

transition with increasing field to the mechanism of the previous paragraph.

SUMMARY

Two mechanisms have been investigated to explain the experimental data on the sidewise motion of 180° domain walls in single crystal BaTiO_3 . A nucleation model which assumes that the wall motion is controlled by the nucleation of triangular steps along existing 180° walls satisfactorily explains much of the data. Over limited field ranges, the model predicts a wall velocity $v \propto \exp(-\delta/E)$, as observed. The theoretical and experimental values of δ agree if the wall energy σ_w is set equal to 0.4 ergs cm^{-2} , a value in order of magnitude agreement with theoretical estimates of the wall energy. The shapes of the domains observed in the low field region are in agreement with the model. Furthermore, provided that slightly different wall energies are assumed for nucleations on parent walls parallel and at 45° to the crystalline a axes, the model

accounts for the change in domain shapes observed with field in the neighborhood of 1000 v cm^{-1} . The measured temperature dependence of the wall velocity is in fair agreement with the nucleation model which gives a variation of the activation field δ with temperature through $P_s^3 T^{-1} \epsilon_a^{-1/2}$.

A screw dislocation mechanism has also been discussed. If it is assumed that the screw dislocations of both senses are randomly distributed in the crystal, and that they are not too close together, then the expected form of the wall velocity is $v \propto \exp(-\text{const}/E^2)$ which is not in agreement with experiment. The possibility that screw dislocation sources may become active at higher fields is suggested. Such a process may account for the observed small increase in $-d \ln v/d(1/E)$ with field.

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Extension of the Madelung Method for the Evaluation of Lattice Sums

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The Madelung formulas for the electrostatic potential of a linear or planar Bravais lattice of ions, neutralized by a uniform distribution of charge, are extended to the lattice sums over a linear or planar Bravais lattice involving two-body interactions of the type R^{-n} (R , interatomic distance; $n > 0$), evaluated at points outside the lattice. The application of these generalized Madelung formulas in the evaluation of the specific face energy for neutral planes of an ionic solid of composition MX is briefly discussed.

1. INTRODUCTION

A WELL-KNOWN method for the evaluation of electrostatic lattice potentials is the so-called *Madelung method*.¹ In essence, the method involves the expansion of the electrostatic potential of a Bravais lattice of point charges, neutralized by a uniform distribution of charge, into a Fourier series of complex exponentials with the required periodicity. The series that one obtains do not converge rapidly inside the lattice itself, and thus the relevant results of the method are the formulas for the electrostatic potential generated by a neutralized linear or planar Bravais lattice in its surroundings. We will show that these formulas can be easily extended to the case of lattice sums over a linear or planar Bravais lattice involving interactions between pairs of atoms which decrease with some power of the distance, such as the van der Waals interactions, evaluated at points outside the lattice. In effect the

formulas given by Hove and Krumhansl² for interaction energies of this type between a semi-infinite cubic or square lattice of atoms and an atom outside it, as well as the expressions given by Benson and his co-workers³ for various lattice sums of interest in the theory of the surface energy of ionic crystals, can be regarded as particular applications of the generalized Madelung method.

2. LINEAR BRAVAIS LATTICE

We consider a linear Bravais lattice of period a along the x axis with lattice points in the positions $x_l = la$ (l , integer) and a point (x, r) , a distance r from the line of the lattice ($r > 0$). To evaluate the sum

$$S_n(x, r) = \sum_{l=-\infty}^{+\infty} \frac{1}{[(x-x_l)^2 + r^2]^{n/2}}, \quad (1)$$

² J. Hove and J. A. Krumhansl, *Phys. Rev.* **92**, 569 (1953).

¹ See, e.g., M. Born, *Atomtheorie des festen Zustandes* (B. G. Teubner, Leipzig, 1923), Sec. 37 and G. Leibfried, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. VII/1, p. 104, Sec. 26.

³ B. M. E. van der Hoff and G. C. Benson, *Can. J. Phys.* **31**, 1087 (1953); G. C. Benson and H. P. Schreiber, *Can. J. Phys.* **33**, 529 (1955); H. P. Schreiber and G. C. Benson, *Can. J. Phys.* **33**, 534 (1955); F. van Zeggeren and G. C. Benson, *J. Chem. Phys.* **26**, 1077 (1957).

with $n > 0$ we expand it into a Fourier series of complex exponentials $e^{i\kappa x}$, $\kappa = (2\pi/a)k_1$ (k_1 , integer), having period a :

$$S_n(x, r) = - \sum_{\kappa=-\infty}^{+\infty} e^{i\kappa x} \int_{-\infty}^{+\infty} \frac{e^{-i\kappa x}}{(x^2 + r^2)^{n/2}} dx. \quad (2)$$

The integrals in Eq. (2), which are invariant with respect to the sign of κ , can be expressed through known functions. Indeed for $k = |\kappa| = 0$ one has, using a well-known formula involving the Γ -function,⁴

$$\int_{-\infty}^{+\infty} \frac{dx}{(x^2 + r^2)^{n/2}} = \frac{\pi^{1/2} \Gamma[(n-1)/2]}{\Gamma(n/2)} \frac{1}{r^{n-1}} \quad (n > 1). \quad (3)$$

For $k > 0$ one has instead

$$\int_{-\infty}^{+\infty} \frac{e^{\pm i\kappa x}}{(x^2 + r^2)^{n/2}} dx = \frac{2\pi^{1/2}}{\Gamma(n/2)} \left(\frac{k}{2r}\right)^{(n-1)/2} K_{(n-1)/2}(kr) \quad (k > 0), \quad (4)$$

a particular form of integral representation of the modified Bessel functions of the second kind.⁵ The final expression of $S_n(x, r)$ is thus

$$S_n(x, r) = \frac{\pi^{1/2} \Gamma[(n-1)/2]}{a \Gamma(n/2)} \frac{1}{r^{n-1}} + \frac{2\pi^{1/2}}{a \Gamma(n/2)} \left(\frac{1}{2r}\right)^{(n-1)/2} \times \sum_{\kappa=-\infty}^{+\infty} k^{(n-1)/2} K_{(n-1)/2}(kr) e^{i\kappa x} \quad (n > 1). \quad (5)$$

For $n \leq 1$ the sum $S_n(x, r)$ diverges. However the terms of Eq. (5) for $\kappa \neq 0$ are valid also for these values of n . In effect for $n = 1$ these terms give simply the Madelung formula for the electrostatic potential of a neutralized, linear Bravais lattice of unit point charges, whose Fourier expansion does not contain the term $\kappa = 0$ owing to Laplace's equation and to the boundary conditions that the potential must satisfy.

3. PLANAR BRAVAIS LATTICE

We consider a planar Bravais lattice of periods \mathbf{a}_1 and \mathbf{a}_2 lying in the plane $z = 0$ with lattice points in the positions $\mathbf{r}_1 = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2$ (l_1, l_2 integers) and a point (\mathbf{r}, z) , a distance z from the plane of the lattice ($z \neq 0$). To evaluate the sum

$$S_n(\mathbf{r}, z) = \sum_{\mathbf{r}_1} \frac{1}{[(\mathbf{r} - \mathbf{r}_1)^2 + z^2]^{n/2}}, \quad (6)$$

with $n > 0$ we expand it into a Fourier series of complex exponentials $e^{i\mathbf{k} \cdot \mathbf{r}}$ of periods \mathbf{a}_1 and \mathbf{a}_2 . The vectors $\mathbf{k} = k_1 \mathbf{a}_1^* + k_2 \mathbf{a}_2^*$, with $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi \delta_{ij}$ and k_1, k_2 integers, are the reciprocal vectors of the planar lattice. The

expansion reads

$$S_n(\mathbf{r}, z) = \frac{1}{|\mathbf{a}_1 \times \mathbf{a}_2|} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \int_{\text{plane}} \frac{e^{-i\mathbf{k} \cdot \mathbf{r}}}{(\mathbf{r}^2 + z^2)^{n/2}} d\mathbf{r}, \quad (7)$$

and the integrals in it can be expressed through known functions. For $\mathbf{k} = 0$ one has immediately

$$\iint_{-\infty}^{+\infty} \frac{dx dy}{(x^2 + y^2 + z^2)^{n/2}} = \frac{\pi}{(n/2) - 1} \frac{1}{|z|^{n-2}} \quad (n > 2). \quad (8)$$

On the other hand for $\mathbf{k} \neq 0$, assuming in particular that the component k_x of \mathbf{k} in a Cartesian frame x, y in the plane of the lattice is different from zero, Eq. (4) gives

$$\begin{aligned} & \int_{-\infty}^{+\infty} e^{-ik_y y} dy \int_{-\infty}^{+\infty} \frac{e^{-ik_x x}}{(x^2 + y^2 + z^2)^{n/2}} dx \\ &= \frac{2\pi^{1/2}}{\Gamma(n/2)} \left(\frac{|k_x|}{2}\right)^{(n-1)/2} \int_{-\infty}^{+\infty} e^{-ik_y y} \\ & \quad \times \frac{K_{(n-1)/2}(|k_x| [y^2 + z^2]^{1/2})}{(y^2 + z^2)^{(n-1)/4}} dy \quad (k_x \neq 0). \quad (9) \end{aligned}$$

However⁶

$$\begin{aligned} & \int_{-\infty}^{+\infty} e^{-ik_y y} \frac{K_{(n-1)/2}(|k_x| [y^2 + z^2]^{1/2})}{(y^2 + z^2)^{(n-1)/4}} dy \\ &= \frac{(2\pi)^{1/2}}{|k_x|^{(n-1)/2}} \left(\frac{k}{|z|}\right)^{(n/2)-1} K_{(n/2)-1}(k|z|) \quad (k_x \neq 0), \quad (10) \end{aligned}$$

where $k = |\mathbf{k}|$. Thus

$$\begin{aligned} \int_{\text{plane}} \frac{e^{-i\mathbf{k} \cdot \mathbf{r}}}{(\mathbf{r}^2 + z^2)^{n/2}} d\mathbf{r} &= \frac{2\pi}{\Gamma(n/2)} \left(\frac{k}{2|z|}\right)^{(n/2)-1} \\ & \quad \times K_{(n/2)-1}(k|z|) \quad (\mathbf{k} \neq 0). \quad (11) \end{aligned}$$

The final expression of $S_n(\mathbf{r}, z)$ is

$$\begin{aligned} S_n(\mathbf{r}, z) &= \frac{\pi}{|\mathbf{a}_1 \times \mathbf{a}_2| [(n/2) - 1]} \frac{1}{|z|^{n-2}} \\ & \quad + \frac{2\pi}{|\mathbf{a}_1 \times \mathbf{a}_2| \Gamma(n/2)} \left(\frac{1}{2|z|}\right)^{(n/2)-1} \\ & \quad \times \sum_{\mathbf{k}}' k^{(n/2)-1} K_{(n/2)-1}(k|z|) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (n > 2). \quad (12) \end{aligned}$$

For $n \leq 2$ the sum $S_n(\mathbf{r}, z)$ diverges. However, the terms of Eq. (12) for $\mathbf{k} \neq 0$ are valid also for these values of n and in effect for $n = 1$ they give simply the Madelung formula for the electrostatic potential of a neutralized,

⁴ See, e.g., W. Magnus and F. Oberhettinger, *Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 4.

⁵ G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1944), Sec. 6.16.

⁶ G. N. Watson, footnote 5, Sec. 13.47.

planar Bravais lattice of unit point charges whose Fourier expansion does not contain the term $\mathbf{k}=0$. Indeed $K_{-1/2}(\mathbf{k}|z|) = K_{1/2}(\mathbf{k}|z|) = (\pi/2k|z|)^{1/2} e^{-k|z|}$.

4. APPLICATIONS

(a) Let us consider a square lattice of atoms with parameter a lying in the plane $z=0$ and extending from $y=0$ to $-\infty$, and an atom located in the point $(\xi a, \eta a, 0)$ ($\eta > 0$) with reference to a Cartesian frame x, y, z . For interactions of the type λR^{-n} (R , interatomic distance), the interaction energy between the atom and each of the linear Bravais lattices in the x direction which compose the semi-infinite planar crystal is given immediately by Eq. (5). Thus the total interaction energy between the atom and the semi-infinite crystal is simply

$$\begin{aligned} \Phi_n(\xi a, \eta a, 0) &= \lambda \sum_{m=0}^{\infty} S_n[\xi a, (m+\eta)a] = \frac{\lambda}{a^n} \frac{\pi^{1/2} \Gamma[(n-1)/2]}{\Gamma(n/2)} \\ &\times \sum_{m=0}^{\infty} \frac{1}{(m+\eta)^{n-1}} + \frac{\lambda}{a^n} \frac{4\pi^{n/2}}{\Gamma(n/2)} \sum_{m=0}^{\infty} \frac{1}{(m+\eta)^{(n-1)/2}} \\ &\times \sum_{k=1}^{\infty} k_1^{(n-1)/2} K_{(n-1)/2}[2\pi k_1(m+\eta)] \\ &\times \cos(2\pi k_1 \xi) \quad (n > 2). \end{aligned} \quad (13)$$

Equation (13) includes the various formulas given in Sec. III of the paper by Hove and Krumhansl.²

It is easy to see that the formulas given by Schreiber and Benson³ for the lattice sums of interest for the calculation of the specific energy of the cube edge in the alkali halides with the NaCl structure are also an immediate consequence of Eq. (5). Thus, in particular, their expression for the lattice sum entering the electrostatic contribution coincides with that obtained originally by Born and Stern⁷ using the Madelung formula for the electrostatic potential of a neutral linear crystal.

(b) Let us consider an ionic crystal of composition MX as formed by neutral planes of ions of periods \mathbf{a}_1 and \mathbf{a}_2 stacked with period \mathbf{a}_3 . The calculation of the specific face energy for the neutral plane $\mathbf{a}_1, \mathbf{a}_2$ requires the evaluation of the interaction energy between a semi-infinite crystal bound by the plane and a column of unit cells of sides $\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{a}_3 sticking out of it along the \mathbf{a}_3 direction.⁷ For interactions of the type $\lambda_{ij} R^{-n}$ (R , interionic distance) for which the coefficient λ_{ij} depends on the nature of the interacting ions, it is relevant to distinguish the interactions between ions of the same sign and of opposite sign. These can be easily expressed through Eq. (12). We take the $\mathbf{a}_1, \mathbf{a}_2$

plane as x, y plane of a Cartesian reference frame x, y, z . The total interaction energy between ions of the same sign is then given by:

$$\begin{aligned} &\sum_{l_3=1}^{\infty} l_3 S_n(l_3 a_{3x}, l_3 a_{3y}, l_3 a_{3z}) \\ &= \frac{\pi}{[(n/2)-1] |\mathbf{a}_1 \times \mathbf{a}_2| |\mathbf{a}_{3z}|^{n-2}} \sum_{l_3=1}^{\infty} \frac{1}{l_3^{n-3}} \\ &+ \frac{2\pi}{\Gamma(n/2) |\mathbf{a}_1 \times \mathbf{a}_2| (2|\mathbf{a}_{3z}|)^{(n/2)-1}} \sum_{l_3=1}^{\infty} \frac{1}{l_3^{(n/2)-2}} \\ &\times \sum'_{\mathbf{k}} k^{(n/2)-1} K_{(n/2)-1}(k l_3 |\mathbf{a}_{3z}|) e^{i l_3 (k_x a_{3x} + k_y a_{3y})} \\ &\quad (n > 4), \end{aligned} \quad (14)$$

apart from the obvious factor $\lambda_{++} + \lambda_{--}$. The factor l_3 in the left-hand side of Eq. (14) accounts for the fact that the interaction between a planar Bravais lattice of positive (or negative) ions and a positive (or negative) ion at a distance $l_3 \mathbf{a}_3$ from it occurs l_3 times in the total interaction energy. The total interaction energy between ions of different sign is given, apart from the obvious factor $2\lambda_{+-}$, by an entirely analogous expression in which $l_3 a_{3x}$ and $l_3 a_{3y}$ are replaced by $l_3 a_{3x} + x_-$ and $l_3 a_{3y} + y_-$, x_- and y_- being the coordinates of the negative ion relative to the positive ion in the planar unit cell. For the electrostatic interactions ($n=1$), the total interaction energy between the semi-infinite crystal and the column of unit cells is simply given by twice the difference between the terms with $\mathbf{k} \neq 0$ in the expressions of the interaction energies between ions of equal and opposite sign, times the square of the ionic charge.

Equation (14) and the analogous equation for ions of different sign include all the special formulas for the NaCl and CsCl structures given by van Zeggeren and Benson,³ and they actually correspond to a more general formulation of the problem than that given in their paper. In particular the expressions that one obtains for the electrostatic contributions to the specific energies of the (100) and (110) planes in the NaCl structure coincide, as one must expect, with those derived originally by Born and Stern,⁷ using the Madelung formula for the electrostatic potential of a neutral planar crystal, apart from obvious printing errors in their formula for the (110) plane. Van Zeggeren and Benson³ simply rewrite these expressions by performing the summation over l_3 to give a closed form.

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⁷ M. Born u. O. Stern, S. B. Preuss. Akad. Wiss. Berlin **48**, 901 (1919).