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¹⁸From the numerical integration of Eq. (2) Kaplan (Ref. 16) finds

$$\tau_D^{-1} = \frac{4(\frac{4}{3}\pi NC^{1/2})(D/C^{1/3})^{3/4}}{[(3/4\pi NC^{1/2})^{1/3}(D/C^{1/3})^{1/4} - 1]^{1/3}},$$

which yields a slightly different functional dependence of τ_D^{-1} even though the values for D are not too different from Eq. (5).

¹⁹The Padé approximant in the brackets is quite closely approximated by $(1 + \pi^{1/2}z)^{3/4}$.

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Surface Mean-Square Amplitudes of Vibration for NaCl[†]

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The mean-square amplitudes and mean-square velocities of vibration have been calculated for the (100) surface of NaCl with the Kellermann rigid-ion model. The calculated value of $\langle u_z^2 \rangle_{\text{surface}} / \langle u_z^2 \rangle_{\text{bulk}}$ (the z direction being perpendicular to the surface) is only about 1.6 at high temperatures, as compared with calculated and experimental values ranging upward from about 2.0 for monatomic metals and noble-gas solids.

There have been a number of calculations of the mean-square amplitudes of vibration near the surfaces of monatomic crystals,¹ but to our knowledge no such calculation has been performed for any ionic crystal. The mean-square amplitudes are of interest because they determine the Debye-Waller factors of the atoms or ions, and thus the temperature dependence of scattering intensities—e. g., the intensities of the “Bragg peaks” in low-energy electron diffraction (LEED). In the present paper we report calculations of the mean-square amplitudes and mean-square velocities for the (100) surface of NaCl.

We will distinguish the Na⁺ and Cl⁻ ions by a label κ and use a label l_3 to distinguish the planes of ions parallel to the surface. The mean-square amplitudes of vibration $\langle u_\alpha^2(l_3\kappa) \rangle$ and the mean-square velocities $\langle v_\alpha^2(l_3\kappa) \rangle$, with $\alpha = x, y, \text{ or } z$, are then given in the quasiharmonic approximation by the standard expressions

$$\langle u_\alpha^2(l_3\kappa) \rangle = \frac{\hbar}{2\bar{N}M_\kappa} \sum'_{\bar{q}, p} |\xi_\alpha(l_3\kappa; \bar{q}p)|^2 \times \frac{\coth[\hbar\omega_p(\bar{q})/2k_B T]}{\omega_p(\bar{q})}, \quad (1)$$

$$\langle v_\alpha^2(l_3\kappa) \rangle = \frac{\hbar}{2\bar{N}M_\kappa} \sum'_{\bar{q}, p} |\xi_\alpha(l_3\kappa; \bar{q}p)|^2 \omega_p(\bar{q}) \times \coth\left(\frac{\hbar\omega_p(\bar{q})}{2k_B T}\right). \quad (2)$$

M_κ is the mass of an ion labeled by κ , \bar{N} is the number of values of the two-dimensional wave vector \bar{q} in the summation, p is a label which distinguishes the different vibrational modes for a given value of \bar{q} , T is the temperature, and k_B is the Boltzmann constant. The vibrational frequencies $\omega_p(\bar{q})$ and eigenvectors $\xi_\alpha(l_3\kappa; \bar{q}p)$ are determined by the standard eigenvalue equation

$$\sum_{l_3'\kappa'} D_{\alpha\beta}(l_3\kappa; l_3'\kappa'; \bar{q}) \xi_\beta(l_3'\kappa'; \bar{q}p) = \omega_p^2(\bar{q}) \xi_\alpha(l_3\kappa; \bar{q}p). \quad (3)$$

It is straightforward to calculate $\langle u_\alpha^2(l_3\kappa) \rangle$ and $\langle v_\alpha^2(l_3\kappa) \rangle$ by numerically solving Eqs. (1)–(3) once the dynamical matrix $D_{\alpha\beta}(l_3\kappa; l_3'\kappa'; \bar{q})$ has been determined. We have calculated the dynamical matrix in exactly the same way as Tong and Maradudin,² except for two differences described in the next paragraph. Although we are really interested in a semi-infinite crystal, we perform the calculations for a 15-layer slab in order to simplify the

problem. The results for a slab of this thickness will closely approximate those for a semi-infinite crystal, since the bulk "bands" are rather densely populated and the surface modes are significantly affected by the finite thickness only for very small values of \bar{q} . We also assume the Kellermann rigid-ion (KRI) model³ with the values of the potential parameters used by Tong and Maradudin² (which are nominally room-temperature values). In this model, the ions are assumed to interact through a pair potential which consists of a point-charge Coulomb potential and a nearest-neighbor Born-Mayer potential; the polarizabilities of the ions are neglected. The surface-mode spectra for the KRI model and for a shell model, which is presumably much more accurate, have been found to differ significantly.⁴ However, the mean-square amplitudes and mean-square velocities represent averages over all the vibrational modes, according to Eqs. (1) and (2), and should therefore not be very sensitive to details in the spectrum of vibrational modes. Furthermore, as can be seen from Eq. (1), the dominant contribution to the mean-square amplitudes comes from the acoustical modes (because of their lower frequencies) which are much better described by the KRI model than are the optical modes. We therefore feel that the KRI model should yield reasonably good estimates for these quantities (or for the surface thermodynamic functions⁵). (But see note added in proof.)

The first difference between our evaluation of the dynamical matrix and that of Ref. 2 involves the method for calculating the Coulomb lattice sums. This matter is discussed in detail elsewhere.⁶ In brief, we find that the method of de Wette and Schacher,⁷ which involves use of the incomplete gamma function, provides much better convergence than the method of Ref. 2, which involves the modified Bessel function. Consequently, we have used the "plane-wise summation method" of Ref. 7, as did Lucas.⁸ The second difference between Ref. 2 and the present work involves the static relaxation of the ions near the surface. Tong and Maradudin permitted both interplanar and intraplanar displacements, as is appropriate if one is interested in doing the calculations consistently for a 15-layer slab. We have, however, permitted only interplanar displacements and held the spacing within the planes fixed at the bulk value, since this is the more appropriate procedure if one is interested in approximating the results for a semi-infinite crystal as accurately as possible. The relaxation of Tong and Maradudin is positive and has a nonzero value near the center of the slab, whereas our relaxation is principally negative and tends to zero with increasing distance from the surface. However, the relaxation is small—less than 1% in either case—and not of great importance. Perhaps

a more serious approximation is the assumption (here and in Ref. 2) that the Na⁺ and Cl⁻ ions in a given plane have equal static displacements, whereas they will in reality undergo different displacements. In the context of the KRI model, however, it is not clear that taking account of this effect would improve the accuracy of the calculation,⁹ and to do so would make the calculation considerably more difficult.

In using Eqs. (1) and (2), we are assuming that the quasiharmonic approximation is valid for the range of temperatures under consideration. Cowley¹⁰ has performed a calculation of the quasiharmonic and lowest-order anharmonic contributions to bulk thermodynamic quantities for NaCl. He finds that, "The quasiharmonic calculation gives good agreement with experiment up to one-quarter of the melting temperature" of 1074 °K. Previous calculations of the surface mean-square amplitudes for noble-gas solids at one-half the melting temperature¹¹ indicated that there are significant, but not enormous, anharmonic contributions at this temperature. It therefore appears that the quasiharmonic approximation should be adequate up to room temperature for the surface mean-square amplitudes in NaCl. In the present work, we also neglect thermal expansion, which should have the effect of increasing the vibrational frequencies by about 3 or 4% between room temperature and 0 °K,⁵ and thus decreasing the mean-square amplitudes at low temperature by roughly 5%.¹²

Our results for the mean-square amplitudes are shown in Figs. 1–3.¹³ It is interesting that the ratio $\langle u_z^2 \rangle_{\text{surface}} / \langle u_z^2 \rangle_{\text{bulk}}$ reaches a value of only about 1.6 even at room temperature and above. (Here, as always, we take the z direction to be normal to the surface.) This value is considerably smaller than the values at high temperatures which have been calculated for model monatomic crystals¹ and measured for monatomic metals¹ and for Xe films,¹⁴ which have ranged upward from about 2.0. The relatively small value of $\langle u_z^2 \rangle_{\text{surface}}$ for NaCl appears to be caused by the relatively high frequencies of the acoustical surface modes¹⁵: According to Eq. (1), large values of ω for the surface modes should produce small values for the surface mean-square amplitudes.

In Fig. 4, the results for the mean-square velocities are shown. Because the equipartition theorem implies that

$$\frac{1}{2} M_{\kappa} \langle v_{\alpha}^2(l_3 \kappa) \rangle = \frac{1}{2} k_B T \quad \text{for } T \rightarrow \infty, \quad (4)$$

and for all κ , α , and l_3 , it follows that there is only a very small difference between the surface and bulk mean-square velocities at room temperature. In the present case, we have

$$\langle v_{\alpha}^2(l_3 \text{Na}^+) \rangle / \langle v_{\alpha}^2(l_3 \text{Cl}^-) \rangle$$

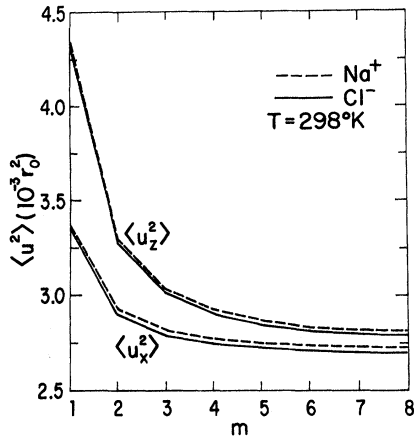


FIG. 1. Mean-square amplitudes of vibration $\langle u_\alpha^2 \rangle$ for Na^+ and Cl^- ions at 298 °K as functions of distance from the surface. Here m labels a plane of ions, with $m=1$ at the surface, and r_0 is the distance between nearest neighbors in the bulk (a Na^+ ion and a Cl^- ion being nearest neighbors) and has the value of 2.814 Å.

$$= (M_{\text{Na}^+}/M_{\text{Cl}^-})^{-1} = 1.54 \quad \text{as } T \rightarrow \infty,$$

as borne out by Fig. 4.

It can be seen in Figs. 1–3 that the mean-square amplitudes for the Na^+ and Cl^- ions are very nearly equal, particularly at high temperatures. In fact, one can show that $\langle u_\alpha^2(l_3 \text{Na}^+) \rangle$ and $\langle u_\alpha^2(l_3 \text{Cl}^-) \rangle$ are exactly equal in the quasiharmonic approximation and the high-temperature limit for our model (i. e., a KRI model in which the Na^+ and Cl^- ions in the same plane have the same static relaxation): For this model, the force-constant matrix for the

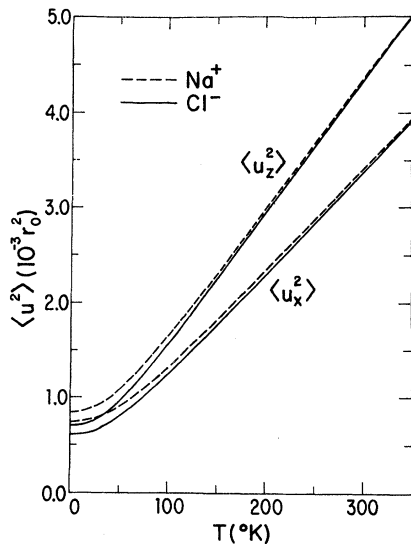


FIG. 2. Dependence of mean-square amplitudes at the surface (i. e., $m=1$) on the temperature T .

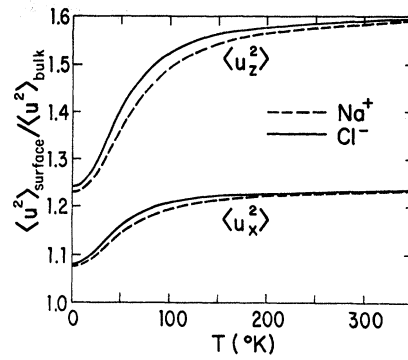


FIG. 3. Ratio of surface to bulk mean-square amplitudes as a function of temperature.

entire crystal¹⁶ is invariant under an interchange of the Na^+ and Cl^- ions. It is known¹⁷ that, for an arbitrary harmonic system in the high-temperature limit, the mean-square amplitudes for a given particle are independent of the particle's mass and depend only on the force constants.¹⁸ Since, within the present model, the force constants are the same for Na^+ and Cl^- ions in the same plane, the mean-square amplitudes must be equal in the high-temperature limit for Na^+ and Cl^- ions in the same plane.¹⁹

Furthermore, an argument²⁰ of Housley and Hess indicates that

$$\begin{aligned} \langle u_\alpha^2(l_3 \text{Na}^+) \rangle / \langle u_\alpha^2(l_3 \text{Cl}^-) \rangle &\approx (M_{\text{Na}^+}/M_{\text{Cl}^-})^{-1/2} \\ &= 1.24 \quad \text{at } T = 0 \text{ °K.} \end{aligned}$$

The actual calculated values for this ratio at the surface are 1.22 and 1.21 for vibrations in the x and z directions, respectively.

It can be seen that both of the above results, i. e.,

$$\langle u_\alpha^2(l_3 \kappa') \rangle = \langle u_\alpha^2(l_3 \kappa) \rangle \quad \text{for } T \rightarrow \infty, \quad (5)$$

$$\frac{\langle u_\alpha^2(l_3 \kappa') \rangle}{\langle u_\alpha^2(l_3 \kappa) \rangle} \approx \left(\frac{M_{\kappa'}}{M_\kappa} \right)^{-1/2} \quad \text{for } T = 0 \text{ °K}, \quad (6)$$

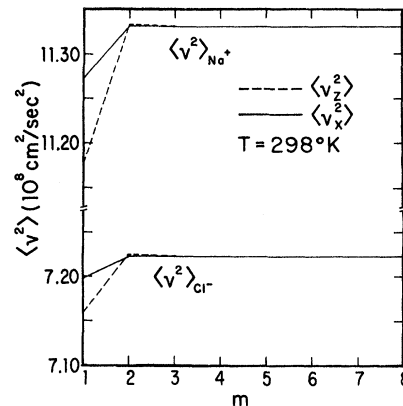


FIG. 4. Mean-square velocities $\langle v_\alpha^2 \rangle$ for Na^+ and Cl^- ions as functions of distance from the surface.

TABLE I. Summary of experimental and theoretical values for bulk Debye-Waller parameters $B_{\kappa} = 8\pi^2 \times \langle u_{\alpha}^2(\kappa) \rangle$ of NaCl at room temperature (R. T.) and at low temperature (L. T.; $\leq 15^\circ\text{K}$), where available.

$B_{\kappa}/\text{\AA}^2$ (R. T.)	$B_{\kappa}/\text{\AA}^2$ (R. T.)	B_{κ}/B_{κ} (R. T.)	B_{κ}/B_{κ} (L. T.)	Method
1.81	1.49	1.21	1.22	Experimental
1.89	1.61	1.17	...	x ray, powder ^a
1.84	1.44	1.28	...	x ray, single crystal ^b
1.64	1.33	1.23	...	x ray, powder ^c
1.63	1.42	1.15	...	x ray, single crystal ^d
				Neutron diffraction, single crystal ^e
				Theoretical
1.62	1.58	1.03	1.22	Deformation-dipole (DD), R. T. parameters ^f
1.59	1.47	1.08	1.26	DD next-nearest-neighbors, 0°K parameters ^f
1.56	1.35	1.15	1.32	Shell model, quasiharmonic ^g
1.71	1.70	1.00	1.22	KRI model (present work)

^aM. Linkoaho, Ann. Acad. Sci. Fennicae **A284** (1968).

^bS. Göttlicher, Acta Cryst. **B24**, 122 (1968).

^cReference 22.

^dS. C. Abrahams and J. L. Bernstein, Acta Cryst. **18**, 926 (1965).

^eH. A. Levy, P. A. Agron, and W. R. Busing, American Crystallography Association Meeting, Cambridge, Mass., Paper E-7, 1963 (unpublished).

^fW. J. L. Buyers and T. Smith, J. Phys. Chem. Solids **29**, 1051 (1968).

^gReference 21.

are valid for any diatomic crystal provided that the force-constant matrix is invariant under an interchange of the two types of particles. This will be the case for models similar to that which we have used, i. e., models in which the ions are arranged in a NaCl structure and interact through point-charge Coulomb forces and nearest-neighbor repulsive forces, and in which the positive and negative ions in a given plane undergo the same static relaxation.

In order to obtain some idea of the reliability of the present results, it is of interest to compare the present values for the *bulk* mean-square amplitudes¹³ with experimental results and with theoretical results obtained from other, presumably more accurate, models. In Table I we give such a comparison in terms of the Debye-Waller parameters $B_{\kappa} = 8\pi^2 \langle u_{\alpha}^2(\kappa) \rangle$ at room temperature and at low temperature. We refer to the paper by Reid and Smith²¹ for a fuller discussion of the comparison

between experimental and theoretical determinations of the Debye-Waller factors for bulk ionic crystals. Here we mention only that the disparity between the two earlier experiments and the later experiments is probably due primarily to a lack of correction for thermal-diffuse scattering (TDS); Merisalo and Paakkari²² suggest that a correction for TDS of about 0.15\AA^2 should be added to the earlier results, which would bring them into much closer agreement with the later TDS-corrected work.

It would be interesting if LEED measurements on alkali-halide crystals could be carried out with the goal of studying the temperature dependence of the Bragg peaks. In the case of NaCl, direct comparison with the results of Figs. 1-3 would be possible. In the case of other alkali halides, it would be possible to test (a) the qualitative conclusion that the ratio of surface to bulk mean-square amplitudes for vibrations normal to the surface should be relatively small, and (b) the degree to which the mean-square amplitudes for positive and negative ions in the same plane should be approximately equal at sufficiently high temperatures. The second point may provide an initial simplification for the approximate analysis of LEED data, in that it may be possible approximately to characterize each plane of ions by a single Debye-Waller factor.

Note added in proof. Although the KRI model is not quantitatively adequate for bulk mean-square amplitudes (MSA)—as shown by Table I—and hence cannot be expected to give accurate *absolute* predictions for surface MSA, such considerations leave open the question of how accurately the KRI model can predict surface MSA *relative* to those of the bulk. Preliminary results have now been obtained by the present authors for a shell model with surface relaxation neglected. For the present purpose, the differences between the KRI results and the preliminary shell-model results can best be summarized in terms of Fig. 3. There exist some noticeable but rather minor differences for the MSA components parallel to the surface. The principal differences appear in the curves for the MSA components normal to the surface: At 0°K the values of the shell-model curves for the Na^+ and Cl^- ions are 1.23 and 1.32, respectively; at 300°K , they are, respectively, 1.54 and 1.73.

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¹For references, see R. E. Allen and F. W. de Wette, Phys. Rev. **188**, 1320 (1969).

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⁷F. W. de Wette and G. E. Schacher, Phys. Rev. **137**,

A78 (1965).

⁸A. A. Lucas, *J. Chem. Phys.* **48**, 3156 (1968).

⁹Benson and co-workers have found that oversimplified models which allow different displacements for different ions tend to overestimate ionic displacements significantly. See G. C. Benson and K. S. Yun, in *The Solid-Gas Interface*, edited by E. A. Flood (Marcel Dekker, New York, 1967), Vol. I, Chap. 8, and references therein.

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¹¹R. E. Allen, F. W. de Wette, and A. Rahman, *Phys. Rev.* **179**, 887 (1969).

¹²If the rate of thermal expansion is larger at the surface than in the bulk, there will be a larger decrease in the surface mean-square amplitudes.

¹³As a check on these results, an independent calculation was performed for the bulk, and good agreement was obtained with the results for the center of the slab. (See Table I.)

¹⁴A. Ignatjevs, T. N. Rhodin, S. Y. Tong, B. I. Lundqvist, and J. B. Pendry, *Solid State Commun.* **9**,

1851 (1971).

¹⁵Compare Fig. 2 of Ref. 4 with Fig. 10 of R. E. Allen, G. P. Alldredge, and F. W. de Wette, *Phys. Rev. B* **4**, 1661 (1971).

¹⁶The force-constant matrix is the matrix K of Ref. 17.

¹⁷R. M. Housley and F. Hess, *Phys. Rev.* **146**, 517 (1966).

¹⁸See Eqs. (10) and (13) of Ref. 17 [with a typographical error to be corrected in Eq. (13), so that $m_r^{-1} \rightarrow m_k$].

¹⁹The high-temperature equality of the Debye-Waller factors for different ions in bulk models having only nearest-neighbor interactions has been conjectured by E. R. Cowley and R. A. Cowley, *Proc. Roy. Soc. (London)* **A292**, 209 (1966).

²⁰See the discussion on p. 521 (right-hand column) of Ref. 17.

²¹J. S. Reid and T. Smith, *J. Phys. Chem. Solids* **31**, 2689 (1970), and references therein.

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PHYSICAL REVIEW B

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Surface Modes of Vibration in the Rigid-Ion Model of NaCl[†]

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A discussion is given of the complete spectrum of vibrational surface modes for the Kellermann rigid-ion model of NaCl. The attenuation with distance from the surface is shown for representative surface and pseudosurface modes. We discuss one interesting feature which has not previously been pointed out: Symmetry requirements can lead to surface modes which are associated with only one species of ion (Na^+ or Cl^-) at the surface.

I. INTRODUCTION

There have been several discussions¹⁻⁵ of surface modes in the Kellermann rigid-ion (KRI) model of NaCl, but as yet no complete and accurate discussion has been given. Although for many purposes the results for the KRI model will be superseded by calculations based on the shell model⁴ and other improved models which are currently in progress, we feel that it is appropriate to give a complete discussion of the surface-mode spectrum for the KRI model before passing on to the shell model. The results for the KRI model yield considerable insight into the qualitative features that can be expected generally of surface and pseudo-surface modes in ionic crystals.

II. RESULTS

The method for calculating the vibrational modes is discussed in detail elsewhere.² Our procedure

differs from that of Ref. 2 in only two respects, as discussed previously.^{3,6} The surface ions relax inward, rather than outward, by a small amount, and a more rapidly convergent method is used to evaluate the Coulomb lattice sums.

In Fig. 1, the calculated frequencies of vibration $\omega_p(\bar{q})$ are shown for a 15-layer slab. Since there are two particles per unit cell and three directions of vibration, there are $2 \times 3 \times 15 = 90$ frequencies for each two-dimensional wave vector \bar{q} ; i. e., $p = 1, 2, \dots, 90$, where p distinguishes the different normal modes which are associated with a given \bar{q} . The values of \bar{q} for which the frequencies were determined lie along the symmetry lines of the two-dimensional Brillouin zone, $\bar{\Gamma}\bar{X}$, $\bar{X}\bar{M}$, and $\bar{M}\bar{\Gamma}$, as shown in Fig. 2(c). In Figs. 2(a) and (b) we show the frequencies for values of \bar{q} along two lines ($\bar{\Gamma}\bar{Y}$) which make angles of 30° and 15° , respectively, with the line $\bar{\Gamma}\bar{M}$. (The endpoints of