state of a pair of ions, coupled either antiferromagnetically or ferromagnetically. In each case, there are four possibilities for coupling two ions of spin $\frac{3}{2}$, leading to a total spin $S=0$, 1, 2, and 3. In a first approximation they take a quadratic isotropic exchange energy $H=J(\mathbf{S}_1\mathbf{S}_2)$, with $J=33$ cm^{-1} for the antiferromagnetic coupling, and in that case the positions of the 4 levels are $0-J=33-3J=99$ and $6J=198$ cm^{-1}. The observed far-infrared lines are interpreted as the $S=0\rightarrow1$ and $S=0\rightarrow2$ transitions. The $S=0\rightarrow3$ would lie at 198 cm^{-1}, where the lattice absorption is considerable. Figures 12 and 13 give the behavior of the population for every level versus temperature, in each type of coupling, calculated from the partition functions. There is a drastic change of the population n_0 of the lower level only in the first type, and it explains quite well the observed variations of intensities of both lines with temperature.[4] The contribution of ferromagnetic pairs would give two lines at 35 and 42 cm^{-1}, which could be mixed with the antiferromagnetic one at 33 cm^{-1}. That would explain the slightly higher wave number observed (37 cm^{-1}), but this contribution is certainly small, and a check at 21 cm^{-1} is planned.

Recently, Kisliuk[6] has considered a more refined antiferromagnetic coupling with a quite different J ($J=11$ cm^{-1}) and a small biquadratic term: $H=J(\mathbf{S}_1\mathbf{S}_2)-j(\mathbf{S}_1\mathbf{S}_2)^2$, with $j/J=2\%$. The new positions of the 4 levels are now 0, 10.3, 32.7, and 67.9 cm^{-1}. They are quite different, but there are so many lines in the red that this scheme is also possible. However, the far-infrared spectra are strikingly in favor of the first one, and are impossible to explain with the second: There is a line at 100 cm^{-1}; there is none near 68 cm^{-1}.

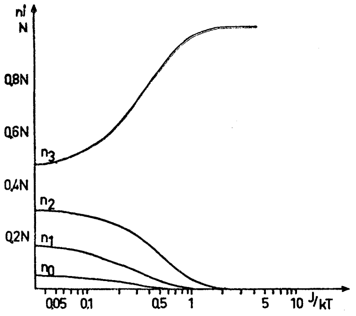

FIG. 13. Variations of the populations $n_0\,n_1\,n_2\,n_3$ of the 4 sublevels of a ferromagnetic pair, versus $1/T$.

ACKNOWLEDGMENTS

We are very grateful to Professor Schawlow and Professor Kastler for stimulating discussions, and to Professor Stoicheff, Dr. Hougen, and Dr. Singh for the single crystals of praseodymium and samarium chloride.

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[6] P. Kisliuk, Appl. Phys. Letters 3, 215 (1963).

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Anisotropic Lattice Absorption by Needle-Shaped Crystals

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Infrared absorption by small needle-shaped ionic crystals of cubic structure has recently been found to be anisotropic. In this note, a single strand is used as a limiting model for such a crystal, and the calculated absorption in both directions is shown to be in qualitative agreement with observations on lithium fluoride. Features of absorptions to be expected from other crystals are discussed.

RECENTLY, Hass[1] prepared small needle-shaped lithium fluoride crystals by evaporating a thin film of lithium fluoride onto an optical grating (rather than onto a plane surface as is usual). The grating spacing, and hence the width of the resulting crystals, was small compared to the infrared absorption wavelength. The resulting absorption was found to be strongly anisotropic.[2]

We may summarize the experimental results by referring to the somewhat idealized rod-shaped crystals of Fig. 1. Let the light wave propagate in the z direction (into the paper); then the "usual" sharp absorption is found if the light is polarized in the x direction (parallel to the long edge of the crystal), but a broad absorption shifted to a higher frequency is found if the light is polarized in the y direction (perpendicular to the long edge of the crystal).

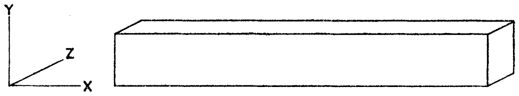

FIG. 1. Model of a needle-shaped crystal.

The simplest, and purely qualitative, theoretical

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[1] M. Hass, Proceedings of the Far Infrared Physics Symposium, Riverside, California, January 1964 (unpublished).

[2] Anisotropic Absorption by Needles of NiSb has also recently been reported by B. Paul and H. Weiss, Solid State Electron (to be published). D. W. Berreman, Phys. Rev. 130, 2193 (1963) has observed similar anisotropy and polarization dependence in the absorption of obliquely incident beams by thin films.

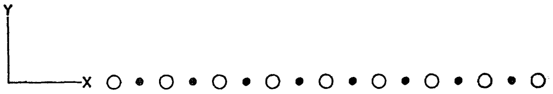

FIG. 2. Limiting model of a needle-shaped crystal (single strand).

explanation for this, is as follows. Each normal vibration has associated with it a dipole moment in the x direction P_x and a dipole moment in the y direction P_y; these depend on the displacements of the atoms during that vibration, in the x direction in one case and in the y direction in the other. As these two displacements are not necessarily the same on account of the lack of symmetry in the crystal of Fig. 1, P_x and P_y will not necessarily be the same either. The absorption of light of the proper frequency and polarized in the x direction depends on the square of P_x, and that of light polarized in the y direction on the square of P_y. In a crystal which is large and cubic in growth shape as well as cubic in internal symmetry, there will be, for any mode with given displacements in the x direction, one mode with the same displacement in the y direction and one with that same displacement in the z direction. Therefore isotropic absorption will result from the total P_x^2, P_y^2, P_z^2 resulting from these three. On the other hand, in a crystal so small in one direction that boundary effects are important, these three symmetrical modes will not necessarily exist, and absorption shown by light of different polarization will therefore not be necessarily the same.

To make quantitative calculations of the quantities P_x and P_y would be by no means easy. Let us therefore idealize the situation even further, and replace the long, thin crystal of Fig. 1 by the even longer and thinner one of Fig. 2. The width and thickness of the crystal have been shrunk to one atom here, and the length in the x direction increased to infinity; in short, a one-dimensional crystal. The light wave is still envisaged in the z direction, into the paper. In this situation, the vibrations in the x direction ("longitudinal")[3] and those in the y direction ("transverse")[3] are separate and distinct; only the former have a dipole moment in the x direction, and only the latter have a dipole moment in the y direction. Let us assume nearest-neighbor interaction and in addition Coulomb interaction between all atoms. Then the frequencies of the longitudinal vibrations are known,[4] and those of the transverse vibrations can be easily calculated in the same way. One has longitudinal

$$\lambda_{\text{long}}(p) = \lambda_0(p) - \sigma S(p)\,, \tag{1}$$

transverse

$$\lambda_{\text{trans}}(p) = (\beta/\alpha)\lambda_0(p) + (\sigma/2)S(p)\,, \tag{2}$$

with

$$\lambda_0(p) = 1 - \cos\pi p\,, \tag{3}$$

$$S(p) = \sum_{k=1}^{\infty} (-)^k k^{-3}(\cos k\pi p - 1)\,. \tag{4}$$

Here λ is proportional to the square of the frequency ω,

$$\lambda = m\omega^2/2\alpha\,,$$

α is the force constant for longitudinal nearest-neighbor interaction and β the force constant for transverse nearest-neighbor interaction, m is the mass of each atom (all atoms are assumed to have the same mass here, for simplicity), p is the wave vector defined so as to run from 0 to 1, and $\sigma = 2e^2/\alpha r_0^3$ is roughly a measure of the ratio of strengths of Coulomb to nearest-neighbor forces; r_0 is the equilibrium distance between atoms, and e is their charge. $\lambda_0(p)$ are thus the squared frequencies in the absence of Coulomb forces—the frequencies of a "one-dimensional metal." Both the functions $\lambda_0(p)$ and $S(p)$ are shown in Fig. 1 of Ref. 4; their general shape is similar although they differ in their analytical behavior near $p=1$.

The two expressions (1), (2) appear surprisingly similar, but there are important qualitative differences. In (1), the function S is preceded by a minus sign, but in (2) by a plus sign (the λ_0 term is positive in both cases). Thus λ_{trans} is positive for all values of the parameters, but λ_{long} becomes negative if σ is large enough. Since a negative λ implies an imaginary vibrational frequency, this means physically that the longitudinally vibrating lattice is unstable for large enough Coulomb forces, or for small enough nearest-neighbor forces, whereas transverse vibrations are always stable, even if nearest-neighbor forces are entirely absent. Direct physical intuition will verify this after a glance at Fig. 2: Imagine one of the atoms displaced longitudinally—to the right, say. This increases the Coulomb attraction from its neighbor to the right and decreases its Coulomb attraction from its neighbor to the left, and thus causes further displacement to the right; in the absence of repulsion between nearest neighbors, the originally displaced atom will therefore move further in the same direction until the lattice collapses. If, on the other hand, an atom is displaced transversely, up, say, the situation is different: The Coulomb forces exerted by the two nearest neighbors are both downward, in a direction opposite to the original displacement, and the lattice is thus stable for transverse vibration under Coulomb forces even in the absence of any nearest-neighbor repulsion. Since, in any physical situation, one would expect the noncentral nearest-neighbor restoring force to be quite small ($\beta/\alpha \ll 1$) if not absent, this seems fortunate.

It may be worth noting parenthetically that the qualitative appearance of $\lambda_{\text{long}}(p)$ and $\lambda_{\text{trans}}(p)$ is quite different, λ_{trans}, being just the sum of two "S-shaped" functions shown in Ref. 4, is itself S-shaped with its

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[3] Let us make clear that throughout this paper "longitudinal" and "transverse" mean lattice vibrations ∥ or ⊥ to the long axis of the crystal, not to a light beam.

[4] H. B. Rosenstock, Phys. Rev. 111, 755 (1958).

minimum at $p=0$ and its maximum at $p=1$, but, as is shown in Ref. 4, $\lambda_{\rm long}$ has its maximum not at $p=1$ but at a smaller value of p, and a minimum at $p=1$. This is illustrated in Fig. 3 for a special set of values of the force constant ratios.

What really interests us here, though, is the behavior of the two functions at $p=1$—the value of p near which optical absorption takes place.[5] At $p=1$, Eqs. (1) and (2) become

$$\lambda_{\rm long}(1)=2-2\xi\sigma\,, \tag{5}$$

$$\lambda_{\rm trans}(1)=2\beta/\alpha+\xi\sigma\,, \tag{6}$$

where

$$\xi=1^{-3}+3^{-3}+5^{-3}+\cdots=1.052\cdots. \tag{7}$$

It follows that $\lambda_{\rm trans}(1)$ will be greater than $\lambda_{\rm long}(1)$ if and only if

$$\sigma>2(1-\beta/\alpha)/3\xi \tag{8}$$

or (since β is probably small and close to unity)

$$\sigma\gtrsim 0.6\,. \tag{9}$$

Values of $\sigma\sim\frac{3}{4}$ seem physically reasonable[4,6] and our crystal can therefore be expected to exhibit absorption of transversely polarized light at frequencies higher than the absorption of longitudinally polarized light. We shall discuss this somewhat more quantitatively later.

Let us review these arguments leading to this result from the physical rather than the mathematical viewpoint. Large restoring forces produce high frequencies, small restoring forces produce low frequencies. In the longitudinal case the restoring force is small because the Coulomb force counteracts the dominant nearest-neighbor force, and the resulting frequencies are low; in the transverse case, both the nearest-neighbor force and the Coulomb force act in the same direction, the restoring force produced is therefore large, as are the resulting frequencies. (Note that this argument will not work in the absence of Coulomb forces, or indeed in the presence of only weak Coulomb force. In that case the longitudinal frequency will be the larger.)

It is, of course, clear that we have taken two rather large steps toward simplification and away from reality as we went from the real crystal first to Fig. 1 and then to Fig. 2; but we may hope that our argument, particularly in its qualitative form of the last preceding paragraph, may have validity in the realistic case as well. It remains to explain the broadness of the observed peak in the transverse case. Here again we hope that a qualitative argument will suffice. We may attribute the difference to the fact that boundaries have larger perturbing effects on "small" crystals than on "large" crystals. (This has been shown elsewhere,[7] but is probably physically obvious to most.) We now return to Fig. 1 but remember that the real crystal will not have the perfect shape depicted there, but will necessarily have somewhat irregular boundaries. It seems plausible that for the same reason the vibrations in the direction in which such a crystal is small will be more strongly perturbed by the boundary irregularities than the vibrations in the direction in which the crystal is large. Since the observed absorption represents the additive effects of many such crystals, each with absorbing properties only slightly different from the ideal in the longitudinal direction but appreciably different in the transverse direction, a broader absorption for transversely polarized light should be expected.

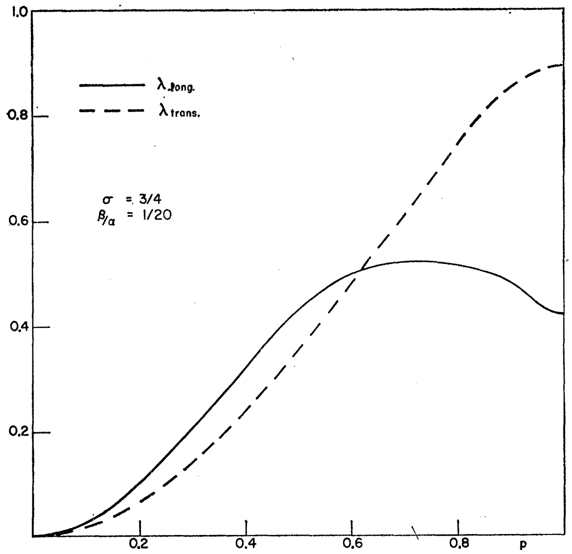

FIG. 3. The squared frequencies $\lambda_{\rm trans}$ and $\lambda_{\rm long}$ as a function of wave vector p.

One restriction in the work above that can be removed is the assumption that both the positively and the negatively charged ion have the same mass m. We now show that the conclusions drawn remain valid, even quantitatively, under the more realistic assumption of two ions with *different* mass.

If one ion (of the lattice shown in Fig. 2) has mass m and the other has mass M, then Eq. (1) for the squared longitudinal frequency is replaced by two equations,

$$\begin{aligned}Am\omega_{\rm long}^2/2=\alpha(A-B\cos\pi p)&\\ -(2e^2/r_0^3)\Big[A\sum_{\text{even }k}k^{-3}\cos(k\pi p-1)&\\ +A\sum_{\text{odd }k}k^{-3}-B\sum_{\text{odd }k}k^{-3}\cos k\pi p\Big]&\end{aligned} \tag{10}$$

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[5] Usually it is said that absorption appears when the wave vector is zero; here it appears at 1, because we have chosen a unit cell with one (rather than the usual 2) particle per unit cell.

[6] See C. Kittel, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (John Wiley & Sons, Inc., New York, 1953), Chap. 2; and Ref. 4 above.

[7] H. B. Rosenstock, J. Chem. Phys. 23, 2415 (1955).

and

$$BM\omega_{\mathrm{long}}^2/2=\alpha(B-A\cos\pi p)$$
$$-(2e^2/r_0^3)\Big[B\sum_{\mathrm{even}\,k}k^{-3}(\cos k\pi p-1)$$
$$+B\sum_{\mathrm{odd}\,k}k^{-3}-A\sum_{\mathrm{odd}\,k}k^{-3}\cos k\pi p\Big].\quad(11)$$

Equation (2) for the squared transverse frequency is also replaced by two equations, but we need not write them down, as they can be obtained from (10) and (11) by simply replacing α and β and e^2 by $-e^2/2$. We then obtain $\lambda(p)$ by solving the determinantal equation of the coefficients of A and B. For $p=0$, which is the value of p at which the "limiting" or optical frequency appears in the diatomic scheme, that determinantal equation is

$$0=\begin{vmatrix}1-\sigma\xi-\lambda_{\mathrm{long}} & -(1-\sigma\xi)\\ -(1-\sigma\xi) & 1-\sigma\xi-M\lambda_{\mathrm{long}}/m\end{vmatrix}.\quad(12)$$

The solutions of this are found to be $\lambda_{\mathrm{long}}=0$ (which is not of interest) and

$$\bar{\lambda}_{\mathrm{long}}=1-\sigma\xi,\quad(13)$$

where

$$\bar{\lambda}_{\mathrm{long}}\equiv mM\omega_{\mathrm{long}}^2/2\alpha(M+m),\quad(14)$$

and for the transverse frequency, by analogy, $\lambda_{\mathrm{trans}}=0$ and

$$\lambda_{\mathrm{trans}}=(\beta/\alpha)+(\sigma/2)\xi,\quad(15)$$

where

$$\bar{\lambda}_{\mathrm{trans}}\equiv mM\omega_{\mathrm{trans}}^2/2\alpha(M+m).\quad(16)$$

Thus (13) and (15) differ from the corresponding expressions (5), (6) of the monatomic case by the same constant factor μ/m where, $\mu=mM/(m+M)$ and relation (8), which is based on their ratios, is entirely unchanged. (To be sure, this simple proportionality would not be retained at points other than $p=0$.)

Let us now consider two points related to experimental observations that have been, or might be, made. As we pointed out, the frequencies we calculated for longitudinal and transverse vibrations are valid only in the limit of the single strand of Fig. 2. In the real case of rod- or needle-shaped small crystals to which the available observations apply,[1,2] the crystals are much more than one strand wide and thick; but it seems reasonable that the relationship between transverse and longitudinal frequencies computed for a single strand will hold in the same sense for a rod of any thickness. Put more precisely, the argument is this: As the one-strand crystal becomes thicker, and finally approaches a cube, the two frequencies ω_{long} and ω_{trans} will come closer together and finally become equal.[8] It seems highly plausible that they would do this without "crossing over"; i.e., that if $\omega_{\mathrm{trans}}>\omega_{\mathrm{long}}$ for the single-strand crystal, the same will hold true for any thickness (until, with infinite thickness, they approach equality).

We can calculate this limiting frequency for infinite thickness—i.e., for a crystal in the shape of an infinite cube—in terms of the same parameters as appear in our one-dimensional equations. The nearest-neighbor interaction term $2\alpha(1-\cos\pi p)$ is replaced by $(2\alpha+4\beta)(1-\cos\pi p)$, because in addition to the two neighbors in the direction of the vibration, there are now four neighbors in directions perpendicular to vibration exerting noncentral forces. The sum of the Coulomb terms becomes, for $p=0$

$$(2e^2/r_0^3)\sum_{l,}\sum_{m,}\sum_{n\ \mathrm{even,\,even,\,odd}}(-)^{l+m+n}(2l^2-m^2-n^2)$$
$$\times(u_{lmn}-u_{000})/(l^2+m^2+n^2)^{5/2}.$$

The secular equation corresponding to (12) then becomes

$$0=\begin{vmatrix}\psi-m\omega^2 & -\psi\\ -\psi & \psi-M\omega^2\end{vmatrix},$$

where

$$\psi=2\alpha+4\beta-(2e^2/r_0^3)V$$

and

$$V=\sum_{l,}\sum_{m,}\sum_{n\ \mathrm{even,\,even,\,odd}}(-)^{l+m+n}$$
$$\times(2l^2-m^2-n^2)/(l^2+m^2+n^2)^{5/2}\quad(17)$$

is a number which has been computed,[9]

$$V=3.754\cdots.\quad(18)$$

The solutions of the secular equation are $\omega=0$ (of no interest) and

$$\mu\omega_{3D}^2/2\alpha=1+2(\beta/\alpha)-(\sigma V/2)$$

or $\quad(19)$

$$\bar{\lambda}_{3D}=1+2\tau-(\sigma/2)V,$$

with $\tau=\beta/\alpha$ and $\bar{\lambda}_{3D}$ by analogy with (17).

Let us summarize: Longitudinal and transverse squared frequencies of the one-strand crystal are, respectively, (13) and (15), viz.,

$$\bar{\lambda}_{\mathrm{long}\,1D}=1-1.052\sigma\quad(20)$$

and

$$\bar{\lambda}_{\mathrm{trans}\,2D}=\tau+0.526\sigma.\quad(21)$$

The three-dimensional limiting frequency which they both approach as the crystal approaches infinite thickness is

$$\bar{\lambda}_{3D}=1+2\tau-1.877\sigma.\quad(22)$$

The magnitude relationships between these three absorbing frequencies are shown graphically in Fig. 4 as a function of the parameters σ and τ.

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[8] When the rod has grown to a cube, the frequency first called transverse will be indistinguishable from the longitudinal one, except for a 90° rotation in the direction of all the displacements (or except for a 90° rotation of the crystal as a whole). For detailed discussion of this point, see H. B. Rosenstock, Phys. Rev. **121**, 416 (1961); A. A. Maradudin and G. Weiss, *ibid.* **123**, 1968 (1961); T. H. K. Barron, *ibid.* **123**, 1995 (1961).

[9] H. B. Rosenstock, Phys. Chem. Solids 4, 201 (1958).

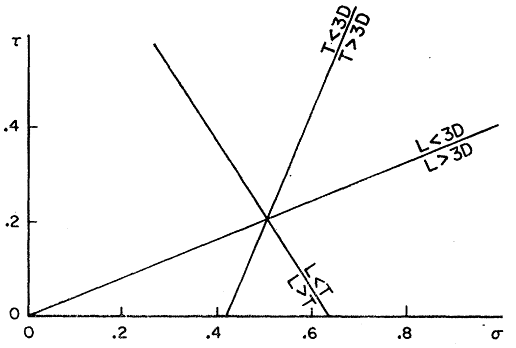

FIG. 4. Magnitude relationships between frequencies as a function of the force constant parameters σ and τ. L, T, and $3D$ have been written for λ_{long}, λ_{trans}, and λ_{3D}.

One physical property that has been ignored so far is electronic polarization. It is known, of course, that this will change the frequencies of vibration, but we can show that under certain reasonable conditions, it will leave the relative magnitudes of the frequencies of optical interest unchanged; i.e., if $\lambda_{\text{trans}} > \lambda_{\text{long}}$ holds in the absence of polarization, then it will hold also when polarization is taken into account. The simplest method of taking polarization into consideration is the shell model.[10] If we let the halide ions consist of a mass point of charge minus e and the metal ions of a shell of charge e' surrounding a mass point of charge $(e-e')$, and let γ be the Hooke's law force constant between metal shell and metal core, the resulting frequency can be expanded in a series in γ^{-1}; one gets

$$\mu\bar{\lambda}_{\text{long}} = \alpha - e^2\xi + \gamma^{-1}(\alpha - ee'\xi)^2 + O(\gamma^{-2}), \quad (23)$$

$$\mu\bar{\lambda}_{\text{trans}} = \beta + \tfrac{1}{2}e^2\xi + \gamma^{-1}(\beta + \tfrac{1}{2}ee'\xi)^2 + O(\gamma^{-2}). \quad (24)$$

The linear terms in each case are seen to be the corresponding frequencies in the absence of polarization ($\gamma = \infty$), and the quadratic ones are seen to be proportional to the same quantities if we set $e' = e$ (i.e., the reasonable situation in which the polarizable charge of the metal ion is that of the one valence electron); one can then deduce from (23), (24) that if $\bar{\lambda}_{\text{trans}} > R_{\text{long}}$ for $\gamma = \infty$, then the same will be true for finite γ if terms up to γ^{-1} are retained.

Next, we should try to get a quantitative estimate of the value of the critical parameter σ for real substances in order to predict, from (9) whether $\lambda_{\text{trans}} > \lambda_{\text{long}}$. Some fairly old semiempirical calculations enable us to do this. Empirically, the short-range interaction in ionic crystals is usually put either into the form br^{-n} or the form $ae^{-r/\rho}$. Our force constant α can be related to these; one finds $\alpha = bn(n+1)r^{-n-2}$ in the former case, and $\alpha = ae^{-r_0/\rho}\rho^{-2}$ in the latter. From these expressions, one can derive, respectively,

$$\sigma = (12/M)(-E_{\text{Coul}}/E_{\text{rep}})/n(n+1)$$

or

$$\sigma = (12/M)(-E_{\text{Coul}}/E_{\text{rep}})\rho^2/r_0^2,$$

where E_{Coul} and E_{rep} are, respectively, the contributions of the Coulomb and the repulsive forces to the cohesive energy, and $M = 1.754$ is the Madelung constant. The E's are given by Seitz[11] as are the n's[12]; ρ and r_0 are given by Mott and Gurney.[13] Results of the calculations appear in Table I; it is pleasing to note that where figures are available for both theories, the σ's agree to at least one significant figure. One concludes that the observation $\lambda_{\text{trans}} > \lambda_{\text{long}}$ for LiF agrees with our criterion (9), as the table gives $\sigma > 0.6$ for that case. Figure 4 also suggests that in this case λ_{long} should differ only slightly from λ_{3D}, also in agreement with experiment. For most other alkali halides, the table suggests that λ_{trans} should be greater than λ_{long} also, though by a lesser amount; for some, near equality should be expected.

TABLE I. Semiempirical values of $\sigma = 2e^2/\alpha r_0^3$ for various alkali halides.

	σ, from r^{-n} potential	σ, from $e^{-r/\rho}$ potential
LiF	1.05	
LiCl	1.01	
LiBr	0.98	
NaCl	0.82	0.81
NaBr	0.79	0.84
NaI		1.00
KCl	0.65	0.59
KBr		0.62
KI		0.69
RbCl		0.77
RbBr		0.64
RbI		0.64

Finally, a different approach to considering this problem should be put into perspective.[1,14] Rather than beginning with the limiting case of a single strand crystal, one can begin with a large cubic crystal, and then consider the effects of the boundary, which provide polarization forces larger in directions in which the crystal is small. Qualitatively similar results can then be obtained.

ACKNOWLEDGMENTS

I should like to thank Dr. Marvin Hass for many discussions which have initiated this work, Dr. H. Weiss for sending me certain data, and Dr. Clifford C. Klick and Dr. James H. Schulman for critical discussions.

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[10] W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959).

[11] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Table 29.

[12] Reference 11, Table 24.

[13] N. F. Mott and R. W. Gurney, *Electronic Processes and Ionic Crystals* (Oxford University Press, New York, 1940), Tables 2 and 8.

[14] See also R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941), Sec. 4.