Breadth of the F Band in NaCl

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The breadth of the F band in NaCl is calculated for various temperatures, primarily in order to investigate the status of the semiempirical configuration coordinate treatment of such problems. The main new feature of the calculation, which involves no adjustable parameters, is the use of the realistic normal modes employed in the Born-Blackman theory of specific heats. The eigenvectors as well as the eigenfrequencies of these modes are used. Modifications of the modes due to the missing ion at the F center are ignored. The coupling to the F center is determined from electrostatic forces on individual ions. Simpson's F center wave functions are used and the calculated breadths are all about 85% of the experimental values. It is found that the main contributions to the breadth come from modes in a fairly small range of frequencies (much lower than the frequencies of the longitudinal optical modes considered in previous calculations) which includes the empirical configuration coordinate frequency. This last result helps to clarify the relation of the hypothetical configuration coordinate mode to the actual modes of lattice vibration.

IN previous attempts[1] at an absolute calculation of the breadth of the F band, only the interactions with the longitudinal optical modes have been considered and these modes have been treated in a continuum approximation. The breadths obtained were much too small unless rather drastic assumptions were made concerning the F center wave functions. This is not very surprising; while it is true that an unscreened charge will interact predominantly with the longitudinal optical modes, the F center is electrically neutral and the electrostatic forces due to it will have a range of only a few lattice spacings.[2] Thus the continuum approximation is hardly appropriate and interaction with other types of mode cannot be excluded.

In the calculation for NaCl described here all types of mode were considered and the coupling of the F center electron to the lattice vibrations was determined from the electrostatic forces exerted by the F center charge distribution on individual ions rather than on a smoothed out charge distribution. Simpson's[3] wave functions for the F center electron were used and no adjustable constants were introduced. The agreement of the results with the experimental breadths at various temperatures is very satisfactory. Moreover, light is thrown on why the semiempirical configuration coordinate analysis[4] of the behavior of the center is so successful and why the empirical frequency of the single hypothetical vibration mode considered in that analysis is much lower than longitudinal optical mode frequencies.

The lattice vibration modes to which the coupling was explicitly calculated were those used by Kellermann[5] in his determination of the lattice vibration spectrum, i.e., six modes for each of 48 values of the wave vector. For the present problem the precise motions of the ions in the various modes were required and these were determined by calculating on an electronic computer the eigenvectors as well as the eigenfrequencies of the appropriate 6×6 matrices.

It was assumed throughout that the anharmonic part of the forces between ions is negligible. The change which a small displacement of an ion produces in the electrostatic force exerted on it by the F center charge distribution was also ignored. More important, it was assumed that modifications in the form of the lattice modes due to the missing ion at the F center could be disregarded; such modifications certainly exist and it is of interest that, at least for the problem considered here, a treatment neglecting them can give reasonable agreement with experiment.

The electrostatic forces exerted on adjacent ions by the F center electron in both its s and p states were required. For simplicity the p state charge distribution was made spherically symmetrical. The screening effect of electronic polarization had to be considered; that of ion displacement is already included in the normal mode analysis. It was checked that reasonable forces on third to sixth nearest neighbor ions inclusive would contribute in total only about 1% to the final results. The forces finally used were obtained by neglecting the forces on fifth and subsequent nearest neighbors

[1] See the reviews by D. L. Dexter, in *Solid-State Physics*, epited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353; and by J. J. Markham, Revs. Modern Phys. **31**, 956 (1959).

[2] M. Lax, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley & Sons, Inc., New York, 1956).

[3] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[4] G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

[5] E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

TABLE I. Breadth of the F band.

	0°K	50°K	100°K	150°K	200°K	250°K	300°K
Theor. (ev)	0.24	0.24	0.27	0.31	0.35	0.39	0.42
Expt. (ev)	0.29	0.29	0.32	0.36	0.41	0.46	0.50
Theor./Expt.	0.83	0.83	0.84	0.86	0.85	0.85	0.84

and treating the polarization by considering the discrete dipoles induced on ions nearer than this.[6]

These electrostatic forces on ions give rise to generalized forces on the normal coordinates associated with the normal modes; the generalized force P on a normal coordinate ξ is by definition such that when ξ alone of the normal coordinates is varied by an amount $\delta\xi$ the work done by the electrostatic forces from the F center on the ions is $P\delta\xi$. It is clearly possible to calculate this work, and so the generalized force P, in terms of the forces on the ions, since the ion displacements in each mode are known.

When the F center electron is excited from the ground s state to a p state, changes in the electrostatic forces on the ions will change the generalized forces on at least some of the modes. If the generalized force on a mode changes, the equilibrium value for the associated normal coordinate will change and phonons may be emitted into the mode. The theory is just that used in the quantum mechanical treatment of the configuration coordinate model.[7] It can be shown that if the change in generalized forces on a mode of angular frequency ω is ΔP, and the kinetic energy of the mode can be written $\frac{1}{2}a\xi^2$, then the mean square fluctuation in the number of phonons emitted into the mode is

$$\tfrac{1}{2}(\Delta P^2/a\hbar\omega^3)\coth(\tfrac{1}{2}\hbar\omega/kT).$$

Phonons are emitted into different modes in a statistically independent manner, as follows from the product form of the expression for the transition probability. Thus the mean square fluctuation in the total energy emitted as phonons is the sum of the mean square fluctuations in the energies emitted into individual modes. This sum over all modes was estimated from a suitably weighted sum over the modes for which calculations had been made. The result gives the mean square breadth of the absorption band; the half-breadth follows on the assumption that the band is nearly Gaussian. In Table I the calculated half-breadths are compared with results estimated from the experimental data of Russell and Klick.[4]

Practically all the discrepancy could be accounted for by assuming that the forces calculated from Simpson's wave functions are about 15% too low. This would also account for a similar calculation of the mean energy emitted as phonons (which depends on the square of the electrostatic forces) giving a result (0.53 ev) about 30% lower than Russell and Klick's semi-empirical value of 0.8 ev.

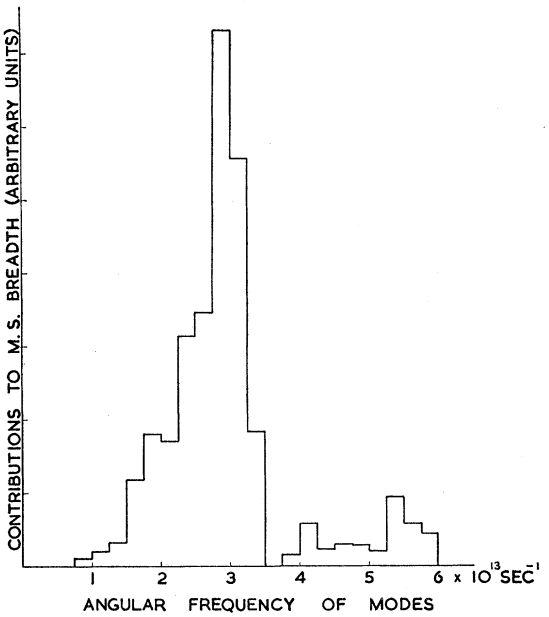

FIG. 1. Histogram of contributions (in arbitrary units) of modes in various frequency ranges to the mean square breadth of the F band at 0°K. The configuration coordinate frequency occurs at $\omega=2.76\times10^{13}$ sec^{-1}.

The form of the histogram (Fig. 1) of the contributions of the modes in the various frequency ranges to the mean square breadth of the F band is insensitive to the F center wave functions used.[8] It is rather similar to a plot of the vibrational frequency spectrum, but is more sharply peaked. The relatively small part of the mean square breadth arising from the high-frequency (longitudinal optical) modes suggests why earlier calculations gave much too small breadths. The concentration of the bulk of the contributions in a fairly small frequency range, which includes the empirical configuration coordinate frequency ($\omega=2.76\times10^{13}$ sec^{-1}), appears to go far in explaining the success of the configuration coordinate approach.

ACKNOWLEDGMENT

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[6] The procedure was essentially that used by N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

[7] See, for example, Markham (reference 1), particularly Sec. 10.

[8] It should, however, be noted that the effect of departures from spherical symmetry in the charge distributions has not yet been investigated.