Acta Cryst. (1958). **11**, 365

The Madelung Constants of Slices and Chains, with an Application to the CdI_2 Structure

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(*Received* 27 *November* 1957)

The Ewald expression for the electrostatic lattice energy is adapted to the calculation of this energy in slices and chains. Application to the CdI_2 structure gives as a new value for the Madelung constant of the Bozorth structure 4·382, of the Hassel structure 4·384 and of a (0001) slice 4·377. The electrostatic attraction energy between the slices in the Bozorth structure amounts to −0·5 kcal.mol.$^{-1}$, the repulsion energy +1·6 kcal.mol.$^{-1}$ (based on Pinsker's value of the total repulsion energy). The van der Waals energy (−8·0 kcal.mol.$^{-1}$ according to Pinsker) far outweighs the other energies.

Introduction

An expression for the Madelung constant of a chain of ions has been given by Kleber (1939). Besides a logarithmic term, it contains the Hankel cylinder function of order zero. The argument of this function is proportional to the projection of the distance between two ions on a plane, perpendicular to the chain direction. When this distance, and hence the argument, approaches zero, the Hankel cylinder function approaches infinity, which makes the calculations very unreliable and lengthy.

A different method was sought to obtain a function that approaches zero, when the aforementioned distance approaches zero. The method of Ewald (1921) for the calculation of Madelung constants furnished formulas that possess the desired property.

The electrostatic energy of an ionic structure can be represented by

$$E = \tfrac{1}{2}\sum_{i=1}^{n} \varepsilon_i \varphi_i \,, \tag{1}$$

when the ions are considered as point charges. Here n is the number of ions in the unit cell, ε_i is the charge of the ith ion and φ_i is the electrostatic potential in the site of that ion.

Ewald (1921) derived the following formulas for the potential:

$$\varphi_i = \varphi_{i1} + \varphi_{i2} \,, \tag{2}$$

$$\varphi_{i1} = \frac{1}{\pi V} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \sum_{j=1}^{n} S_{hklj} \times \exp\,(-\pi^2\lambda^2/d^2_{hkl}) \,.\, d^2_{hkl} - 2\varepsilon_i/\lambda\sqrt{\pi} \,, \tag{3}$$

$$\varphi_{i2} = \frac{1}{\lambda} \sum_{q=1}^{\infty} \varepsilon_q \frac{1-H(r_{iq}/\lambda)}{r_{iq}/\lambda} \quad (q \neq i) \,. \tag{4}$$

Here

V = volume unit cell,
λ = arbitrarily chosen length,
$S_{hklj} = \varepsilon_j \exp 2\pi i(hx_j + ky_j + lz_j)$,
r_{iq} = distance between the ions i and q,

$$H(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp\,(-t^2)\,dt \,.$$

The summation in φ_{i1} should not include the term with $h = k = l = 0$ and the summation in φ_{i2} is to be extended over all the ions in the infinite structure.

Electrostatic potential of an ion in a slice†)

This potential can be derived from the general expression in the following way.

A unit cell is chosen in such a way that the a and b axes are parallel to the slice. Its origin is in the site of the ith ion.

For the sake of convenience we take the c axis perpendicular to the slice. In this case $V = abc \sin\gamma$ and

$$1/d^2_{hkl} = h^2a^{*2} + k^2b^{*2} + 2hka^*b^* \sin\gamma^* + l^2c^{*2} \,,$$

where the starred symbols denote reciprocal-lattice elements.

The structure is now stretched out in the direction of the c axis, but the positions of the ions belonging to the slice should remain fixed in space. The potential of an ion in the slice is then obtained when c becomes infinite, or when c^* becomes zero. So we have to calculate

$$\lim_{c^*\to 0} \varphi_{i1} = \frac{1}{\pi ab \sin\gamma} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{j=1}^{n} \varepsilon_j \exp 2\pi i(hx_j + ky_j) \times \exp\,\{-\pi^2\lambda^2(h^2a^{*2} + k^2b^{*2} + 2hka^*b^* \sin\gamma^*)\} \times \lim_{c^*\to 0} \sum_{l=-\infty}^{+\infty} \frac{\exp\,(2\pi i l Z_j c^*)\, \exp\,(-\pi^2\lambda^2 l^2 c^{*2}) \,.\, c^*}{h^2a^{*2} + k^2b^{*2} + 2hka^*b^* \sin\gamma^* + l^2c^{*2}} - \frac{2\varepsilon_i}{\lambda\sqrt{\pi}} \,. \tag{5}$$

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† The term slice was first used by Hartman & Perdok (1955) to indicate a stoichiometric portion of a crystal structure that is parallel to a lattice plane and that contains two or more periodic bond chains. The term layer is used here exclusively for a two-dimensional array of coplanar ions.

In this formula we substituted $z_j = Z_j c^*$, where Z_j is the distance of the jth ion to a plane parallel to the slice and going through the ith ion.

Further we substitute

$$A^2 = \pi^2\lambda^2(h^2a^{*2}+k^2b^{*2}+2hka^*b^*\sin\gamma^*)\,. \qquad (6)$$

At the limit $c^* = 0$ the summation over l changes into an integral:

$$\lim_{c^*\to 0}\varphi_{i1} = \frac{1}{\pi ab\sin\gamma}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{j=1}^{n} S_{hkj}\exp(-A^2)$$
$$\times\lim_{c^*\to 0}\int_{-\infty}^{+\infty}\frac{\exp(2\pi ilZ_jc^*)\exp(-\pi^2\lambda^2l^2c^{*2}).c^*}{A^2/\pi^2\lambda^2+l^2c^{*2}}\,dl$$
$$-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (7)$$

Here S_{hkj} stands for $\varepsilon_j\exp 2\pi i(hx_j+ky_j)$.

Now we put $u = \pi\lambda lc^*$. With this substitution, c^* disappears from the integral, so that the limit is the integral itself:

$$\lim_{c^*\to 0}\varphi_{i1} = \frac{\lambda}{ab\sin\gamma}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{j=1}^{n} S_{hkj}\exp(-A^2)$$
$$\times\int_{-\infty}^{+\infty}\frac{\exp(2iZ_ju/\lambda)\exp(-u^2)}{A^2+u^2}\,du-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (8)$$

This integral can be further evaluated (see Appendix). We find

$$\varphi_{i1}(\text{slice}) = \frac{\lambda\pi}{ab\sin\gamma}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{j=1}^{n} S_{hkj}\frac{\{1-H(A)\}}{A}$$
$$+\frac{2\lambda}{ab\sin\gamma}\sum_{h=-\infty}^{+\infty}\sum_{k=-\infty}^{+\infty}\sum_{j=1}^{n} S_{hkj}\exp(-A^2)$$
$$\times\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p)!}\left(\frac{2Z_j}{\lambda}\right)^{2p}\int_0^{\infty}\frac{u^{2p}\exp(-u^2)}{A^2+u^2}\,du-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (9)$$

The first summation over h and k in this formula should not include the term with $h = k = 0$, which is infinite. The omission of this infinite term does not affect the value of the total electrostatic energy, because they all cancel out in expression (1). The second summation, which depends on Z_j, includes also the term with $h = k = 0$.

Formula (4) still holds for the second part of the potential (φ_{i2}(slice)), so that the complete potential is the sum of (9) and (4).

If λ is given such a value that $A^2 > 14$ for all terms with either $h \neq 0$ or $k \neq 0$, then these terms are negligible (smaller than 10^{-6}) and the expression (9) reduces to

$$\varphi_{i1}(\text{slice};\ A^2>14)\ \cdot$$
$$= \frac{2\lambda\sqrt{\pi}}{ab\sin\gamma}\sum_{j=1}^{n}\varepsilon_j\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p-1)p!}\left(\frac{Z_j}{\lambda}\right)^{2p}-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (10)$$

The j-dependent part in (10) represent the term in (9) for which $h = k = 0$.

Electrostatic potential of an ion in a chain

An expression for this potential is obtained in much the same way as in the case of a slice. We take a Cartesian set of axes, of which the a axis runs parallel to the chain. The origin is in the site of the ith ion. The potential is then derived from expression (3), by taking the double limit with $c \to \infty$ and $b \to \infty$ or with $c^* \to 0$ and $b^* \to 0$.

Taking into account that $V = abc$ and that $1/d^2_{hkl} = h^2a^{*2}+k^2b^{*2}+l^2c^{*2}$, and substituting $y_j = Y_jb^*$ and $z_j = Z_jc^*$, we obtain

$$\lim_{\substack{c^*\to 0\\ b^*\to 0}}\varphi_{i1} = \frac{1}{\pi a}\sum_{h=-\infty}^{+\infty}\sum_{j=1}^{n}\varepsilon_j\exp(2\pi ihx_j)\exp(-\pi^2\lambda^2h^2a^{*2})$$
$$\times\lim_{\substack{c^*\to 0\\ b^*\to 0}}\sum_{k=-\infty}^{+\infty}\sum_{l=-\infty}^{+\infty}\frac{\exp 2\pi i(kY_jb^*+lZ_jc^*)\times\exp(-\pi^2\lambda^2k^2b^{*2}-\pi^2\lambda^2l^2c^{*2}).b^*c^*}{h^2a^{*2}+k^2b^{*2}+l^2c^{*2}}$$
$$-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (11)$$

The limit is approximated by the double integral

$$\lim_{\substack{c^*\to 0\\ b^*\to 0}}\varphi_{i1} = \frac{1}{\pi a}\sum_{h=-\infty}^{+\infty}\sum_{j=1}^{n}S_{hj}\exp(-\pi^2\lambda^2h^2a^{*2})$$
$$\times\lim_{\substack{c^*\to 0\\ b^*\to 0}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{\exp 2\pi i(kY_jb^*+lZ_jc^*)\times\exp(-\pi^2\lambda^2k^2b^{*2}-\pi^2\lambda^2l^2c^{*2}).b^*c^*}{h^2a^{*2}+k^2b^{*2}+l^2c^{*2}}$$
$$\times\,dk\,dl-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (12)$$

We substituted

$$S_{hj} = \varepsilon_j\exp(2\pi ihx_j)\,.$$

Now put

$$B = \pi\lambda ha^*\,. \qquad (13)$$

Change of variables by taking $u = \pi\lambda kb^*$ and $v = \pi\lambda lc^*$ does remove b^* and c^* from the integral, so that the limit equals the integral:

$$\lim_{\substack{c^*\to 0\\ b^*\to 0}}\varphi_{i1} = \frac{1}{\pi a}\sum_{h=-\infty}^{+\infty}\sum_{j=1}^{n}S_{hj}\exp(-B^2)$$
$$\times\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{\exp 2i(Y_ju/\lambda+Z_jv/\lambda)\exp(-u^2-v^2)}{B^2+u^2+v^2}\,du\,dv$$
$$-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,. \qquad (14)$$

This double integral can be reduced (see Appendix), and we obtain

$$\varphi_{i1}(\text{chain}) = -\frac{1}{a}\sum_{h=-\infty}^{+\infty}\sum_{j=1}^{n}S_{hj}Ei(-B^2)$$
$$+\frac{1}{a}\sum_{h=-\infty}^{+\infty}\sum_{j=1}^{n}S_{hj}\exp(-B^2)\sum_{p=1}^{\infty}\frac{(-1)^p}{(p!)^2}\left(\frac{R_j}{\lambda}\right)^{2p}$$
$$\times\int_0^{\infty}\frac{t^p\exp(-t)}{B^2+t}\,dt-\frac{2\varepsilon_i}{\lambda\sqrt{\pi}}\,, \qquad (15)$$

in which $R_j^2 = Y_j^2+Z_j^2$.

The first summation over h in (15) should not include the term with $h = 0$.

If λ is given such a value that $B^2 > 14$ for $h = 1$, the expression (15) contains only the term with $h = 0$ and it reduces to

$$\varphi_{i1}(\text{chain};\ B^2 > 14)$$
$$= \frac{1}{a} \sum_{j=1}^{n} \varepsilon_j \sum_{p=1}^{\infty} \frac{(-1)^p}{p^2(p-1)!} \left(\frac{R_j}{\lambda}\right)^{2p} - \frac{2\varepsilon_i}{\lambda\sqrt{\pi}} . \qquad (16)$$

The second part of the potential (φ_{i2}(chain)) is still represented by formula (4). The sum of (4) and (15) gives the total potential.

The final formulas (9) and (15) have the same structure: in both cases the first summation minus the constant term $2\varepsilon_i/\lambda\sqrt{\pi}$ represents the potential in a slice, where all ions are located in the same mathematical plane and the potential in a straight chain, respectively. The second summation is a correction for those cases in which not all Z_j's and R_j's are zero.

The choice of λ

The occurrence of the power series of Z_j/λ in formula (9) and of R_j/λ in formula (15) puts a practical limit on the choice of λ. To ensure a good convergence of these series, λ should be larger than 1·1 times the maximum value of Z_j or R_j. In that case the term with $p = 5$ is about one-tenth of the term with $p = 4$, so that at most 11 terms will give an accuracy of six decimals.

Whenever possible λ should be given a value that makes A^2 or $B^2 > 14$ (cf. equations (10) and (16)). This gives the desirable condition $\lambda > 1{\cdot}2/a^*$.

On the other hand the number of terms involved in the calculation of φ_{i2} is small when λ is small. A particular condition for the choice of λ cannot be given because the number of different terms depends on the symmetry and on the number of ions in the asymmetric unit.

Application to the CdI_2 layer lattice

Recently the interlayer bonding in this structure was discussed by Holser (1956). The Madelung constant of one slice (0001), consisting of two layers of iodine atoms with a layer of cadmium atoms in between, was calculated by the method of Højendahl (1938).

Holser found for this Madelung constant the value 4·457, which is higher than the Madelung constant of the whole structure, evaluated by Pinsker (1943*a*) to be 4·394. Pinsker calculated the potentials of the ions separately for two values of λ (see formulas (3) and (4)). The two values of each of these potentials, which should be exactly equal, showed differences of the order of 0·3%. This may be due to rounding-off errors. It was therefore decided to recalculate the Madelung constant of CdI_2 with sufficient accuracy in order to exclude computational and rounding-off errors.

(*a*) *The Madelung constant of the Bozorth* CdI_2 *structure*

The space group of this structure is $P\bar{3}m$ with Cd in (0, 0, 0) and I in $(\frac{1}{3}, \frac{2}{3}, u)$ and $(\frac{2}{3}, \frac{1}{3}, \bar{u})$.

The cell dimensions are $a = 4{\cdot}240$, $c = 6{\cdot}855$ Å, and the parameter $u = \frac{1}{4}$ (Pinsker, 1941).

The S_{hklj} values were first summed over j and the whole set of symmetrically equivalent hkl values. Then we calculated $E_1 = \frac{1}{2}\sum_{i=1}^{n} \varepsilon_i \varphi_{i1}$ for two values of λ. For the calculation of $E_2 = \frac{1}{2}\sum_{i=1}^{n} \varepsilon_i \varphi_{i2}$ the necessary $H(x)$ values were taken from *Tables of Probability Functions* (1941).

All calculations were carried out in six decimal places on a desk calculating machine. From the crystal energy $E = E_1 + E_2$, in units e.^{2}Å^{-1}, the Madelung constant A_B was obtained by multiplication by the shortest Cd–I distance (2·988 Å). The result is:

$$\text{with } \lambda = \tfrac{1}{2}a, \quad A_B = -4{\cdot}381890\ ,$$
$$\text{with } \lambda = \tfrac{1}{4}a\sqrt{2}, \quad A_B = -4{\cdot}381890\ .$$

(*b*) *The Madelung constant of the Hassel* CdI_2 *structure*

The space group of this structure is $P6mc$. Two Cd atoms are in $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z)$, with $z = 0$. Two I atoms are in the same positions with $z = \frac{5}{8}$ and two other I atoms are in $(0, 0, z)$ and $(0, 0, \frac{1}{2}+z)$ with $z = \frac{3}{8}$.

The lattice parameters are $a = 4{\cdot}240$ and $c = 13{\cdot}710$ Å. The values quoted for c by several authors do not agree. Therefore the c axis was provisionally taken twice the c axis of the Bozorth structure. The result is:

$$\text{with } \lambda = \tfrac{1}{2}a, \quad A_H = -4{\cdot}384071\ ,$$
$$\text{with } \lambda = \tfrac{1}{3}a\sqrt{3}, \quad A_H = -4{\cdot}384074\ .$$

(*c*) *The Madelung constant of a* (0001) *slice*

With $\lambda = \frac{3}{2}a$, all terms containing $H(A)$ in formula (9) could be neglected, while five terms of the power series of Z_j had to be calculated. The calculation of the φ_{i2}'s involved 54 different terms.

With $\lambda = \frac{5}{4}a$, again all terms containing $H(A)$ were negligible, but now six terms of the power series had to be calculated and 38 terms were needed for the φ_{i2} calculation.

The result is:

$$\text{with } \lambda = \tfrac{3}{2}a, \quad A_L = -4{\cdot}377467\ ,$$
$$\text{with } \lambda = \tfrac{5}{4}a, \quad A_L = -4{\cdot}377461\ .$$

(*d*) *Discussion of the interlayer bonding*

Contrary to Holser, we find that a weak electrostatic attraction exists between the slices (0001) in the crystal. The larger attraction is found in the Hassel structure and it amounts to $-0{\cdot}73$ kcal.mol.$^{-1}$. For the Bozorth structure it is $-0{\cdot}49$ kcal.mol.$^{-1}$.

The repulsion energy between the slices is estimated by assuming a r^{-10} function. The total repulsion energy B_B was calculated by Pinsker (1945) to be $+115$ kcal.mol.$^{-1}$. The part of it that is due to repulsion between the slices is denoted by B_L and is calculated from the following equation:

$$\frac{B_L}{B_B} = \frac{6r_1^{-10}}{12r_1^{-10}+12r_2^{-10}+12r_3^{-10}+6r_4^{-10}}\,.$$

Here $r_1 = 4{\cdot}212$ Å, the distance between two nearest I ions in adjacent layers; $r_2 = 2{\cdot}988$ Å, the distance between neighbouring Cd and I ions; $r_3 = r_4 = 4{\cdot}240$ Å, the distance between nearest I ions and nearest Cd ions in the same layer.

We find that

$$B_L = +1{\cdot}72 \text{ kcal.mol.}^{-1}.$$

A more refined treatment, in which Pinsker's exponential form of the repulsion energy is used, gives the value $B_L = +1{\cdot}56$ kcal.mol.$^{-1}$.

The repulsion and attraction energies are thus found to be very weak and of the same order of magnitude. Hence for the interlayer bonding the van der Waals energy must be mainly responsible; Pinsker (1943*b*) estimated this energy to be $-8{\cdot}0$ kcal.mol.$^{-1}$.

The author gratefully acknowledges the help of Dr P. C. Sikkema (Mathematical Institute of this University) specially for pointing out the possibility to change the limits (5) and (11) to the integral forms (8) and (14), respectively.

APPENDIX

(1) Evaluation of the integral in formula (8)

$$I_1 = \int_{-\infty}^{+\infty} \frac{\exp(2iZ_ju/\lambda)\exp(-u^2)}{A^2+u^2}\,du$$

$$= 2\int_0^\infty \frac{\exp(-u^2)\cos 2Z_ju/\lambda}{A^2+u^2}\,du\,.$$

Expansion of the cosine in a series gives

$$I_1 = 2\int_0^\infty \frac{\exp(-u^2)}{A^2+u^2}\,du + 2\sum_{p=1}^{\infty}\frac{(-1)^p}{(2p!)}\left(\frac{2Z_j}{\lambda}\right)^{2p}\int_0^\infty \frac{u^{2p}\exp(-u^2)}{A^2+u^2}\,du\,.$$

A recurrence relation is valid for the last integral:

$$\int_0^\infty \frac{u^{2p+2}\exp(-u^2)}{A^2+u^2}\,du$$

$$= \int_0^\infty u^{2p}\exp(-u^2)\,du - A^2\int_0^\infty \frac{u^{2p}\exp(-u^2)}{A^2+u^2}\,du$$

$$= \frac{1.3.5\ldots(2p-1)}{2^{p+1}}\sqrt{\pi} - A^2\int_0^\infty \frac{u^{2p}\exp(-u^2)}{A^2+u^2}\,du\,. \quad (17)$$

For $p = 0$ we obtain

$$\int_0^\infty \frac{\exp(-u^2)}{A^2+u^2}\,du = \frac{\pi}{2}\exp(A^2)\frac{\{1-H(A)\}}{A}\,. \quad (18)$$

Substitution of relations (17) and (18) gives (9).

(2) Evaluation of the double integral in formula (14)

We put $f = 2Y_j/\lambda$ and $g = 2Z_j/\lambda$. Then

$$I_2 = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \frac{\exp i(fu+gv)\exp(-u^2-v^2)}{A^2+u^2+v^2}\,du\,dv\,,$$

$$I_2 = 2\left[\int_0^\infty\int_0^\infty \frac{\cos(fu+gv)\exp(-u^2-v^2)}{A^2+u^2+v^2}\,du\,dv + \int_0^\infty\int_0^\infty \frac{\cos(fu-gv)\exp(-u^2-v^2)}{A^2+u^2+v^2}\,du\,dv\right]. \quad (19)$$

Now the cosines are expanded into series and polar coordinates are introduced: $u = r\cos\theta$ and $v = r\sin\theta$. After separation of the variables (19) changes into

$$I_2 = 2\left[2\int_0^{\frac{\pi}{2}} d\theta\int_0^\infty \frac{r\exp(-r^2)}{A^2+r^2}\,dr + \sum_{p=1}^{\infty}\int_0^\infty \frac{r^{2p+1}\exp(-r^2)}{A^2+r^2}\,dr\int_0^{\frac{\pi}{2}}\frac{(-1)^p}{(2p)!} \times\{(f\cos\theta+g\sin\theta)^{2p}+(f\cos\theta-g\sin\theta)^{2p}\}\,d\theta\right]. \quad (20)$$

In the first integrals we substitute $A^2+r^2 = s^2$ and obtain

$$2\int_0^{\frac{\pi}{2}} d\theta\int_0^\infty \frac{r\exp(-r^2)}{A^2+r^2}\,dr = \frac{\pi}{2}\exp(A^2)\int_{A^2}^\infty \frac{e^{-s}}{s}\,ds$$

$$= -\frac{\pi}{2}\exp(A^2)Ei(-A^2)\,. \quad (21)$$

The second integral over the function of r in (20) is given a more convenient form by substituting $t = r^2$:

$$\int_0^\infty \frac{r^{2p+1}\exp(-r^2)}{A^2+r^2}\,dr = \tfrac{1}{2}\int_0^\infty \frac{t^p\exp(-t)}{A^2+t}\,dt\,. \quad (22)$$

The integral (22) can be evaluated by means of a recurrence relation:

$$\int_0^\infty \frac{t^{p+1}\exp(-t)}{A^2+t}\,dt$$

$$= \int_0^\infty t^p\exp(-t)\,dt - A^2\int_0^\infty \frac{t^p\exp(-t)}{A^2+t}\,dt$$

$$= p! - A^2\int_0^\infty \frac{t^p\exp(-t)}{A^2+t}\,dt\,. \quad (23)$$

For $p = 0$ we find

$$\int_0^\infty \frac{\exp(-t)}{A^2+t}\,dt = -\exp(A^2)Ei(-A^2)\,. \quad (24)$$

Finally, the last integral in (20) can be evaluated by integrating each term separately. We find then

$$\int_0^{\frac{\pi}{2}} \frac{(-1)^p}{(2p)!} \{(f\cos\theta+g\sin\theta)^{2p}+(f\cos\theta-g\sin\theta)^{2p}\}\,d\theta = \frac{(-1)^p\pi}{4^p(p!)^2}(f^2+g^2)^p. \quad (25)$$

Now we put $Y_j^2+Z_j^2 = R_j^2$, so that

$$f^2+g^2 = 4R_j^2/\lambda^2\,. \quad (26)$$

When all the expressions from (21) to (26) are substituted into (20) and this into (14) we obtain formula (15).

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Präzisionsbestimmung der Gitterkonstanten von $A^{\mathrm{III}}B^{\mathrm{V}}$-Verbindungen

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(*Eingegangen am* 24. *Dezember* 1957)

Precision cell dimensions of compounds of the type $A^{\mathrm{III}}B^{\mathrm{V}}$ have been determined from powder photographs, using the asymmetric method of Straumanis. Without correction for refraction the following values were obtained:

InSb: $a = 6{\cdot}47877 \pm 0{\cdot}00005$ Å; InAs: $a = 6{\cdot}0584 \pm 0{\cdot}0001$ Å; InP: $a = 5{\cdot}86875 \pm 0{\cdot}0001$ Å;
GaSb: $a = 6{\cdot}0954 \pm 0{\cdot}0001$ Å; GaAs: $a = 5{\cdot}6534 \pm 0{\cdot}0002$ Å; GaP: $a = 5{\cdot}4505 \pm 0{\cdot}0001$ Å;
AlSb: $a = 6{\cdot}1355 \pm 0{\cdot}0001$ Å.

The corrections for refraction are given.

Einleitung

Die im Zinkblende- (bzw. Wurtzit-) Gitter kristallisierenden AB-Verbindungen aus Elementen der III. und V. Hauptgruppe des periodischen Systems haben durch die grundlegenden Arbeiten von Welker (1952, 1953) grosses Interesse für die Halbleiterphysik erlangt. Dies führte dazu, dass Kristalle sehr hoher Reinheit hergestellt wurden, und es soll im folgenden über die Präzisionsbestimmung der Gitterkonstanten von einigen durch besondere chemische und physikalische Methoden gereinigten $A^{\mathrm{III}}B^{\mathrm{V}}$-Verbindungen berichtet werden.

Verwendetes Probenmaterial

Die untersuchten Verbindungen wurden in unserem Forschungslaboratorium von Dr O. G. Folberth durch Zusammenschmelzen der Komponenten hergestellt. Die Ausgangsstoffe hierfür sind durch spezifische von Dr G. Iwantscheff und Mitarbeitern ausgearbeitete chemische Verfahren gereinigt worden. Ausserdem wurden die Verbindungen noch durch Zonenziehen nachgereinigt. Die von Dr E. Golling durchgeführte Spektralanalyse der Proben liess keinerlei Verunreinigungen erkennen.

Durchführung der Gitterkonstantenbestimmung

Die Gitterkonstanten wurden aus Pulveraufnahmen nach der asymmetrischen Methode von Straumanis & Ievins (1940) bestimmt. Die Kamera hatte einen Durchmesser von 57,3 mm. Die stäbchenförmigen Pulverpräparate waren 0,1–0,15 mm. dick. Sie sind durch Aufbringen der zu untersuchenden Substanz auf 0,05 mm. dicke Quarzglasfäden hergestellt worden. Um Temperaturschwankungen während der Aufnahme auszuschliessen, befand sich die Kamera in einem Luftthermostaten, dessen Wände mit Wasser von kon-