PHYSICAL REVIEW VOLUME 178, NUMBER 3 15 FEBRUARY 1969

Phonon Dispersion Relations in NaCl

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(Received 10 August 1968)

Phonon dispersion relations in NaCl at 80°K have been determined in the crystallographic [100], [101], and [111] symmetry directions using inelastic neutron scattering. Some measurements have also been made at 300°K, and at (1.0, 0.5, 0) in reciprocal space. The results are compared with theoretical calculations: those of Karo and Hardy for their "deformed-dipole" model, those of Schröder and Nüsslein for a "breathing-shell" model, and those of Caldwell and Klein for a shell model. Satisfactory agreement is obtained in many places, but significant discrepancies still remain, particularly close to the zone boundaries. Comparison is also made with earlier x-ray work on NaCl. The work was performed on a new crystal spectrometer at the R2 reactor at Studsvik, which is equipped with a two-crystal monochromator.

I. INTRODUCTION

OVER a number of years a considerable amount of theoretical work has been devoted to the lattice dynamics of NaCl and other alkali halides. There are many reasons for this interest, e.g., the relatively simple crystal and electronic structures, which facilitate theoretical calculations, and the fact that a great deal of experimental work has been carried out on thermodynamical, optical, electrical, and other properties of NaCl, providing a good starting point for calculations on lattice dynamics. Since Kellermann[1] published his pioneer work on NaCl, a number of people have worked out increasingly more sophisticated models to describe the ionic interactions in this solid.[2–5] An early attempt by Lundqvist *et al.*[2] to calculate phonon dispersion relations in NaCl from first principles could not properly account for the observed specific heat and the temperature dependence of the Debye temperature, but their results indicated that a true model should lie somewhere between their version and Kellermann's rigid-ion model.

The first experimental determination of phonon dispersion relations in an alkali halide using inelastic scattering of neutrons was that by Woods *et al.*[6] in NaI, later followed by measurements on KBr and extended work on NaI.[7] Using the now well-established "shell-model" (SM) approach, originally due to Dick and Overhauser[8] and later applied to phonon calculations by Cochran,[9] Woods *et al.* obtained good agreement between theory and experiment. In recent years a number of other alkali halides have been investigated by neutron inelastic scattering, e.g., KI,[10] NaF,[11] and LiF.[12] So far, however, NaCl had not been investigated by this method except for a brief report by Schmunk.[13]

There are several reasons for this neglect, the most important probably being the high absorption cross section of the Cl for thermal neutrons. Another difficulty is the rather high incoherent scattering cross section of NaCl which in some situations may give rise to a troublesome background intensity. Another factor to take into account is the comparatively high frequencies of the optical phonons, because the cross section for one phonon scattering falls off markedly with frequency. These difficulties for neutron experiments are not present in the case of x rays and measurements on NaCl using the method of thermal diffuse scattering of x rays have been performed for a few branches by Buyers and Smith.[14] Their results are compared with the present data in Sec. IV.

Karo and Hardy[4] and Nüsslein and Schröder[15] kindly put their numerical data at our disposal, thereby making possible a direct comparison of the experimental results with their "deformed-dipole" (DD) and "breathing-shell" (BSM) variants of the SM, respectively. This is done in Sec. IV. We have also utilized the eigenvectors given by Karo and Hardy[16] for their next-nearest-neighbor (DDNNN) model to calculate the structure factor for one-phonon scattering of neutrons, which is important in choosing the most favorable conditions for making measurements. This factor can be written in a reduced form as

$$g_j^2=(\xi_j\cdot\mathbf{Q})^2\frac{b_1^2}{m_1\nu_j}\left|\xi_{1j}\pm\frac{b_2}{b_1}\left(\frac{m_1}{m_2}\right)^{1/2}\xi_{2j}\right|^2 .$$

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[*] From the Chalmers University of Technology, Gothenburg, Sweden.

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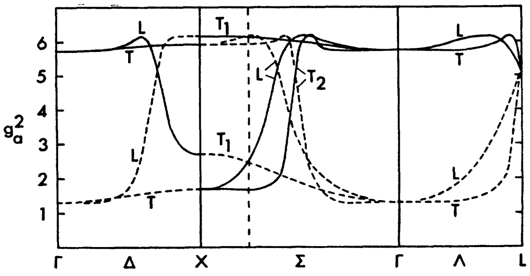

FIG. 1. Reduced inelastic structure factors for the acoustic branches. For the optical branches we have the relation $g_0^2=6.15-g_a^2$. The structure factors are calculated from the Karo-Hardy (Ref. 16) DDNNN data. Solid lines, even reciprocal zones; dashed lines, odd reciprocal zones.

The plus sign refers to reciprocal lattice points with even indices, the minus sign to those with odd indices, b_s are the atomic scattering lengths, m_s are the masses, and ξ_{sj} are the eigenvectors of the sth ion in the unit cell, j signifying the mode of vibration. Figure 1 shows the structure factors in units of $(\hat{\xi}_j\cdot\mathbf{Q})^2b_1^2/m_1\nu_j$ for the acoustic modes. For the optical modes we have for the same polarizations $g_0^2=1+b_2^2m_1/b_1^2m_2-g_a^2$.

In Sec. II a brief discussion of experimental details is given. The results are given in Sec. III, while Sec. IV contains some comments on the data obtained.

TABLE I. Phonon frequencies in NaCl at 80°K. Except for the higher frequencies, the relative error is usually not greater than about 0.5%.

Direction	Wave vector $(2\pi/a)$	Phonon frequencies (10^{13} rad sec^{-1})					
		TA	LA	TO	LO		
[100]	0.2	0.541	1.14	3.26	4.80		
	0.4	0.999	2.15	3.31	4.32		
	0.6	1.35	2.94	3.34	3.76		
	0.7	···	3.19	···	···		
	0.8	1.54	2.97	3.38	3.46		
	1.0	1.64	2.67	3.39	3.62		
		TA	LA	TO	LO		
[111]	$0.1\sqrt{3}$	0.584	0.913	3.23	···		
	$0.2\sqrt{3}$	1.12	1.72	3.12	4.73		
	$0.3\sqrt{3}$	1.60	2.48	3.00	4.58		
	$0.4\sqrt{3}$	2.03	3.09	2.82	···		
	$0.5\sqrt{3}$	2.27	3.36	2.68	4.33		
		T_1A	T_2A	LA	T_1O	T_2O	LO
[110]	$0.1\sqrt{2}$	···	···	···	3.25	···	···
	$0.2\sqrt{2}$	0.799	1.04	1.45	3.27	···	4.82
	$0.4\sqrt{2}$	1.53	1.93	2.58	3.36	···	4.23
	$0.5\sqrt{2}$	···	2.26	2.96	···	···	···
	$0.6\sqrt{2}$	2.24	2.25	3.04	3.48	2.77	3.51
	$0.7\sqrt{2}$	···	···	2.71	···	···	···
	$0.8\sqrt{2}$	2.56	1.82	2.26	3.58	3.23	3.46
	$0.9\sqrt{2}$	···	···	1.81	···	···	···
	$1.0\sqrt{2}$	2.68	1.64	1.64	3.62	3.39	3.39

II. EXPERIMENTAL

The measurements were carried out on one of two new spectrometers operating at one of the horizontal beam tubes of the R2 research reactor at Studsvik. This is a 30-MW reactor with a maximum thermal flux of about 3.10^{14} n cm^{-2} sec^{-1}. A complete description of the instrument will soon be published,[17] so we limit ourselves here to a few characteristic features. The spectrometers, which are mirror twins, are equipped with two parallel monochromating crystals. This arrangement has advantages, which in our case outweigh the inevitable loss of intensity caused by the second reflection. First, the direction and position of the beam incident on the sample is always the same. This makes it possible to mount the sample on a stationary axis of rotation, and thereby facilitates the mounting of the cryostat and analyzer. Furthermore, there is a very low background of fast neutrons and γ radiation and low contamination of higher-order neutrons in the beam after two reflections in the monochromator unit. The reflectivity (peak reflectivity) of the monochromators being used at present (Cu 220) is about 40–60%, depending on neutron energy. The operation of the spectrometer is fully automatic, the movements of the arms and tables being controlled by a punched paper tape delivered by a computer. In addition to the tape, the computer also supplies a table of all angle settings during a run, and a table of the different contributions to the energy and wave-vector resolution of the recorded phonon, taking into account the collimation of the neutron beam before and after the sample and the mosaic widths of the monochromator and the analyzer. A focusing technique[18] was applied throughout in order to obtain the best possible resolution, although focusing conditions were not always rigidly adhered to, because they sometimes conflict with the interests of intensity. The computed program sheet contains a table of energy resolutions for values of the analyzer setting and of the slope of the dispersion curve which lie in the neighborhood of the respective values that are expected to be appropriate; this table serves both as a check on the suitability of the chosen spectrometer setting and as a guide for possible modifications.

The sample was a slab 60×40×7 mm,[3] with a mosaic spread of about 0.1°. It was mounted in a cryostat above a container for liquid nitrogen, adjusted in the neutron beam at room temperature, and then cooled down. One filling of the cryostat (about 10 liters) kept the sample at liquid-nitrogen temperature for 3–4 days.

Situations where the combined beam path for incident and scattered directions was long had to be avoided, because of the large absorption in NaCl. This, together with the requirements on the structure factor, considerably complicated the programming in comparison with measurements on simple nonabsorbing substances with a single atom in the unit cell.

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[17] R. Stedman, L. Almqvist, G. Raunio, and G. Nilsson, Rev. Sci. Instr. (to be published).

[18] R. Stedman, Rev. Sci. Instr. 39, 878 (1968).

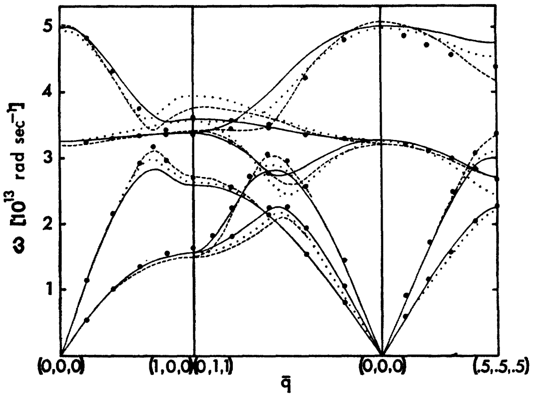

FIG. 2. Phonon frequencies obtained experimentally compared with three different theoretical models; solid lines, shell model, Caldwell and Klein (Ref. 23); dotted lines, DD model, Karo and Hardy (Ref. 4); dashed lines, BSM, Nüsslein and Schröder (Ref. 5).

III. RESULTS

The experimental results are presented in Table I and in Fig. 2. It should be noted that the designatiosn of branches refer to polarization. Thus the T_1 branch in the $(1\bar{1}0)$ plane has its polarization in that plane, while the T_2 branch is perpendicular to it and frequencies in the same branch vary smoothly along the symmetry directions even at "crossover" singularities.

On most branches, measurements have been made for five different q values including the zone boundary points. This number represents a compromise between the desire for a large number of experimental points and the necessity to limit the duration of the experiment. In some branches, e.g., [220] LA, extra points have been included as a check on the curves estimated from the five "standard" points. These results confirm that the chosen number of points provides reasonable accuracy on most branches. Most phonons were measured in the $(1\bar{1}0)$ plane but the T_2 branches in the [220] direction were obtained in the (100) plane. After the crystal had been turned into this plane, some checks were made on phonons previously measured in the $(1\bar{1}0)$ plane. The results always agreed within the experimental errors, which thus supported the estimated accuracy of the measurements. The experimental errors are $<0.5\%$ for most phonons except for some of the LO ones, where the errors are between 0.5 and 1%.

A short preliminary report on part of this work is presented in Ref. 19. Some measurements on phonons at the zone boundary were performed with the sample at room temperature. These give some information on temperature shifts of phonon frequencies, and may also be compared with the results of Schmunk[20] for this temperature (see Table II).

A computer program based on simple statistical considerations for weak resonances[21] was used to analyze the observed peaks, giving phonon energies and phonon widths. The program also gives the errors of these quantities due to counting statistics. A comparison between the results of the program and the results of the visual inspection shows that the energy values agree very well but that the visual method tends to overestimate the statistical errors.

Systematic errors associated with calibration and measurement of angles are small, since various and repeated checks indicate that all significant angles are correct to within about 0.02° (maximum). Where the error in phonon frequency from this source is comparable to the random error, it has been taken into account in an appropriate manner, so the errors quoted may be regarded as total probable errors.

Since the main purpose of this experiment was to obtain the dispersion relations, comparatively little effort was devoted to measurement of widths, which requires rather higher statistical counting accuracy. A comment on this is made in Sec. IV. To examine the possible effect of factors that may contribute to the background, a background measurement was made between $\omega = 5.3\times10^{13}$ rad sec^{-1} and $\omega = 3.0\times10^{13}$ rad sec^{-1} at the zone boundary in the [111] direction (point L) using very long counting times. Although some variation in the background level was observed which was believed mainly to be due to incoherent inelastic scattering, this check proved that this variation is not a serious problem for measurements on one-phonon resonances. Repeated checks were carried out during the course of the measurements to assure that the adjustments of the spectrometer were still correct. No deviations from the initial conditions were observed.

IV. COMMENTS

The three different models with which the experiment is compared (see Fig. 2) are similar in that they all take into account the deformation of the ions due to their relative motions. In the DD model of Karo and Hardy,[4] the deformation of the negative ions is taken into account as an oscillating dipole moment at the ion site, the dipole moment being attributed to distortion of the outer electron shell of the negative ion in the region of maximum overlap with its neighbors. In the SM the dipoles are introduced by letting the outer shell of the ion be displaced relative to the ion core, connected to it by a spring constant. The BSM of Nüsslein and Schröder[5] in addition allows the shell of the negative ion to "breathe," i.e., to contract and expand under the influence of the movements of its neighbors. The difference between the SM and the BSM may be expected to be small in alkali halides with small negative ions. In calculations on LiF,[12] the two models produce very similar results. For NaCl the difference appears to be somewhat more pronounced,

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[19] L. Almqvist, G. Raunio, and R. Stedman, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 295.

[20] R. E. Schmunk (private communication).

[21] R. Stedman and J. Weymouth (unpublished).

TABLE II. Comparison of frequencies of some zone-boundary phonons at different temperatures (in units of 10^{13} rad sec^{-1})

q	Branch	Ref. 20 ω (300°K)	This expt. ω (300°K)	This expt. ω (80°K)	This expt. ω (300°K) $-\omega$ (80°K)	Ref. 24 ($Z=0.9$) ω (300°K) $-\omega$(0°K)	Ref. 16 ω (300°K) $-\omega$ (0°K)
(1, 0, 0)	LO	3.43	3.51±0.015	3.62±0.015	−0.11±0.021	−0.24	+0.01
	TO	3.28	3.26±0.01	3.39±0.01	−0.13±0.014	−0.27	−0.09
	LA	2.69	2.69±0.015	2.67±0.015	+0.02±0.021	+0.04	−0.02
	TA	1.67	1.61±0.01	1.64±0.01	−0.03±0.014	−0.01	+0.003
(0.5, 0.5, 0.5)	TO		2.59±0.015	2.68±0.015	−0.09±0.021	−0.15	−0.17
	LA	3.28	3.25±0.015	3.36±0.01	−0.11±0.018	−0.08	−0.12
	TA	2.22	2.19±0.01	2.27±0.01	−0.08±0.014	−0.23	−0.10
(0, 0, 0)	LO	4.93		4.98±0.05			
	TO	3.08		3.25±0.02			

but still is not very large. In this connection it should be pointed out that the good agreement between experiment and theory is obtained without any fitting of the theoretical data to the experimental dispersion curves.

The DD model by Karo and Hardy[4] was used as a guide when this work was started. The agreement was found to be rather good for the acoustic branches except in the vicinity of the zone boundaries, where the DD values were too low, especially for the [111] LA and the [100] LA branches, the deviations being 5–8%. This observation is supported by optical work by Pierce.[22] For the optical branches the agreement is somewhat worse, particularly near the zone boundary in the [110] direction. The TO modes are found to be flatter than predicted by theory. This has also been observed by Buyers in NaF.[11]

A SM calculation by Caldwell and Klein,[23] used for an experiment on thermal conductivity, agrees very well with our results. They assumed a van der Waals force of the form $V=a/r^6$ between next-nearest neighbors and used this instead of the Szigeti relation used by Karo and Hardy to obtain the high-frequency dielectric constant which is needed as an input parameter in the calculations. This improves the agreement considerably, e.g., at the point X, where the agreement appears to be almost perfect. The main deviations still remaining are then confined in five areas. The [111] LO branch is up to 10% too high and also too flat. The LA branch at point L is about 10% too low, as was also the case for the DD model. The [110] LO branch has a broad shoulder between $q=0.2\sqrt{2}$ and the zone boundary which is not present in the experimental results. The maximum in the LA branches in the [100] and [110] directions are 6–8% too low. Otherwise the agreement is remarkably good, for example, for all of the TO branches. In their calculation, Caldwell and Klein used an effective ionic charge $Z=1$, which is worth noticing (see comments on the BSM below). In Table III a comparison is made between the different model results and the experiments for the point W (1.0, 0.5, 0). One finds that none of the models is able to reproduce all four frequency values very well, although the BSM shows the best over all agreement. If the DD model and the SM calculations by Caldwell and Klein for NaCl are compared to the BSM, the latter gives a somewhat better fit. For the LO branch in the [110] direction and the T_1O branch in the [110] direction, a discrepancy of some 4% still remains, however. In this calculation an ionic charge $Z=1$ was used. In a later calculation by these authors[24] using an ionic charge $Z=0.9$ the agreement is considerably poorer in many places indicating that the proper value of the ionic charge is much closer to 1.0 than to 0.9 in NaCl. This result is also supported by a comparison with the two BSM values in Table III. It is worth mentioning that in measurements on KCl, now nearing completion at this laboratory, the agreement with the $Z=0.9$ calculations is much better than is the case for NaCl.

In their work on LiF, Dolling *et al.*[12] reported a deviation between the slopes of the dispersion curves for small q values obtained from their neutron data and the slopes calculated from ultrasonic measurements of the elastic constants. When the present work on NaCl was compared with the calculations by Karo and Hardy, a similar effect was at first believed to be descernible. However, this apparent discrepancy disappeared when more recent data on the elastic constants of NaCl at 77°K, reported by Fugate and Schuele,[25] were used in the calculation. The present

TABLE III. Comparison of experimental and theoretical frequency values (in units of 10^{13} rad sec^{-1}) at point W (1.0, 0.5, 0). The values for Refs. 5 and 23 have been taken from the graphs in those papers.

Mode	This expt. ω (80°K)	Ref. 4 (DD) ω (0°K)	Ref. 5 (BSM) $Z=1.0$ ω (0°K)	Ref. 24 (BSM) $Z=0.9$ ω (0°K)	Ref. 23 (SM) ω (0°K)
TA	2.267±0.004	2.278	2.28	2.153	2.20
LA	2.65 ±0.01	2.544	2.58	2.63	2.48
TO	3.00 ±0.015	2.993	2.96	3.09	3.25
LO	3.51 ±0.015	3.783	3.64	3.415	3.46

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[22] C. B. Pierce, Phys. Rev. **135**, A83 (1964).

[23] R. F. Caldwell and M. V. Klein, Phys. Rev. **158**, 851 (1967).

[24] V. Nüsslein and U. Schröder (private communication).

[25] R. Q. Fugate and D. E. Schuele, J. Phys. Chem. Solids **27**, 493 (1966).

neutron results and their results agree within the experimental errors, indicating that the anharmonic effects which may cause a difference between the sound velocity at the ultrasonic frequencies (10^9–10^{10} cps) and at the phonon frequencies studied by neutron scattering (10^{12}–10^{13} cps) must be small in NaCl at 80°K. This effect has recently been discussed by Cowley and by Svensson *et al.*[26]

The method of thermal diffuse scattering of x rays has been applied to NaCl in a study by Buyers and Smith[14] on the [100] TA and the [111] LO and LA branches at 300°K. Their results agree quite well with our data considering the difficulties of this method, particularly for the [100] TA branch. In the [111] direction the agreement is somewhat less satisfactory, their LO results being about 5% too high and the LA results 10–15% too low.

In earlier work on alkali halides, many people have reported difficulties in measuring the high-energy LO phonons. This was again observed in this work on NaCl, where these phonons are 2–3 times broader than those in most other branches, indicating strong damping and consequently short lifetimes of these vibrations. Especially the phonons of the [111] LO branch are rather poor. The TA branch in the [111] direction offered unexpected difficulties, the intensities being low and the widths of the peaks larger than expected. The same effect has also been observed in work on KCl now in progress. It is interesting that in work on lithium by Smith *et al.*[27] double peaks were observed in this same branch which they were not able to eliminate.

The explanation seems to be that the measured frequency is of course an average value for a region around the [111] direction, and includes contributions from both transverse branches; if the degeneracy between these branches on the [111] axis is one of rather sharp or abrupt contact between the two dispersion surfaces, the average frequency will not be well defined. The data of Karo and Hardy[16] do in fact show that the T_1 and T_2 branches cross on the [111] axis, and that, as one would expect at a crossover singularity, the polarization varies discontinuously in the neighborhood. An example of the unusual dispersion behavior is that the lower transverse branch has minima when q is approximately (0.1, 0.25, 0.25), (0.1, 0.2, 0.3), and (0.3, 0.2, 0.1), i.e., in a ring round the point (0.2, 0.2, 0.2). It is then not surprising that the neutron experiments, which deal with a sample of phonons on and near the [111] axis with polarization vectors near the plane of scattering, give a blurred picture. Unfortunately, measurements on the T_2 branch in the $(1\bar{1}0)$ plane require rather laborious reorientations of the sample, and we do not have experimental data to illustrate frequency variations near the [111] axis. A fuller account of this kind of behavior near the [111] axis will be given in a forthcoming paper on KCl.

Seven zone-boundary phonon frequencies were also measured at 300°K. A comparison between these and the results at 80°K is given in Table II, as well as the shifts calculated by Nüsslein and Schröder and by Karo and Hardy. One finds a relative energy shift of 3–4% for five frequencies, in reasonable agreement with what has earlier been found in KBr.[7] Exceptions are the [100] TA mode, where the change is about 2%, and the [100] LA mode, where a small upward change was observed. The latter effect was rather unexpected, but repeated measurements have confirmed it. When we received the theoretical data of Nüsslein and Schröder,[15] we found that this behavior was predicted by their model. As can be seen from Table II, the predicted shifts of the model are generally larger than those determined experimentally. This can not be explained by the fact that the model shifts are between 300 and 0°K instead of 80°K but is probably due to some deficiency of the model itself. The shifts for the DD model are in some cases in better agreement with experiment, in some cases in worse.

It should be pointed out that the theoretical calculations referred to above[4,5,23] were made for 0°K, which should introduce a small positive deviation from the experimental frequencies in most cases. It turns out, however, that the deviations for branches where a good fit is obtained are small and alternatively positive and negative. The difference between 80 and 0°K has therefore been disregarded. No broadening of the phonon widths outside the resolution of the instrument was observed in the measurements at 300°K, but it should be pointed out that the resolution was relatively poor for these phonons, which were at the zone boundary and not amenable to focusing.

In calculations on the phonon frequency distribution, Karo and Hardy[4] obtained a singularity on the low-frequency side of the first critical point (TA X). They ascribe this to a curve of contact between two acoustic branches in a ⟨100⟩ plane, stating that for small q vectors the transverse branches in the [110] direction should be above the longitudinal one. However, their explanation on this point can hardly be correct, and does not agree with the experimental observation that, for small q, phonon frequencies are always higher for phonons with longitudinal polarization.

It is interesting to compare the neutron results with available data from infrared absorption measurements and, through the Lyddane-Sachs-Teller (LST) relation,[28] with the high- and low-frequency dielectric constants. The value for ω_{TO} at $q=0$ obtained through extrapolation from our neutron results is 3.25±0.02

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[26] R. A. Cowley, Proc. Phys. Soc. (London) **90**, 1127 (1967); E. C. Svensson and W. J. L. Buyers, Phys. Rev. **165**, 1063 (1968); R. A. Cowley, W. J. L. Buyers, E. C. Svensson, and G. L. Paul, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 281.

[27] H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 149; and (private communication).

TABLE IV. Comparison of optical data and neutron data for a few principal phonon frequencies (in units of 10^{13} rad sec^{-1}).

q	Branch	Opt. data (Ref. 22)	Calc. data (Ref. 4)	This expt.
(1, 0, 0)	TA	1.67	1.56	1.64
	LA	2.58	2.73	2.67
	TO	3.33	3.48	3.39
(1, 1, 1)	LA	3.04	3.04	3.36
	TO	2.28	2.28	2.68

(in units of 10^{13} rad sec^{-1}). This can be compared with the values given by Martin[29] ($\omega_{\mathrm{TO}}=3.30$) and by Robinson and Hallett[30] ($\omega_{\mathrm{TO}}=3.20$), showing a very satisfactory agreement. Through the LST relation

$$\left(\frac{\omega_{\mathrm{LO}}}{\omega_{\mathrm{TO}}}\right)^2=\frac{\epsilon_{st}}{\epsilon_\infty}$$

and using the value $\epsilon_{st}=5.53$ from Ref. 30 (neglecting the small anisotropy of this quantity reported there), combined with the value for ϵ_∞ given by Martin[29] (2.31) one obtains $\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}}=1.547\pm0.015$. Using the value given by Kittel[31] (2.25) for ϵ_∞, $\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}}=1.568\pm0.015$. The value calculated from our extrapolated neutron data ($\omega_{\mathrm{LO}}=4.98\pm0.05$) is 1.532 ± 0.025, which agrees fairly well with the values just mentioned. The errors of the dielectric constants are about 1% and this value has been used above. In this connection it should be pointed out that the temperature dependence of ϵ_∞ is expected to be rather small in the alkali halides.[32]

From infrared measurements, Klein and Macdonald[33] found that phonon energy values calculated by Caldwell and Klein[23] for the LA mode at X and the TA mode at L were too low by about 6%. This observation is supported by the present results, although the difference appears to be somewhat smaller.

In Table IV a comparison is made between a few zone-boundary phonons obtained by Pierce[22] from optical absorption measurements and the Karo-Hardy data used by this author as a guide, and also with our results. The agreement is satisfactory for the [100] direction, but not very good in the [111] direction.

V. CONCLUSIONS

Phonon dispersion relations at 80°K have been obtained for the symmetry directions in NaCl. The results are in most cases in fairly good agreement with various SM types of calculation, particularly for the BSM of Nüsslein and Schröder, but some discrepancies remain. Frequency shifts have been measured for a few phonons between 80 and 300°K and they are in general agreement with the BSM as regards signs and magnitudes. Thus the BSM is superior to the other models considered here, though, since the superiority is not very pronounced, it cannot be regarded as decisive support for the new feature in this model, the expansive-contractive motion of the negative ion's outer shell. The slopes of the dispersion curves for small q values agree with sound velocities obtained from ultrasonic measurements within the experimental errors. The data are also in good agreement with results from infrared and optical measurements.

ACKNOWLEDGMENTS

Two of us (G. R. and L. A.) gratefully acknowledge research grants and other financial support from the Swedish Atomic Research Council. We are grateful to Professor H. P. Myers for his strong support throughout this work and to Professor S. O. Lundqvist for valuable discussions on this and other problems. Dr. Karo and Dr. Hardy and Dr. Nüsslein and Dr. Schröder kindly sent us their numerical data. K.-O. Isaxon gave us skilful technical assistance during the performance of these measurements.

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