

CONCLUSIONS

It has been experimentally demonstrated that there is a transition from impurity band conduction to conventional conduction via the conduction band in rutile as the oxygen vacancy density is decreased. Temperature versus resistivity measurements in the “*a*” and “*c*” crystal directions of rutile have been made over a wide variation in nonstoichiometric compositions of titanium and oxygen. An anisotropy of conduction greater than 1000 to 1 was observed at room temperature, increasing to more than 10 000 to 1 at -60°C . The results of this study indicate that associated with each crystal direction there is a continuous transition from impurity band conduction to conventional conduction via the conduction band, which is determined by the oxygen vacancy

density. However, the nature of this dependency on the oxygen vacancy density differs in the “*a*” and “*c*” crystal directions, allowing large anisotropies in the intermediate region of the transition. It is hoped that much of the published experimental data can now be reinterpreted with respect to the crystal directions and more unanimity of understanding achieved.

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Metallic Transitions in Ionic Crystals: Some Group Theoretical Results

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In view of a discrepancy between results available in the literature, the problem of finding the different irreducible representations for points on the surface of the Brillouin zone in NaCl and CsCl type lattices is re-examined for particular points of high symmetry. The lattice harmonics to be included in cellular-type calculations are listed up to and including $l=10$ for two points on the surface of the Brillouin zone in each case. Our results confirm the earlier work of Bell up to $l=6$, and extend her tables somewhat. The present findings however are at variance with Behringer's work on LiH for one of the points (*W*) which he considers.

1. INTRODUCTION

BEHRINGER¹ has recently reported a theoretical investigation designed to predict the pressure at which a metallic transition might occur in the ionic crystal LiH. Independently, two of us (M. F. and N. H. M.) have been working on the general problem of metallic transitions in ionic crystals, but with two essential differences from Behringer's work. Firstly, we have been considering the CsCl structure, rather than the NaCl structure adopted by Behringer. Although Behringer comments in his paper that the CsCl structure may be an important feature in discussing the metallic transitions, he does not deal quantitatively with this case. Secondly, from the point of view of the methods used in the band structure calculation, Behringer uses expansions in symmetrized plane waves, whereas so far all our work has made use of the cellular method.

However, both methods utilize the symmetry of the wave functions; in Behringer's calculation the form of the appropriate symmetrized plane waves is thereby fixed, whereas in our cellular treatment we determine in this way the allowed spherical harmonics in the expan-

sion of the wave function for a given \mathbf{k} within each cell. It is this group theoretical aspect of the problem on which we focus attention in this note. The compelling reason for a re-examination of existing work resides in the discrepancy which we find between the results of Behringer for the point *W* (see Sec. 2) and those given by Bell² on which our work is based. Behringer states that for the representation W_1 (W_s in the notation of Howarth and Jones), the wave function is *s*-like around both the nuclei in the LiH crystal, assuming the NaCl structure. On the other hand, Bell's tables indicate that the function is *p*-like around the second nucleus for this point in the Brillouin zone, if *s*-like around the first. It is the main purpose of this note to resolve the discrepancy, and then to extend the available results in certain directions.

2. NaCl STRUCTURE

(a) Point *W*. $\mathbf{k} = (\pi/2a)(2,1,0)$

To avoid repetition, we shall refer the reader to Behringer's notation. However, it is convenient for the purposes of the present argument to reproduce the

¹ R. E. Behringer, Phys. Rev. **113**, 787 (1959).

² D. G. Bell, Revs. Modern Phys. **26**, 311 (1954).

TABLE I. Character table for point W . $\mathbf{k} = (\pi/2a)(\pm 2, \pm 1, 0)$.

W	E	C_2	$2S_4$	$2C_2'$	$2\sigma_d$
$W_1(W_s)$	1	1	1	1	1
$W_2(W_f)$	1	1	1	-1	-1
$W_1'(W_d)$	1	1	-1	1	-1
$W_2'(W_p^1)$	1	1	-1	-1	1
$W_3(W_p^2)$	2	-2	0	0	0

$E \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$	$C_2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ -z \end{pmatrix}$
$S_4 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \pm z \\ -y \\ \mp x \end{pmatrix}$	$C_2' \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \pm z \\ -y \\ \pm x \end{pmatrix}$
$\sigma_d \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \pm x \\ y \\ \mp z \end{pmatrix}$	

character table for the point W , and this is shown in Table I.

In order to elucidate the point at issue, namely the nature of the wave function about different sites in the NaCl crystal, we shall begin by an argument based on an empty lattice assumption. Into this we will insert the correct symmetry of the lattice, and then discuss directly the form of the wave function about a nucleus of the second type. Since we are dealing with the basic plane wave

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = \exp[(i\pi/2a)\{2x+y\}], \quad (1)$$

we see from the character table that for the non-degenerate representation W_1 , the linear combination of plane waves with the correct symmetry is

$$\exp[(i\pi/2a)\{2x+y\}] + \exp[(i\pi/2a)\{-2x+y\}] + \exp[(i\pi/2a)\{2z-y\}] + \exp[(i\pi/2a)\{-2z-y\}]. \quad (2)$$

We now consider this wave function centered on a Na nucleus, and enquire what the nature of this function will be when it is viewed from a Cl site. To be definite, the origin will be transferred to the Cl nucleus sitting at the point $(a,0,0)$, and introducing the new co-ordinate $X = x - a$ we see that the wave function (2) becomes

$$-\exp[(i\pi/2a)\{2X+y\}] - \exp[(i\pi/2a)\{-2X+y\}] + \exp[(i\pi/2a)\{2z-y\}] + \exp[(i\pi/2a)\{-2z-y\}]. \quad (3)$$

We see then immediately that the wave function in (3) is zero when evaluated at the point $(X=0, y=0, z=0)$ and cannot therefore be s -like around the Cl nucleus. This argument is sufficient then to reveal that Behringer's result is at variance with the basic character table, and in fact it may now be seen from Table I that the appropriate irreducible representation corresponding to (3) is $W_2'(\equiv W_p^1)$, in essential agreement with Bell's work.

In the cellular calculations now in progress, it is of considerable value to have available all the lattice harmonics which occur up to high values of l in the general case when the empty lattice approximation is transcended. We show below how these harmonics may be obtained by a fairly straightforward generalization of the above plane wave argument. We write, instead of the basic plane wave $\exp[(i\pi/2a)\{2x+y\}]$, the function $f(x,y,z)$ and the properly symmetrized wave function corresponding to the irreducible representation W_1 is

$$\psi = f(x,y,z) + f(-x, y, -z) + f(z, -y, -x) + f(-z, -y, x) + f(z, -y, x) + f(-z, -y, -x) + f(x, y, -z) + f(-x, y, z). \quad (4)$$

We now expand $f(x,y,z)$ in the form adopted in cellular

TABLE II. Lattice harmonics for point W (NaCl lattice). $\mathbf{k} = (\pi/2a)(2,1,0)$.

l	W_s	W_p^1
0	1	...
1	...	$p = y$
2	$d = 2y^2 - x^2 - z^2$	$d = x^2 - z^2$
3	$f = y(x^2 - z^2)$	$f = y^3 - \frac{3}{5}p$
4	$g_1 = g(\Gamma_s)$	$g = x^4 - z^4 - 6d/7$
5	$g_2 = 2y^4 - x^4 - z^4 - 6d/7$	$h_1 = y^5 - (10/9)f - (3/7)p$
6	$h = y^3(x^2 - z^2) - f/3$	$h_2 = y(x^4 - 6x^2z^2 + z^4)$
7	$i_1 = i(\Gamma_s)$	$i_1 = x^6 - z^6 - 15g/11 - (5/7)d$
8	$i_2 = 2y^6 - x^6 - z^6 - 15g_2/11 - 5d/7$	$i_2 = (x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$
9	$j_1 = y^5(x^2 - z^2) - 10h/13 - (5/33)f$	$j_1 = y^7 - (21/13)h_1 - (35/33)f - p/3$
10	$j_2 = y(x^2 - z^2)(x^4 + z^4 - 14x^2z^2)$	$j_2 = y^3(x^4 - 6x^2z^2 + z^4) - (3/13)h_2$
11	$k_1 = k(\Gamma_s)$	$k_1 = x^8 - z^8 - (28/15)i_1 - 210g/143 - 20d/33$
12	$k_2 = 2y^8 - x^8 - z^8 - 28i_2/15 - 210g_2/143 - (20/33)d$	$k_2 = x^2y^2z^2(x^2 - z^2) - (8/31)k_1 + i_1/15 + 2g/143 - d/231$
13	$k_3 = x^2y^2z^2(2y^2 - x^2 - z^2) - (8/31)k_2 + i_2/15 + 2g_2/143 - d/231$	$l_1 = y^9 - (36/17)j_1 - (126/65)h_1 - (140/143)f - (3/11)p$
14	$l_1 = y^7(x^2 - z^2) - (21/17)j_1 - (7/13)h - (35/429)f$	$l_2 = y^5(x^4 + z^4 - 6x^2z^2) - (10/17)j_2 - (1/13)h_2$
15	$l_2 = y^3(x^2 - z^2)(x^4 + z^4 - 14x^2z^2) - (3/17)j_2$	$l_3 = y\{x^8 + z^8 - 28x^2z^2(x^4 + z^4) + 70x^4z^4\}$
16	m_1 . As for Γ_s .	$m_1 = x^{10} - z^{10} - (45/19)k_1 - (42/17)i_1 - 210g/143 - 75d/143$
17	$m_2 = 2y^{10} - x^{10} - z^{10} - (45/19)k_2 - (42/17)i_2 - (210/143)g_2 - (75/143)d$	$m_2 = x^2y^2z^2(x^4 - z^4) - (2/29)m_1 - (89/589)k_1 - (15/19)k_2$
18	$m_3 = x^2y^2z^2(2y^4 - x^4 - z^4) - (2/29)m_2 - (89/589)k_2 - (15/19)k_3$	$+ (14/255)i_1 + g/143 - 10d/3003$
19	$+ (14/255)i_2 + g_2/143 - 10d/3003$	$m_3 = (x^2 - y^2)(y^2 - z^2)(z^2 - x^2)(x^4 + y^4 + z^4) - (11/17)i_2$

TABLE III. Lattice harmonics for point L (NaCl lattice). $\mathbf{k} = (\pi/2a)(1,1,1)$.

L_s	L_p^1
l	l
0 1	1 $p = x + y + z$
2 $d = xy + yz + zx$	3 $f_1 = x^3 + y^3 + z^3 - \frac{3}{2}p$ $f_2 = xyz$
4 $g_1 = g(\Gamma_s)$ $g_2 = xyz(x + y + z) - d/7$	5 $h_1 = x^5 + y^5 + z^5 - (10/9)f_1 - 3p/7$ $h_2 = (y^4 + z^4 - 6y^2z^2)x + (z^4 + x^4 - 6z^2x^2)y + (x^4 + y^4 - 6x^2y^2)z$
6 $i_1 = i(\Gamma_s)$ $i_2 = (x^3 + y^3 + z^3)xyz - 6g_2/11 - d/21$ $i_3 = [y^4 + z^4 - (10/3)y^2z^2]yz + [z^4 + x^4 - (10/3)z^2x^2]zx$ $+ [x^4 + y^4 - (10/3)x^2y^2]xy$	7 $j_1 = x^7 + y^7 + z^7 - (21/13)h_1 - (35/33)f_1 - \frac{1}{3}p$ $j_2 = xyz(x^4 + y^4 + z^4) - 5f_2/11$ $j_3 = (y^4 + z^4 - 6y^2z^2)x^3$, etc., $-(3/13)h_2$
8 $k_1 = k(\Gamma_s)$ $k_2 = (x^5 + y^5 + z^5)xyz - i_2 - (45/143)g_2 - (5/231)d$ $k_3 = [y^4 + z^4 - (10/3)y^2z^2]x^2yz$, etc., $-i_3/15$	9 $l_1 = x^9 + y^9 + z^9 - (36/17)f_1 - (126/65)h_1 - (140/143)f_1$ $- (3/11)p$ $l_2 = x^3y^3z^3 + 3j_2/34 - 3f_2/143$ $l_3 = (y^4 + z^4 - 6y^2z^2)x^5$, etc., $-(10/17)j_3 - (1/13)h_2$ $l_4 = \{y^8 + z^8 - 28(y^6z^2 + y^2z^6) + 70y^4z^4\}x$, etc.
10 m_1 . As for Γ_s . $m_2 = (x^7 + y^7 + z^7)xyz - (28/19)k_2 - (14/17)i_2 - (28/143)g_2$ $m_3 = [y^4 + z^4 - (10/3)y^2z^2]x^4yz$, etc., $-(6/19)k_3 - i_3/85$ $m_4 = \{y^8 + z^8 - 12(y^6z^2 + y^2z^6) + (126/5)y^4z^4\}yz$, etc.	

calculations

$$f(x, y, z) = \sum A_{lm} R_l(r) P_{lm}(\cos\theta) e^{im\phi}, \quad (5)$$

and to obtain ψ in a simple form we choose y as the polar axis. Using the results³

$$\exp(i\phi) = (z + ix)/(1 - y^2)^{1/2}, \quad y = \cos\theta$$

it is easily shown by direct analytical methods that the terms appearing in the expansion of ψ have the form

$$(d^m/dy^m) P_l(y) [(z + ix)^m + (z - ix)^m], \quad (6)$$

where, for l odd, $m=2, 6, 10$, etc., and for l even, $m=0, 4, 8$, etc. Combinations of terms for a given l have been found which lead to a completely symmetrical function⁴ and orthogonal functions, and the results are collected in Table II. By an obvious modification of the above argument we have found the harmonics for W_p^1 , and these are also listed in Table II. These functions must be used in conjunction with one another in cellular calculations: for the extension of (3), based on plane waves, to Bloch functions, reference should be made to the Appendix.

(b) Point L . $\mathbf{k} = (\pi/2a)(1,1,1)$

Table III records similar results for the point L , which is the other case Behringer considers for NaCl. In this case, the present symmetry arguments agree with those used by Behringer, and the detailed harmonics are in accordance with Bell's results, which extend, however, only as far as $l=6$.

3. CsCl STRUCTURE

Turning now to the CsCl lattice, we shall consider here two wave vectors which are of interest in the numerical calculations which are at present in progress.

³ From this point we shall use x, y, z as direction cosines, except in the Appendix, where they again denote coordinates.

⁴ Actually this is the same as Γ_s ; compare Sec. 3 and Table IV.

(a) Point Γ . $\mathbf{k} = (\pi/a)(1,1,1)$

We consider first the representation Γ_s . All the harmonics up to $l=10$ are listed in Table IV. The form of the correctly symmetrized wave function, by arguments entirely analogous to those discussed earlier, shows that with Γ_s symmetry round one nucleus, say Cs, the wave function must have Γ_f symmetry when viewed from a Cl nucleus. All harmonics for $l \leq 10$ are listed for Γ_f in Table IV.

(b) Point X . $\mathbf{k} = (\pi/a)(1,0,0)$

We consider the representation X_s around one nucleus; this corresponds to X_p when viewed from a nucleus of the second kind. Independent tables are not in fact required for this case. The results may be obtained from those for W_s in the case of X_s by omitting the odd l values entirely, and by interchanging x and y in the even l harmonics. The results for X_p are similarly obtained from Table II, by omitting the even harmonics in W_p^1 and interchanging x and y .

4. COMMENTS ON TABLES

Use of our tables in conjunction with those of Bell will allow certain of her results to be immediately extended. Thus, her representation A_i (Γ_i in the notation

TABLE IV. Lattice harmonics for point Γ (CsCl lattice). $\mathbf{k} = (\pi/a)(1,1,1)$.

Γ_s	Γ_f
l	l
0 1	1 ...
2 ...	3 $f = xyz$
4 $g = x^4 + y^4 + z^4 - \frac{3}{2}$	5 ...
6 $i = x^2y^2z^2 + g/22 - 1/105$	7 $j = xyz(x^4 + y^4 + z^4) - 5f/11$
8 $h = x^8 + y^8 + z^8 - 28i/5 - 210g/143 - \frac{1}{3}$	9 $x^3y^3z^3 + 3j/34 - 3f/143$
10 $x^{10} + y^{10} + z^{10} - 45h/19 - 126i/17$ $- 210g/143 - 3/11$	

of this paper) may be seen by inspection of our Table II to contain no eighth-order term, the next term of order $l=10$ being given by

$$(x^2-y^2)(y^2-z^2)(z^2-x^2)(x^4+y^4+z^4-11/17). \quad (7)$$

In addition, the following extensions of Bell's results may readily be obtained from our Tables II and III:

$$\begin{array}{ll} A_d(1) \text{ and } A_{f'}(x) & \text{from } W_s, \\ A_p(x) \text{ and } A_d(2) & \text{from } W_p^1, \\ A_{d'}(x) & \text{from } L_s. \end{array}$$

5. FINAL REMARKS

The results for the CsCl structure are being utilized in the detailed study at present in progress on the CsI crystal, for which the experimental results of Alder and Christian⁵ indicate a metallic transition at about 250 000 atmospheres. We hope to report fully on these band structure calculations at a later date.

We conclude by remarking here that for LiH assuming the NaCl structure, Behringer's estimate of the pressure at which a metallic transition might occur must now be viewed with caution, in the light of the symmetry arguments for the point W presented in this work.

Note added in proof.—Dr. Behringer has now re-examined his calculations and has kindly given us permission to say that he agrees with our conclusions.

The revised energy calculation for the point W in the LiH crystal is now being undertaken in this Department.

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⁵ B. J. Alder and R. H. Christian, Phys. Rev. **104**, 550 (1956).

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APPENDIX

We show here how the argument based on plane waves, and leading to Eq. (3) above may be generalized to deal with Bloch functions. Equation (4) embodies the symmetry requirements for the irreducible representation W_s and we can clearly rewrite this, about the point (0,0,0) say, as

$$\begin{aligned} \psi(x,y,z) &= \{u(x,y,z) + u(x,y,-z)\}e^{(i\pi/2a)(2x+y)} \\ &\quad + \{u(-x,y,z) + u(-x,y,-z)\}e^{(i\pi/2a)(-2x+y)} \\ &\quad + \{u(z,-y,x) + u(z,-y,-x)\}e^{(i\pi/2a)(2z-y)} \\ &\quad + \{u(-z,-y,x) + u(-z,-y,-x)\}e^{(i\pi/2a)(-2z-y)}, \end{aligned} \quad (A.1)$$

where, utilizing Bloch's theorem, $u(x,y,z)$ has the period of the lattice. (A.1) reduces to (2) when we take the free-electron limit, i.e., $u \rightarrow \text{constant}$. Following the method of Sec. 2, we now transfer the origin to the point $(a,0,0)$. Using the periodicity of $u(x,y,z)$, and writing $u(x-a,y,z) \equiv v(x,y,z)$ we have

$$\begin{aligned} \psi(x-a,y,z) &= -\{v(x,y,z) + v(x,y,-z)\}e^{(i\pi/2a)(2x+y)} \\ &\quad - \{v(-x,y,z) + v(-x,y,-z)\}e^{(i\pi/2a)(-2x+y)} \\ &\quad + \{v(z,-y,x) + v(z,-y,-x)\}e^{(i\pi/2a)(2z-y)} \\ &\quad + \{v(-z,-y,x) + v(-z,-y,-x)\}e^{(i\pi/2a)(-2z-y)}, \end{aligned} \quad (A.2)$$

where we have used relations of the type

$$u(z,-y,x-a) = u(z-a,-y,x) = v(z,-y,x).$$

The function (A.2) is easily seen to have p symmetry about the point $(a,0,0)$. Similar arguments hold for the points $(0,a,0)$ and $(0,0,a)$.