸ D. J. Howarth and H. Jones, *Proc. Phys. Soc. (London)* **A65**, 355 (1952).

lattice test in choosing suitable sets of boundary conditions.

3. THE CRYSTAL POTENTIAL

The ion-core potential in each cell was taken to contain the contributions from the nucleus and the 46 inner electrons out to, and including, the 4*d* shell. A Hartree field was available for Cs⁹ and for I a field was calculated using an interpolation scheme suggested by Ridley.¹⁰ Briefly the basis for this method consists in the fact that for heavy atoms, if $Z(nl:r)$ is the contribution to the effective charge $Z(r)$ for the electric field from an electron described by an (*nl*) wave function, the quantities $Z(nl,r)$ vary systematically with atomic number and as this becomes large the $Z(nl,r)$ tend to the corresponding hydrogen-like functions. Ridley has obtained a two-parameter method of fitting the curve of $Z(nl,r)$ to the hydrogen results. In the present case it was only necessary to consider the screening constant $\sigma(nl)$ when interpolating from the Cs Hartree field, the variation in the slope constant

TABLE I. Effective charge for potential of iodine due to nucleus and 1*s*-4*d* electrons. (*r* in atomic units.)

<i>r</i>	<i>r</i>	<i>r</i>	<i>r</i>
0.000	53.000	0.32	19.074
0.001	52.696	0.34	18.351
0.002	52.394	0.36	17.692
0.003	52.093	0.38	17.086
0.004	51.796	0.40	16.524
0.005	51.502		
0.006	51.212	0.45	15.264
		0.50	14.154
0.008	50.644	0.55	13.154
0.010	50.094	0.60	12.250
		0.65	11.440
0.015	48.797	0.70	10.724
0.020	47.602	0.75	10.100
0.025	46.491	0.80	9.564
0.030	45.445		
0.035	44.452	0.9	8.725
0.040	43.501	1.0	8.140
0.045	42.587	1.1	7.746
0.050	41.707	1.2	7.486
		1.3	7.314
0.06	40.038	1.4	7.202
0.07	38.488	1.5	7.129
0.08	37.052	1.6	7.083
0.09	35.723		
0.10	34.489	1.8	7.033
0.11	33.341	2.0	7.013
0.12	32.267	2.2	7.005
0.13	31.255	2.4	7.002
0.14	30.298	2.6	7.001
		2.8	7.000
0.16	28.522		
0.18	26.902		
0.20	25.423		
0.22	24.075		
0.24	22.853		
0.26	21.752		
0.28	20.763		
0.30	19.874		

⁹ D. R. Hartree, Proc. Roy. Soc. (London) A143, 506 (1934).
¹⁰ E. C. Ridley, Proc. Cambridge Phil. Soc. 51, 693 (1955).

TABLE II. Eigenvalues for CsI (in atomic units).

k	Representation about		Normal lattice	Compressed lattice
	Cs	I		
Conduction band				
0	<i>A_s</i>	<i>A_s</i>	0.04±0.01	0.36±0.01
(π/a)(1,0,0)	<i>C_s</i>	<i>C_p</i>	0.16±0.01	0.45±0.03
(π/a)(0,1,1)	<i>C_s</i>	<i>C_d</i>	0.10±0.03	0.45±0.05
(π/a)(1,1,1)	<i>A_s</i>	<i>A_f</i>	0.23±0.01	0.61±0.03
Valence band				
0	<i>A_p</i>	<i>A_p</i>	-0.19±0.01	0.06±0.01
(π/a)(1,0,0)	<i>C_s</i>	<i>C_p</i>	-0.24±0.02	0.02±0.02
	<i>C_{d'}</i> (1)	<i>C_{p'}</i> (2)	-0.18±0.01	0.10±0.02
(π/a)(0,1,1)	<i>C_{f'}</i>	<i>C_p</i>	-0.32±0.02	0.06±0.02
	<i>C_{p'}</i> (2)	<i>C_{p'}</i> (1)	-0.21±0.01	0.06±0.02
(π/a)(1,1,1)	<i>A_{d'}</i>	<i>A_p</i>	-0.21±0.01	-0.01±0.01

$\alpha(nl)$ being unimportant. The potential thus obtained is tabulated in Table I and should be a good starting point for accurate self-consistent calculations should they eventually be deemed worthwhile.

The crystal was further assumed to be completely ionic and a crude potential representing the valence electrons was obtained by simply smearing eight electrons in the equal volume spheres around each ion. We finally added the appropriate Madelung potential corresponding to this completely ionic model.

4. ELECTRONIC ENERGY LEVELS IN CsI

With the field described above we have carried out detailed calculations at the following points of high symmetry in the fundamental Brillouin zone:

$$\pi^{-1}a\mathbf{k}=0, (1,0,0), (0,1,1), \text{ and } (1,1,1).$$

A very crude estimate using semi-empirical methods led us to examine, to simulate pressures of the order of 250 000 atmospheres, a lattice spacing given by $a=7.3$ atomic units. It was also of interest to extend our calculations to the normal lattice spacing $a=8.6$ atomic units.

We record the eigenvalues obtained in Table II, for both the conduction and valence bands. The states are classified according to the notation of Bell.⁷

5. CONCLUSION

At both lattice spacings, our results show that for the conduction band the lowest level investigated is non-degenerate and at $\mathbf{k}=0$. The top of the valence band is somewhat more difficult to locate with certainty, but with the present potential the indications are that, of the levels we have studied, the highest is a doubly degenerate state at $\pi^{-1}a\mathbf{k}=(1,0,0)$. Again this situation is true for both lattice parameters considered, although without compression, a triply degenerate state at $\mathbf{k}=0$ is only slightly lower.

For the normal lattice parameter we estimate the band gap as (6 ± 1) ev and the width of the valence

band as (4 ± 1) ev. It is a little puzzling that our results for the smaller spacing indicate a slightly larger band gap and somewhat narrower valence band. However, in view of (a) the spread in the eigenvalues for different sets of matching conditions and (b) the relatively crude potential used, we would only infer from this that any variation in the gap over this pressure range is small compared with the total width of the gap.

Recently, Philipp, Taft, and Apker have reported the results of photoemission experiments for CsI which may be compared with our findings in the case of the normal lattice spacing. These workers estimate the width of the valence band to lie between 3 and 4 ev and state that the energy gap is about 6 ev. The agreement with our calculations is better than could reasonably be expected in view of the errors which must be present in our potential.

However, there is evidently no possibility of explaining the findings of Alder and Christian¹ along the present lines, and in this respect our work supports the later conclusions of Griggs *et al.*⁵ Very much higher

static pressures would be needed according to the present theoretical treatment before any metallic transition can occur.

Finally we should remark that in a heavy ionic crystal like CsI, spin-orbit coupling effects will doubtless eventually require consideration. However, until more detailed experiments have been carried out to determine the band structure of CsI, we have not thought it profitable to embark on a full treatment of this effect. Certainly, it does not in any way change our principal conclusions, as the spin-orbit splitting will be small compared with the band gap we have obtained.

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