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# Lattice Vibrations in Deuterated Ammonium Chloride at 85 °K. II. Theoretical*

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A shell model is shown to provide a good fit to the phonon dispersion curves in $ND_4Cl$. The model contains 22 parameters of which 13 are fitted to the experimental measurements. The ionic charge on the chlorine, and the electronic polarizabilities of the ions, are not fitted to the experiments. The $ND_4$ group is not treated as rigid, but it is shown that an effective dynamical matrix can be set up, which does not contain the internal coordinates explicitly, but which describes their effect on the external dispersion curves to a very good approximation. The dispersion curves in $NH_4Cl$ are also calculated. A group-theoretical analysis of the symmetry of the normal modes is given in the Appendix.

## I. INTRODUCTION

In the preceding paper[1] the phonon dispersion curves in the ordered phase of deutero-ammonium chloride, $ND_4Cl$ are described and compared with theoretical curves, calculated by Parlinski,[2] based on the rigid-ion and rigid-molecule approximations. A number of discrepancies exist between the experimental and calculated curves, and it is not possible *a priori* to absolve either of the above approximations. In this paper we describe a model which contains neither approximation, and which provides a satisfactory description of the experimental curves.

The most straightforward method of including all of the effects required is to abandon the concept of the $ND_4$ ion as a useful unit and to regard the unit cell as containing six independent atoms or ions. This is the approach initially adopted here. The polarizabilities of the ions are taken into account in the shell-model formalism.[3,4] A shell model containing simplifications appropriate to $ND_4Cl$ is described in Sec. II, and the results of a least-squares fit to the experimental data are given in Sec. III. The model contains 22 parameters, but the values of some of them can be deduced from other data, and a model in which 13 of the parameters are adjusted to fit the phonon dispersion curves provides satisfactory agreement with experiment.

The procedure described above is the safest way of ensuring that all of the effects associated with both ionic and molecular polarizability are included, but it does not contain the intuitively appealing separation of the dispersion curves into external and internal branches. In Sec. IV we describe an approximation to the dynamical matrix in which the internal coordinates of the $ND_4$ group are eliminated from the equation for the external branches, but the effects of the internal deformations on the external branches are well represented.

Some of the features of the model are discussed in Sec. V, and the model is also used to predict the form of the dispersion curves in $NH_4Cl$.

## II. SHELL-MODEL FORMALISM

The equations of motion of the shell model can be written in the form[3,4]

$$\underline{m}\omega^2\underline{U} = (\underline{R} + \underline{ZCZ})\underline{U} + (\underline{T} + \underline{ZCY})\underline{W},$$

$$0 = (\underline{T}^{\dagger} + \underline{YCZ})\underline{U} + (\underline{s} + \underline{Y}\,\underline{\mathcal{C}}\,\underline{Y})\underline{W} .$$

$\underline{U}$ and $\underline{W}$ are column vectors describing the ionic displacements and deformations; $\underline{m}$, $\underline{Z}$, and $\underline{Y}$ are diagonal matrices ($18\times18$ in the present case) of ionic masses, ionic charges, and shell charges, respectively, the value for each ion being repeated three times. In the model described below, the deuterium ions are treated as point ions, so that their shell charges drop out of the calculations. $\underline{\mathcal{C}}$ is a matrix of Coulomb coefficients calculated using the Ewald transformation,[5] and $\underline{C}$ is a similar matrix except that the terms in which it appears satisfy translational invariance conditions, e.g.,

$$\sum_{K'} Z(K)Z(K')C_{\alpha\beta}(KK', q=0) = 0 .$$

The distinction between the matrices $\underline{C}$ and $\underline{\mathcal{C}}$ is apparent in Eq. (35.13) of Ref. 5, where a simpler model is treated, but is otherwise not usually pointed out. For the most common diatomic cubic lattices the two matrices are of course equal. Since the electronic polarizabilities of only the chlorine and nitrogen ions are included, and these ions are fairly well separated in the crystal, it seems reasonable to ignore any non-Coulomb shell-shell interactions. The matrix $\underline{s}$ then takes the form[6]

$$s_{xy}(KK', \vec{q}) = \delta_{xy}\,\delta_{KK'}\,\alpha_K^{-1}\,Y_K^2 ,$$

where $\alpha_K$ is the electronic polarizability of the $K$th ion. It is then possible to write the final equation of motion, obtained by eliminating the shell coordinates $\underline{W}$, as

$$\underline{m}\omega^2\underline{U} = [(\underline{R} + \underline{ZCZ}) - (\underline{TY}^{-1} + \underline{ZC})\alpha(\underline{1} + \underline{\mathcal{C}}\alpha)^{-1}(\underline{Y}^{-1}\underline{T}^{\dagger} + \underline{CZ})]\underline{U} .$$

Here $\underline{\alpha}$ is a diagonal matrix of polarizabilities.

A common approximation for the matrix $\underline{T}$ is to set it equal to $\underline{R}$, and it is well known that this is a method of defining implicitly the shell charges, which are otherwise undetermined. This can be seen clearly in the above form of the equations of motion where the shell charges enter only as scaling factors multiplying $\underline{T}$. In our model of $ND_4Cl$ we include short-range ion-shell forces, which are described by the $\underline{T}$ matrix, only between the chlorine shell and its deuterium neighbors. We therefore set $\underline{T} = \underline{R}$ for those elements of $\underline{T}$ corresponding to the chlorine-shell displacement and the deuterium displacements, and zero otherwise. Mathematically this can be achieved by setting the nitrogen- and deuterium-shell charges to infinity. This is, however, a consequence of the fact that, as noted above, the shell charges enter the equations of motion only as scaling factors for the $\underline{T}$ matrix, and are not defined when short-range polarizability effects are omitted. The values of the $N$ and $D$ shell charges thus have no physical significance in our model.

The matrix $\underline{R}$ is defined in terms of the short-range force constants between atoms, $\phi_{\alpha\beta}(lK, l'K')$, as

$$R_{\alpha\beta}(KK', \vec{q}) = \sum_{l'} \phi_{\alpha\beta}(lK, l'K')e^{i\vec{q}\cdot[\vec{r}(l'K') - \vec{r}(lK)]} ,$$

where $\vec{r}\,(lK)$ is usually taken to be the equilibrium position of the $K$th ion in the $l$th unit cell. It is convenient in the present calculation to take $\vec{r}\,(lK)$ to be the equilibrium position of the center of the molecule containing the ion in question, and similar phases must then be used in the Coulomb coefficients. The equilibrium positions and sublattice numbering used in the present work are given in Table I. We include short-range forces between a chlorine ion and its four nearest-neighbor deuteriums, between a nitrogen ion and its four nearest-neighbor deuteriums, between all pairs of deuterium ions in one $ND_4$ group, between chlorine ions in adjacent unit cells, and between nitrogen ions in adjacent unit cells. This last contribution is intended to represent the over-all translation-translation interaction between $ND_4$ groups. No short-range translation-rotation or rotation-rotation force constants between $ND_4$ groups are included. The short-range forces are then completely described in terms of 17 independent force constants. The choice made for these is indicated in Table II. All other short-range force constants in the model can be found from these by the use of the symmetry transformations of the structure and the usual invariance conditions.[6] It is common in calculations on simpler materials to carry out the sum indicated above for the elements of $\underline{R}$ analytically to give a relatively simple expression for the wave-vector dependence of the matrix. In the present case the simplification is slight and it was more convenient to perform the sum with the computer.

## III. DETERMINATION OF THE PARAMETER VALUES

The model described in Sec. II contains 22 parameters: 17 short-range force constants, two independent ionic charges, say, $Z$(Cl) and $Z$(D), electron-

TABLE I. Atomic positions in $ND_4Cl$.

| Sublattice index (K) | Atomic species | Position in unit cell[a] |
|---|---|---|
| 1 | Cl | 0, 0, 0 |
| 2 | N | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| 3 | D | $\frac{1}{2}+u, \frac{1}{2}+u, \frac{1}{2}+u$[b] |
| 4 | D | $\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}-u$ |
| 5 | D | $\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}+u$ |
| 6 | D | $\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}-u$ |

[a] In units of the cube edge, 3.819 Å at 90 °K.
[b] $u = 0.155$ in $ND_4Cl$ at 90 °K.

ic polarizabilities for Cl and N, and a shell charge $Y$(Cl) for the chlorine ion. It is clearly necessary to determine the values of as many of these as possible from data independent of the phonon dispersion curves. With the approximations contained in the model the refractive index and high-frequency dielectric constant are additive functions of the polarizabilities of the chlorine and nitrogen ions (they would not be if short-range shell-shell forces were included), and the analysis carried out by Tessman, Kahn, and Shockley[7] to separate the individual electronic polarizabilities is applicable. We therefore adopt the values 2.974 Å$^3$ for the chlorine polarizability and 2.0 Å$^3$ for the nitrogen polarizability. The latter value is the average ammonium polarizability given by Tessman *et al.* and in our model it sits entirely on the nitrogen. The use of these polarizabilities, which are based initially on data for the alkali halides, implies the adoption of an ionic picture and we assume that the charge on the chlorine is $-|e|$. The charge on the deuteriums need not assume a simple value and we treat it as an adjustable parameter.

We expect the external branches of the dispersion curves to be only weakly dependent on the values of the intramolecular force constants of the $ND_4$ group, $\alpha$ to $\mu$ in Table II, so that an approximate determination of these values should be adequate. An isolated $ND_4$ group has four independent frequencies. In the crystal some of these are split into transverse and longitudinal modes, but the splitting is of the order of 1% and can be neglected in a first approximation. In an isolated $ND_4$, the force constants satisfy the rotational invariance condition

$$\alpha - \beta + 2\gamma + 2\delta - 2\mu + 2\epsilon = 0$$

so that there are five independent force constants.

TABLE II. Independent short-range force constants in the model.

| $-\phi_{\alpha\beta}(lK, l'K')$ | $K$ | $K'$ | $\alpha\beta$ | $\vec{r}(l'K') - \vec{r}(lK)$ |
|---|---|---|---|---|
| $A$ | 1 | 3 | $xx$ | $-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$ |
| $B$ | 1 | 3 | $xy$ | $-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$ |
| $C$ | 1 | 5 | $xx$ | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| $D$ | 1 | 5 | $zz$ | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| $E$ | 1 | 5 | $xy$ | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| $F$ | 1 | 5 | $xz$ | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| $G$ | 1 | 5 | $zx$ | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| $\alpha$ | 2 | 3 | $xx$ | 0, 0, 0 |
| $\beta$ | 2 | 3 | $xy$ | 0, 0, 0 |
| $\gamma$ | 3 | 4 | $xx$ | 0, 0, 0 |
| $\delta$ | 3 | 4 | $yy$ | 0, 0, 0 |
| $\epsilon$ | 3 | 4 | $xy$ | 0, 0, 0 |
| $\mu$ | 3 | 4 | $yz$ | 0, 0, 0 |
| $A_{11}$ | 1 | 1 | $xx$ | 1, 0, 0 |
| $B_{11}$ | 1 | 1 | $yy$ | 1, 0, 0 |
| $A_{22}$ | 2 | 2 | $xx$ | 1, 0, 0 |
| $B_{22}$ | 2 | 2 | $yy$ | 1, 0, 0 |

TABLE III. Experimental and calculated frequencies (in units of $10^{12}$ Hz) in isolated $NH_4$ and $ND_4$ groups. All experimental values are taken from Ref. 8.

| Frequency | Symmetry | $NH_4$ | | $ND_4$ | |
|---|---|---|---|---|---|
| | | Expt | Calc | Expt | Calc |
| $\nu_1$ | $\Gamma_1$ | 91.44 | 91.43 | 65.4 | 64.68 |
| $\nu_2$ | $\Gamma_{12}$ | 51.48 | 50.95 | 35.7 | 36.04 |
| $\nu_3$ | $\Gamma_{15}$ | 93.78<br>94.14 | 95.09 | 70.05 | 68.71 |
| $\nu_4$ | $\Gamma_{15}$ | 42.09<br>42.60 | 42.10 | 31.86 | 32.24 |

It follows that if the internal-mode frequencies in both $ND_4Cl$ and $NH_4Cl$ are considered, the intramolecular force constants can be completely determined, and are in fact overdetermined. It is possible to choose values for the five independent constants to reproduce all of the eight experimental frequencies[8] to within 2%, and the sixth constant is given by the above invariance condition. The agreement between the calculated frequencies and infrared and Raman scattering measurements is shown in Table III.

The values obtained in this way are listed in Table IV, but some caution is needed in using them. These values represent total force constants including short-range terms, rigid-ion Coulomb terms, and polarizability, or shell-model, corrections. If the values given in Table IV were used directly in the $\underline{R}$ matrix the internal frequencies could have values very different from the experimental values. The procedure we therefore used was to calculate the extra contributions for a given set of ionic charges and polarizabilities and hence to determine the short-range parts. This procedure was carried out in the computer programs, and the values given in Table IV were always used as input data. In point of fact, in the best model obtained, the charge on the deuterium ions is very small, and the corrections to the short-range constants then all disappear, but in some earlier models we obtained, the corrections were very important. Even if corrections of this type are made, the values of the internal frequencies are not exactly equal to the values for an isolated $ND_4$ group given in Table III because of intermolecular interactions, but this effect is small, the largest deviation in the final model being 3%, so that again it can be ignored if we are interested in the effects on the external vibrations.

The remaining 13 parameter values were determined in a nonlinear least-squares fit, which gave the remaining numbers listed in Table IV. The fitted values are given to many more figures than are physically significant to avoid rounding errors. The value of the fitting parameter $\chi$, defined by

$$\chi^2 = \sum_{\text{obs}} \frac{[(\nu_{\text{obs}} - \nu_{\text{calc}})/\sigma]^2}{N_{\text{obs}} - N_{\text{parameters}}} ,$$

where $\sigma$ is the estimated error on the observed frequency, was obtained as 1.384, which we consider to represent a satisfactory fit. We did attempt to reduce the number of parameters by imposing axial symmetry conditions on the chlorine-deuterium force constants $C$ to $G$. The least-squares procedure was then much better conditioned, but the fit obtained was significantly worse.

The most noteworthy feature of the values given in Table IV is the very low value for the deuterium charge. Essentially the whole of the charge on the $ND_4$ group is placed on the nitrogen. In our model the entire rotation-rotation coupling between $ND_4$ groups arises from the charges on the deuterium ions. The low fitted value is then a consequence of the experimental observation that the rotational branches are almost perfectly flat. In a series of models containing different assumptions about other features of the forces, the fitted magnitude of the deuterium charge was never found to be greater than $0.1|e|$, and its sign varied from model to model.

The dispersion curves of the model in the principal symmetry directions are compared with the experimental results[1] in Fig. 1. The splitting between the three rotational branches is too small to be shown there.

## IV. SEPARATION OF EXTERNAL BRANCHES

The frequencies plotted in Fig. 1 were obtained from the lowest nine eigenvalues of an $18\times18$ dynamical matrix $\underline{D}$. Values for nine branches of the dispersion curves corresponding to internal vibrations of the $ND_4$ group, with frequencies in the range $30-60\times10^{12}$ cps, were obtained at the same time. We describe here a method of avoiding this extra calculation by reducing the problem to the solution of a $9\times9$ matrix which yields the frequencies of the external branches only, but which incorporates the effects of the internal distortions of the $ND_4$ group.

It is convenient to make a transformation of coordinates from individual ionic displacements along Cartesian axes to linear combinations of such displacements so that the first nine coordinates describe rigid molecular translations and rotations and the second nine describe internal deformations of the $ND_4$. The transformation can be effected by introducing a unitary matrix $\underline{U}$ such that $U(K\alpha,i)$ is proportional to $m(K)^{1/2}$ times the $\alpha$ component of the displacement of the $K$th ion in the $i$th linear combination. The choice of $\underline{U}$ is not unique. The use of the phase factors described in Sec. II has the result that the elements of $\underline{U}$ are independent of the wave vector, which would not otherwise be the case. The transformed dynamical matrix $\underline{\mathfrak{D}}$ can then be partitioned into four $9\times9$ blocks:

$$\underline{\mathfrak{D}} = \underline{U}^\dagger \underline{D} \underline{U} = \begin{pmatrix} \underline{A} & \underline{B} \\ \underline{B}^\dagger & \underline{C} \end{pmatrix} .$$

$\underline{C}$ here should not be confused with the matrix of Coulomb coefficients used in Sec. II. Diagonalization of the complete matrix $\underline{\mathfrak{D}}$ yields the same 18 eigenvalues as before, but with rotated eigenvectors. Diagonalization of the matrix $\underline{A}$ is equivalent to neglecting all internal deformations of the $ND_4$ group, allowing it only to translate and rotate rigidly. It is not hard to show that this leads to errors in the external frequencies of the order of $(\nu_{\text{ext}}/\nu_{\text{int}})^2$, up to 5% in the present case. In fact this is not a large effect, and indicates that most of the discrepancy between Parlinski's calculation[2] and the experimental results is due to his use of the rigid-ion model. However, it is possible to set up a $9\times9$ matrix which describes very accurately the external branches of the dispersion curves by eliminating the internal coordinates adiabatically from the equations of motion, in a manner reminiscent of the elimination of the shell coordinates in the shell model.[3] The effective dynamical matrix is then obtained as

$$\underline{A} - \underline{B}\underline{C}^{-1}\underline{B}^\dagger ,$$

and the eigenvalues of this matrix differ from the lowest nine eigenvalues of the full matrix $\underline{D}$ by terms of the order of $(\nu_{\text{ext}}/\nu_{\text{int}})^4$. We have programmed this calculation and verified that the approximation is a good one, which leads to a substantial saving

TABLE IV. Fitted parameter values. Short-range force constants are in units of $10^5$ dyn/cm, ionic and shell charges in units of $|e|$, and electronic polarizabilities in units of $10^{-24}$ cm$^3$.

| Parameter | Value |
|---|---|
| $A$ | 0.41892 ± 0.019 |
| $B$ | 0.68974 ± 0.076 |
| $C$ | 0.39642 ± 0.191 |
| $D$ | −0.02374 ± 0.369 |
| $E$ | 0.18828 ± 0.045 |
| $F$ | 0.24906 ± 0.123 |
| $G$ | 0.33971 ± 0.171 |
| $\alpha$ | 16.072 |
| $\beta$ | 11.672 |
| $\gamma$ | 1.207 |
| $\delta$ | 3.443 |
| $\epsilon$ | −3.170 |
| $\mu$ | 3.680 |
| $A_{11}$ | 0.16765 ± 0.065 |
| $B_{11}$ | −0.01657 ± 0.011 |
| $A_{22}$ | 0.48539 ± 0.085 |
| $B_{22}$ | 0.07063 ± 0.025 |
| $Z$(Cl) | −1.0 |
| $Z$(D) | 0.00631 ± 0.161 |
| Cl Polarizability | 2.974 |
| N Polarizability | 2.0 |
| $Y$(Cl) | −2.40143 ± 0.193 |

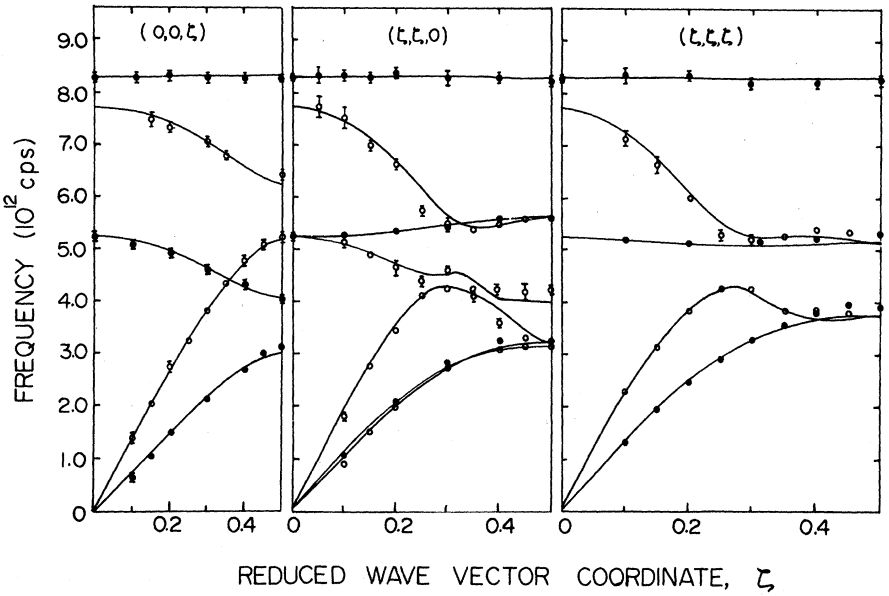


FIG. 1. Dispersion curves for $ND_4Cl$ at 85 °K. The lines are the best shell-model fit and the points are the experimental measurements of Teh and Brockhouse.

in computing time.

An additional attractive feature of this approach is that the symmetry properties of the dynamical matrix obtained are identical with those of the rigid-molecule dynamical matrix $\underline{A}$. Group-theoretical analyses are often used to discuss the symmetry of the external branches based on the rigid-molecule approximation. The treatment given here shows that such symmetry based conclusions are more accurate than the rigid-molecule approximation, and can be expected to be valid for quite small spacings between the external- and internal-dispersion curves.

## V. DISCUSSION

The model described above provides a good over-all representation of the dispersion curves. In fact, since we have used standard values for the electronic polarizabilities, fixed the value of the chlorine charge at its formal value, and set $\underline{T} = \underline{R}$, the model can reasonably be described as a simple shell model in the sense of Ref. 4 and as such the agreement with experiment is excellent. There are a number of small discrepancies however, notably in the optical branches in the [110] direction, and we have made some attempts to remove these. Allowing the chlorine charge to vary does not improve the fit significantly. Apart from this simple possibility the most successful attempt to improve on the shell model has been the breathing-shell model of Schröder.[9] In this model as it has been applied to the alkali halides, an extra scalar degree of freedom, corresponding to the shell radius, is associated with the halogen ion. The improvement in the calculated dispersion curves in the vicinity of the point $L$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, in the Brillouin zone is then considerable.

A little thought shows that no such dramatic improvements can be expected in the present case. A scalar variable on one ion per unit cell can couple only to phonons transforming according to one-dimensional irreducible representations. In particular if the chlorine ion is taken to be at the origin, the shell radius couples only to phonons transforming according to the identity representation at each wave vector. The results of an analysis of the symmetry properties of the vibrations are given in the Appendix, and it may be seen that very few of the frequencies at special points in the zone can be affected. If the crystal had the $m3m$ symmetry of its high-temperature modification, the frequencies of *all* the external-zone-boundary phonons would be unaffected by the breathing motion. We can therefore expect only a secondary effect from the inclusion of this degree of freedom. Some frequencies at intermediate points in the symmetry directions are affected; the remaining parameters must then be readjusted and thus all the frequencies are eventually changed. By actual calculation we find that the over-all agreement is not improved, although some of the trends are correct. The same type of argument can be used to show that the off-diagonal elements of the quadrupole moment of the chlorine ion can couple more strongly to the optical branches of the dispersion curves in both the [110] and [111] directions, but the inclusion of these effects would almost certainly involve more extra unknown parameters than could reliably be determined.

Two features of the fitted parameter values are noteworthy. The first is the large uncertainties associated with the chlorine-deuterium force constants $C$ to $G$. If these force constants are related

to the chlorine-$ND_4$ translation-translation and translation-rotation force constants, only three combinations of the five force constants occur. In other words, two of the constants (or two linear combinations of them) appear only in the matrix $\underline{B}$ which describes the coupling between the external and internal branches. It is thus not surprising that these parameters are not well defined. As described in Sec. III, we did attempt to remove this indeterminancy by imposing axial symmetry conditions on the parameters, but this led to a significant worsening of the fit.

This same difficulty arises if nitrogen-chlorine forces are included in the model, since for the same reasons these must be highly correlated with the deuterium-chlorine forces. The relatively large values for the nitrogen-nitrogen force constants given in Table IV represent total translation-translation force constants between neighboring ammonium ions, including all intermolecular non-Coulomb deuterium-deuterium forces.

The second feature is the absence of rotational coupling between the $ND_4$ groups. In setting up the model we neglected non-Coulomb rotation-rotation force constants, and the very small value we obtained for the deuterium charge corresponds to zero Coulomb rotational coupling. Non-Coulomb coupling terms could be included in the model, but then almost certainly the deuterium charge would be strongly correlated to them and neither could be well determined from the fit. Basically, the lack of rotational coupling is indicated directly by the flatness of the rotational branches of the dispersion curves but it is hard to understand why the crystal undergoes an order-disorder phase transition if such coupling is really absent. It should be noted that the data obtained with the second, more highly deuterated, specimen described in the previous paper were not included in the least-squares fit.

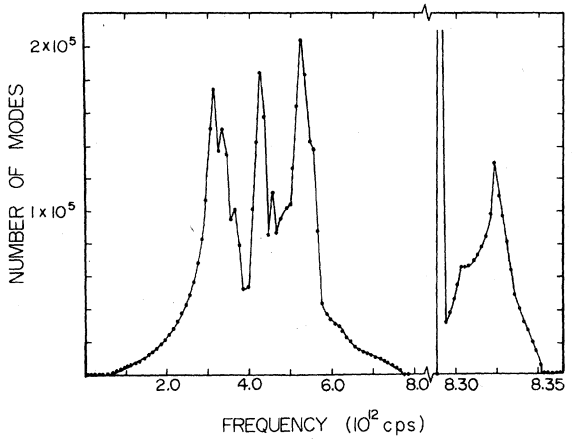


FIG. 2. Frequency distribution function (unnormalized) for $ND_4Cl$.

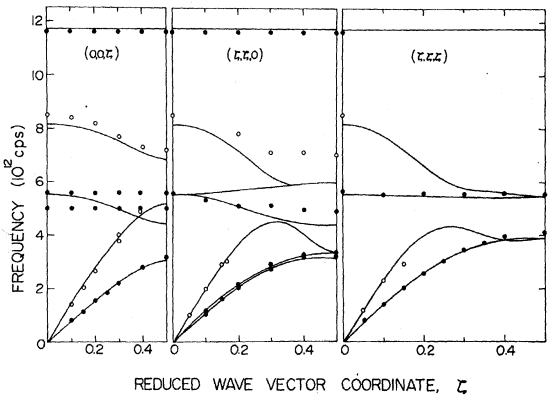


FIG. 3. Dispersion curves for $NH_4Cl$ calculated from the model fitted to $ND_4Cl$. The points are the experimental measurements of Smith *et al.*

Possibly more accurate measurements of the rotational branch, and particularly the measurement of the splitting at the point $M$, will allow a better determination of the value of the deuterium charge. The remaining branches of the dispersion curves are extremely insensitive to the value of this parameter, in the sense that an adjustment of the deuterium-chlorine short-range force constants can compensate for wide variations in the deuterium charge. In view of these considerations and the large error associated with the fitted value of the deuterium charge, we do not consider the value obtained to be inconsistent with estimates such as the value of $0.18|e|$ given by Pauling.[10]

A frequency distribution for the fitted model is shown in Fig. 2. The frequencies were calculated at a set of 56 wave vectors in the irreducible volume of the Brillouin zone, corresponding to 1000 wave vectors in the whole zone. A quadratic interpolation was then used to generate the frequencies on a mesh 729 times as dense, and these frequencies were sorted into a histogram. The bin width used for the histogram was $0.1\times10^{12}$ cps, which is larger than the largest errors due to the interpolation. We believe all of the structure remaining in the histogram is real. On this scale the rotational branches plot as a single point. In the right-hand part of the figure, the bin width has been decreased by a factor of 40 to show the shape of the rotational peak, but one-third of the frequencies still fall into a single bin.

It is plausible that the force constants in ammonium chloride $NH_4Cl$ are almost unchanged from $ND_4Cl$. We have already made this assumption to derive values for the intramolecular force constants, and we can also use it to obtain the external dispersion curves in $NH_4Cl$. They are shown in Fig. 3, compared with some results obtained directly by Smith *et al.*[11] This is a very difficult ex-

TABLE V. Symmetry properties of the external branches of the dispersion curves.

| Wave vector | Representation and degeneracy | $n_j$ | Cl translation direction | $ND_4$ translation direction | $ND_4$ rotation axis | Compatible representations |
|---|---|---|---|---|---|---|
| (0, 0, 0) | $\Gamma_{15}$[a] (3) | 2 | 1, 0, 0 | 1, 0, 0 | | $\Delta_1+\Delta_3+\Delta_4$; $\Lambda_1$ |
| | | | 0, 1, 0 | 0, 1, 0 | | $+\Lambda_3$; $2\Sigma_1+\Sigma_2$ |
| | | | 0, 0, 1 | 0, 0, 1 | | |
| | $\Gamma_{25}$ (3) | 1 | | | 1, 0, 0 | $\Delta_2+\Delta_3+\Delta_4$; $\Lambda_2$ |
| | | | | | 0, 1, 0 | $+\Lambda_3$; $\Sigma_1+2\Sigma_2$ |
| | | | | | 0, 0, 1 | |
| (q, 0, 0) | $\Delta_1$ | 2 | 1, 0, 0 | 1, 0, 0 | | |
| | $\Delta_2$ | 1 | | | 1, 0, 0 | |
| | $\Delta_3$[b] | 3 | 0, 1, −1 | 0, 1, −1 | 0, 1, 1 | |
| | $\Delta_4$[b] | 3 | 0, 1, 1 | 0, 1, 1 | 0, 1, −1 | |
| (½, 0, 0) | $X_1$ | 1 | | 1, 0, 0 | | $\Delta_1$; $S_1$; $Z_1$ |
| | $X_3$ | 1 | 1, 0, 0 | | | $\Delta_1$; $S_1$; $Z_2$ |
| | $X_4$ | 1 | | | 1, 0, 0 | $\Delta_2$; $S_2$; $Z_1$ |
| | $X_5$ (2) | 3 | 0, 0, 1 | 0, 1, 0 | 0, 1, 0 | $\Delta_3+\Delta_4$; $S_1+S_2$; |
| | | | 0, 1, 0 | 0, 0, 1 | 0, 0, 1 | $Z_1+Z_2$ |
| (q, q, 0) | $\Sigma_1$ | 5 | x, x, z | x, x, z | 1, −1, 0 | |
| | $\Sigma_2$ | 4 | 1, −1, 0 | 1, −1, 0 | x, x, z | |
| (½, ½, 0) | $M_1$ | 1 | 0, 0, 1 | | | $\Sigma_1$; $T_1$; $Z_2$ |
| | $M_3$ | 1 | | 0, 0, 1 | | $\Sigma_1$; $T_1$; $Z_1$ |
| | $M_4$ | 1 | | | 0, 0, 1 | $\Sigma_2$; $T_2$; $Z_1$ |
| | $M_5$ (2) | 3 | 1, −1, 0 | 1, −1, 0 | 1, 1, 0 | $\Sigma_1+\Sigma_2$; $T_3+T_4$; |
| | | | 1, 1, 0 | 1, 1, 0 | 1, −1, 0 | $Z_1+Z_2$ |
| (q, q, q) | $\Lambda_1$ | 2 | 1, 1, 1 | 1, 1, 1 | | |
| | $\Lambda_2$ | 1 | | | 1, 1, 1 | |
| | $\Lambda_3$ (2) | 3 | 1, −1, 0 | 1, −1, 0 | −1, −1, 2 | |
| | | | −1, −1, 2 | −1, −1, 2 | 1, −1, 0 | |
| (½, ½, ½) | $R_{15}$ (3) | 2 | 1, 0, 0 | 1, 0, 0 | | $\Lambda_1+\Lambda_3$; $2S_1+S_2$; |
| | | | 0, 1, 0 | 0, 1, 0 | | $T_1+T_3+T_4$ |
| | | | 0, 0, 1 | 0, 0, 1 | | |
| | $R_{25}$ (3) | 1 | | | 1, 0, 0 | $\Lambda_2+\Lambda_3$; $S_1+2S_2$; |
| | | | | | 0, 1, 0 | $T_2+T_3+T_4$ |
| | | | | | 0, 0, 1 | |
| (q, q, ½) | $S_1$ | 5 | x, x, z | x, x, z | 1, −1, 0 | |
| | $S_2$ | 4 | 1, −1, 0 | 1, −1, 0 | x, x, z | |
| (½, ½, q) | $T_1$ | 2 | 0, 0, 1 | 0, 0, 1 | | |
| | $T_2$ | 1 | | | 0, 0, 1 | |
| | $T_3$[c] | 3 | 1, 1, 0 | 1, 1, 0 | 1, −1, 0 | |
| | $T_4$[c] | 3 | 1, −1, 0 | 1, −1, 0 | 1, 1, 0 | |
| (½, q, 0) | $Z_1$ | 5 | 0, 1, 0 | x, 0, z | x, 0, z | |
| | $Z_2$ | 4 | x, 0, z | 0, 1, 0 | 0, 1, 0 | |

[a]The $\Gamma_{15}$ optical modes are split by the macrosopic electric field.
[b]$\Delta_3$ and $\Delta_4$ modes are degenerate in pairs owing to time-reversal symmetry.
[c]$T_3$ and $T_4$ modes are degenerate in pairs owing to time-reversal symmetry.

periment to carry out because of the large incoherent scattering cross section of the protons. Some of the points shown for the [001] direction are presumably due to this cause. The energy distribution of incoherently scattered neutrons can be expected to resemble the frequency distribution function. We have calculated this in the same manner as for $ND_4Cl$, and obtain a similar result, with three sharp peaks in the translational part, at frequencies of about 3.15, 4.45, and 5.60. It may be that some of the extra peaks reported by Smith *et al.* are due to incoherent scattering, particularly at the last frequency mentioned.

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## APPENDIX

Table V contains the results of a group-theoretical analysis[12] of the symmetry properties of the external branches of the dispersion curves in $ND_4Cl$, i.e., only the nine-dimensional space of Cl displacements and rigid-$ND_4$ translations and rotations

is considered. The notation used is that of Koster,[13] and the chlorine ion is taken to be at the origin of the unit cell. In the table, $n_j$ is the number of times the $j$th irreducible representation occurs. The figure in brackets after a representation label is the degeneracy of the representation, and if no figure is given the representation is singly degenerate.

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# Dynamics of Interacting Photon-Phonon Fields in Dielectric Crystals*

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The dynamic interaction between electromagnetic waves and transverse optical phonons in dielectric crystals has been studied by means of the Green's-function method. Emphasis has been given to the line shapes of the absorption bands at finite temperatures. The spectral functions for the photon and phonon fields are found to consist of the superposition of symmetric and asymmetric Lorentzian lines even if the frequency dependence of the energy shift and damping functions is neglected. The source of the asymmetry is the anharmonic coupling between the transverse photons and transverse optical phonons. General expressions for the energy shift and the damping functions are derived. The possible mechanisms that may occur in the physical process of Raman scattering are examined in detail, and expressions for the corresponding scattering amplitudes are developed. In the limiting case of absence of dispersion of the electromagnetic waves in the medium, the bare excitation spectra for both fields are also discussed.

## I. INTRODUCTION

The excitation spectrum of interacting polaritons in dielectric crystals has been recently studied[1] by means of the Green's-function method. In a dielectric medium and for certain values of wave vectors of the electromagnetic field, the polariton spectrum arises from the interaction between transverse photons and transverse optical (TO) phonons. The polarization operator for the interacting polariton system has been calculated in successive approximations and the excitation spectrum has been discussed in detail. The polariton spectral function arising from polariton-polariton interactions is found to have a Lorentzian line shape, while asymmetric broadening will arise only when the frequency variation of the damping function is taken into consideration. We refer to I for details as well as for polariton literature.

Benson and Mills[2] have recently developed a theory of light scattering from polaritons in the presence of lattice damping. Their calculation is based on the assumption that the lattice anharmonicity is the dominant factor in the damping process and the anharmonic coupling between the electromagnetic field and TO phonons has been completely ignored. For the process of Raman scattering, they found that the spectral functions for the photon and phonon fields are described by Lorentzian lines. Asymmetric broadening results only when the frequency dependence and the variation of the linewidth with respect to the scattering angle are taken into account.[2] Barker[3] studied the Raman scattering spectrum of TO phonons in GaP. He found that the TO phonon mode showed considerable asymmetric broadening.[3] The purpose of this study is to show that the line shape of the spectrum arising from photon-phonon[4] in-