

Shape of the F -Aggregate Bands in KCl and KBr. II. Analysis

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A theory for the broad optical-absorption bands of defects in solids is developed and applied to the F and F -aggregate bands in the alkali halides. An analysis of the data for these bands is carried out by fitting their temperature-dependent moments with the predictions of the theory. In this way parameters are evaluated which indicate the complexity of the interactions between the defect and phonons, and which measure the effect of phonons of different symmetries and different frequencies. It is found that the data for KCl can be fitted only if linear and bilinear terms in the interaction Hamiltonian are considered and if vibrations of many symmetries and frequencies are included. The consequence of the Jahn-Teller effect for the shape and structure of some of the bands receives special attention.

INTRODUCTION

THE F band, the main optical-absorption band associated with the F center in the alkali halides, is typical of broad structureless bands. It is a bell-shaped curve which narrows and shifts to shorter wavelengths as the temperature is lowered. Konitzer and Markham¹ made careful measurements of the F band in KCl and found that: (1) The integrated area under the band is independent of temperature, (2) the shape is slightly asymmetrical, but approximately Gaussian, (3) the shape is independent of temperature when normalized to a fixed position, height, and half-width, (4) the half-width can be approximated by $0.163 \coth^{1/2}(142.0^\circ/2T)$ eV, and (5) the peak position can be approximated by $[2.340 - 0.027 \coth(142.0^\circ/2T)]$ eV. Similar results have been found for the F band in most of the other alkali halides and for many other defect centers in many hosts.²

There is general agreement that the finite width of these absorption bands is largely a result of the motion of the lattice ions around the defect, but there is a lack of agreement as to the exact nature of this motion. Ideally, one should be able to calculate from first principles the details and consequences of the vibrational modes that involve the defect. Progress has been made in this direction, but in most cases one is forced to work backwards by comparing the results of experiments such as the determination of band shape with the predictions of theories based on various simplified treatments of the lattice vibrations and their interaction with the defect center. In this way a judgment of the validity of the theories can usually be made.

Most theories of this kind assume the validity of the Born-Oppenheimer, Condon, and harmonic approximations.³ At least three additional assumptions are us-

ually made before a complete theory is developed. These involve a description of the types, i.e., symmetries, of lattice vibrations which interact with the defect, the nature of the interaction energies, and the frequencies of the vibrations. The simplest theories assume that vibrations of only one symmetry and one frequency are involved and use the simplest possible form of interaction energy. These assumptions are often expressed by the use of a configuration-coordinate diagram composed of two displaced but otherwise identical parabolic curves corresponding to the electronic ground and excited states. The details of transitions between these states in the presence of vibrations of the lattice coordinate can then be calculated either "exactly" using a quantum-mechanical description of the vibrational states or approximately using various classical assumptions. In this way the shape of an absorption (or emission) band and its dependence upon temperature and other variables can be determined. The analysis of the shape of the F band by Konitzer and Markham as well as many other measurements made on this and other bands is based upon such a simple approach.

When enough detailed measurements are made, however, one often finds some property of an absorption or emission band which cannot be explained by the simple theory; then some of the assumptions made above must be relaxed. For example: To explain the change in the shape of the F band due to an applied stress, Schnatterly⁴ modified the simple assumptions by including vibrations of at least two different symmetries; to explain the skewed shape of the F band Russell and Klick⁵ allowed the second derivatives of the two curves of the configuration-coordinate diagram to differ; and to explain the temperature dependence of the half-width of the F band, Karo, McCombie, and Murray⁶ used a large number of vibrations with a distribution of frequencies.

The first two assumptions of the simple theory could be eliminated by including vibrations of all types allowed by the point-symmetry group of the defect and by allow-

¹ J. D. Konitzer and J. J. Markham, *J. Chem. Phys.* **32**, 843 (1960).

² Reviews discussing these and related topics are found in C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 97; J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962), p. 69.

³ Reviews discussing these approximations and related topics are found in J. J. Markham, *Rev. Mod. Phys.* **31**, 956 (1963); and D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353.

⁴ S. E. Schnatterly, *Phys. Rev.* **140**, A1364 (1965).

⁵ G. A. Russell and C. C. Klick, *Phys. Rev.* **101**, 1473 (1956).

⁶ A. M. Karo, C. W. McCombie, and A. M. Murray, *Phys. Rev.* **119**, 504 (1960); an important erratum is found in *Phys. Rev.* **121**, 1864 (1961).

ing interaction energies of a very general form. In the language of configuration-coordinate diagrams this corresponds to adding a new dimension to the diagram for each type of vibration and to allowing the ground- and excited-state sheets to differ in curvature and have any other nonparabolic distortions. There has been a lasting controversy concerning the third assumption, which involves the frequency range covered by the lattice vibrations which interact strongly with the F center. Two extreme possibilities are either that a single localized vibration with a well-defined frequency is involved, or that a distribution of frequencies essentially the same as that found in the unperturbed lattice is involved. We feel that most of the evidence supports the latter view. Some of this evidence is presented below:

(1) Calculations show that localized modes can be expected only when the number of normal lattice vibrations with the same frequency is small⁷ or when, for some reason, the localized vibrations are weakly coupled to the rest of the lattice. Experiments verify this; for instance localized modes are found at very low frequencies,⁸ or at very high frequencies,⁹ or in special places within the normal phonon spectrum where the density of phonon states is low,¹⁰ or they involve vibrations within molecularlike defects which are loosely coupled to the lattice.¹¹ Because of these restrictions it appears that the localized-mode assumption cannot be used with the F band since the frequency (3.0×10^{12} for KCl) which must be used with this assumption to fit the data of Konitzer and Markham¹ satisfies none of these conditions.

(2) Optical Raman experiments of Worlock and Porto¹² on the F center show that vibrations with a broad spread of frequencies interact with the F center. No evidence is found for a localized mode.

(3) Pierce¹³ has found that the many peaks observed in the absorption bands of some of the closely related F -aggregate centers cannot be explained by the excitation of a single vibrational mode with a well-defined frequency but can be by a model involving interactions with many of the vibrations of the unperturbed lattice.

(4) Spin-lattice-relaxation measurements on the F center by Feldman *et al.*¹⁴ have been explained using the assumption that a Debye distribution of phonons causes the relaxation. Subsequent calculations of ours show that the data cannot be fitted by an alternative model involving a localized mode of a well-defined frequency.

(5) Calculations carried out by McCombie, Matthew, and Murray¹⁵ of the vibrational modes in a small KCl crystal before and after the introduction of an F center indicate that no localized mode is introduced with the F center and that the change in the modes is relatively minor, consisting of an accentuation of the low-frequency and a reduction of the high-frequency vibrations in much the same manner predicted for a massive-impurity ion by Dawber and Elliot.⁷

From the arguments presented above it is clear that a "good" theory for the band shape of an optical transition of a defect center should be a fully quantum-mechanical treatment, should include realistic interactions between the defect and phonons, and should include phonons of many different symmetries and a wide frequency range. The development of such a theory is one of the purposes of this paper. We have drawn heavily upon previous works including especially those of Lax,¹⁶ Markham,¹⁷ Silsbee,¹⁸ and Longuet-Higgins, Öpik, Pryce, and Sack.¹⁹ A very recent review by Maradudin²⁰ covers some of the points discussed by us. We refer the reader to these authors for a more complete treatment of many of the details raised in this article. Our second purpose is to apply the theory we have developed to the data measured by Konitzer and Markham¹ for the F band and by us for the aggregate bands (presented in the preceding paper, hereafter called I). Our ultimate aim is to answer the following questions for the F and F -aggregate centers: (1) How complex are the defect-phonon interactions? (2) Are the effects of phonons of different symmetries evident in the shape of the bands? (3) Can the frequency spread of the phonon spectrum be deduced, and how does it compare with the spectrum of the unperturbed lattice? (4) Can the differences in shape, width, fine structure, etc., among the aggregate bands be understood in terms of the differences in the defect-phonon interactions?

THEORY

We will base our analysis upon the following assumptions:

(1) When the defect is in its ground state, the modes of vibration of the surrounding lattice can be approximated by harmonic oscillators of different symmetry types, indexed by k , and different frequencies ω_k . The number of symmetry types is equal to the total number of basis functions belonging to all of the irreducible

⁷ P. G. Dawber and R. J. Elliot, Proc. Roy. Soc. (London) **A273**, 222 (1963).

⁸ A. J. Sievers, Phys. Rev. Letters **13**, 310 (1964).

⁹ G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960).

¹⁰ M. Wagner and W. E. Bron, Phys. Rev. **139**, A223 (1965).

¹¹ J. Rolfe, F. R. Lipsett, and W. J. King, Phys. Rev. **123**, 447 (1961).

¹² J. M. Worlock and S. P. S. Porto, Phys. Rev. Letters **15**, 697 (1965).

¹³ C. B. Pierce, Phys. Rev. **135**, A83 (1964).

¹⁴ D. W. Feldman, R. W. Warren, and J. G. Castle, Jr., Phys. Rev. **135**, A470 (1964).

¹⁵ C. W. McCombie, J. A. D. Matthew, and A. M. Murray, J. Appl. Phys. Suppl. **33**, 359 (1962).

¹⁶ M. Lax, J. Chem. Phys. **20**, 1752 (1952).

¹⁷ J. J. Markham, Rev. Mod. Phys. **31**, 956 (1963).

¹⁸ R. H. Silsbee, Phys. Rev. **128**, 1726 (1962).

¹⁹ H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).

²⁰ A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273.

representations of the point-symmetry group of the defect.

(2) The defect has only a small effect upon the phonons of the unperturbed lattice; they change in the way described for the F center by McCombie, Matthew, and Murray,¹⁵ i.e., by an enhancement in the amplitude of the phonons in one frequency range at the expense of those in another. The altered distribution of amplitude or strain at the defect versus frequency is assumed to be identical with that of a Debye distribution whose Debye temperature Θ_D is the same for vibrations of all symmetry types. The presence of the defect can be accounted for by allowing Θ_D to differ from Θ_{SH} , the specific-heat Debye temperature. The magnitude of the inequality indicates the strength of the perturbation and reflects upon the validity of the approximation. This Debye approximation is admittedly crude, but the sensitivity of experiments to the exact distribution is very low.

(3) When the defect is excited electronically, its interaction with its neighbors is changed. This is a short-range interaction, extending only as far as the electronic wave functions do. The change in the interaction is directly related to the total strain at the defect. It can be expressed in terms of the vibrational normal coordinates x_{ki} of the defect crystal appropriate to the electronic ground state. One finds that if the change in the interaction is assumed to be limited to the nearest neighbors, it can be expressed by the interaction Hamiltonian H' given by $H' = H'(\sum_i \omega_i x_{ki})$ or, when expressed in a power series, by

$$H' = \sum_k [A_k' \sum_i \omega_i x_{ki} + B_k' (\sum_i \omega_i x_{ki})^2 + C_k' (\sum_i \omega_i x_{ki})^3 + \dots], \quad (1)$$

where a sum is taken over all symmetry types k and all frequencies ω_i . Expressions very similar to H' have been used by Silsbee¹⁸ and Yen *et al.*²¹ for other purposes. The parameters A' , B' , etc., have resulted from an integration over the electronic coordinates. They are related to certain familiar characteristics of configuration-coordinate diagrams— A' to the horizontal displacement of the two parabolas, B' to their difference in curvature, and C' , etc., to nonparabolic distortions. In Eq. (1) we have neglected cross terms between normal modes of different symmetry types. Ultimately, in our analysis all terms in the Hamiltonian higher than second order will be neglected; thus only the second-order cross terms are of concern. They will be discussed later in this paper.

(4) The Born-Oppenheimer and Condon approximations are applicable. These approximations merit further discussion. The Born-Oppenheimer approximation is valid only when electronic states are well

separated from each other.²² It does not apply to electronically degenerate states,²³ but such a situation will be discussed later along with the Jahn-Teller effect. The Condon approximation takes two possible forms: In one the dipole-matrix element for the electronic transition is assumed to be independent of the vibrational coordinates²⁴; in the other it is the oscillator strength, which differs from the matrix element by a frequency factor, which is assumed to be independent.¹⁷ Konitzer and Markham¹ used the latter approach for the F center and we will do so for the aggregate centers because if the former assumption were correct or if the oscillator strength depended upon the vibrational coordinates, the moments of the band would display, among others, the following characteristics¹⁷: The zeroth moment of the band would depend upon temperature; the first moment would increase with temperature; and the second moment would increase with temperature less rapidly than linearly at high temperatures. None of these characteristics were observed in the measurements of the aggregate centers reported in paper I.

The assumptions (1)–(4) are about the simplest ones we can make and still retain the features of a complex interaction involving vibrations of many symmetries and many frequencies. Similar assumptions have been used to describe various other properties of defects in solids such as phonon scattering,²⁵ nuclear²⁶ and electronic¹⁴ spin-lattice relaxation, zero-phonon-line strength and width,²⁷ and Mössbauer effects.²⁸ They are often quite successful in predicting at least the temperature dependence of the phenomena being investigated. The approximations made should be most appropriate for those materials like KCl which have a phonon density of states similar to a Debye distribution.

MOMENTS CALCULATIONS

We will use two different analytical techniques with these assumptions to discuss band shapes. The first, especially useful for a broad band, involves the calculation of its moments. Lax¹⁶ and Markham¹⁷ have presented general discussions of such calculations. Silsbee¹⁸ uses moment calculations as well as many of the assumptions presented above to discuss the broadening of zero-phonon lines. His paper can be used as an example of the techniques employed by us. The advantage of moment calculations is that although transition occurs between ground and excited states whose vibra-

²² D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 365.

²³ C. H. Henry, S. E. Schnatterly, and C. P. Slichter, *Phys. Rev.* **137**, A583 (1965).

²⁴ Reference 22, p. 36.

²⁵ C. T. Walker and R. O. Pohl, *Phys. Rev.* **131**, 1433 (1963).

²⁶ M. J. Weber, *Phys. Rev.* **130**, 1 (1963).

²⁷ D. B. Fitchen, R. H. Silsbee, T. A. Fulton, and E. L. Wolf, *Phys. Rev. Letters* **11**, 275 (1963).

²⁸ V. A. Bryukhanov, N. N. Delyagin, and Yu. M. Kagan, *Zh. Eksperim. i Teor. Fiz.* **46**, 825 (1964) [English transl.: *Soviet Phys.—JETP* **19**, 563 (1964)].

²¹ W. M. Yen, W. C. Scott, and A. L. Schawlow, *Phys. Rev.* **136**, A271 (1964).

tional parts differ because of H' , it is not necessary to determine the excited-state vibrational wave functions. Instead, the moments can be derived from the ground-state vibrational wave functions and H' alone and can ultimately be given in terms of the Debye temperature Θ_D and the parameters appearing in H' . To put these latter parameters in dimensionless form we rewrite H' as follows:

$$H' = \hbar\omega_D \sum_k [A_k e_k + B_k e_k^2 + C_k e_k^3 + \dots], \quad (2)$$

where $\hbar\omega_D = k\Theta_D$ and e_k , which is proportional to the strain at the defect due to all vibrations of symmetry k , is given by

$$e_k = (N_k \omega_D)^{-1/2} \sum_i \omega_i^{1/2} (a_{ki}^\dagger + a_{ki}). \quad (3)$$

a_{ki}^\dagger and a_{ki} are the creation and destruction operators for the mode of symmetry k and frequency ω_i . The summations are made over all N_k of the normal modes of symmetry type k and then over all of the symmetry types. The moments can now be calculated by inserting these expressions for H' into the relations given by Lax and Silsbee. For vibrations of a given symmetry one finds the following:

$$M_1 = \hbar\omega_D \left\{ \frac{3}{4} BU + \frac{27}{16} DU^2 + \dots \right\}, \quad (4)$$

$$M_2 - M_1^2 = \bar{M}_2 = (\hbar\omega_D)^2 \left\{ \frac{3}{4} A^2 U + \frac{27}{16} (B^2 + 3AC) U^2 + \frac{405}{64} (C^2 + 2BD + 2AE) U^3 + \dots \right\}, \quad (5)$$

$$M_3 - 3M_2 M_1 + 2M_1^3 = \bar{M}_3 = (\hbar\omega_D)^3 \left\{ \frac{3}{5} A^2 + \frac{9}{5} (B^2 + \frac{3}{2} AC) U + \frac{27}{8} \times \left[A^2 B + \frac{9}{10} (C^2 + \frac{16}{9} BD + \frac{10}{9} AE) \right] U^2 + \frac{27}{8} (B^3 + 9ABC + \frac{9}{2} A^2 D + \dots) U^3 + \dots \right\}, \text{ etc.} \quad (6)$$

When a bar appears over the various moments, e.g., \bar{M}_2 , it indicates that this moment is calculated by using the value of the first moment M_1 as a reference point. U is the normalized total energy of a Debye solid. It depends parametrically upon Θ_D and is a function of temperature. It is given by

$$U(T) = \sum_i \hbar\omega_i (2n_i + 1) / \sum_i \hbar\omega_i = \frac{4}{\omega_D^4} \int_0^{\omega_D} \omega^3 \coth(\hbar\omega/2kT) d\omega. \quad (7)$$

Examples of this function are shown in Fig. 6 of paper I, where all of the curves are proportional to U and have the different Θ_D values given there. Tabulated values of $C[U(T)-1]$ are available in the literature²⁹; in the reference cited $C = (9/8)R\Theta_D$. If a single mode whose frequency is given by $\omega_c = k\Theta_c/\hbar$ were coupled to the defect instead of a Debye distribution of modes these formulas for the moments would be relatively unchanged. Some of the constants would differ, especially in the formulas for the higher moments, and the function $U(T)$ would be replaced by $\coth\Theta_c/2T$. $U(T)$ and $\coth\Theta_c/2T$ are experimentally indistinguishable if $\Theta_D = 4\Theta_c/3$.

In calculating Eqs. (4)–(6) we have neglected to sum H' over k , the different symmetry types. Gold and Keil³⁰ have shown that ordinarily such a sum in H' leads to moments which are sums of the partial moments for each symmetry type given by Eqs. (4)–(6). When this sum is taken, the number of coupling parameters in the moments formulas is very large—a complete set for each symmetry.

If the experimental data were extensive enough and the coupling parameters converged rapidly enough (in the sense $A_k > B_k > C_k$, etc.), these parameters could, in principle, be uniquely determined. If, on the other hand, only a few of the moments could be measured, for instance the first three, and if we assumed that $0 = C_k = D_k$, etc., then only five relations among the A_k and B_k could be determined by fitting Eqs. (4)–(6) to the data, namely the values of $\sum_k B_k$, $\sum_k A_k^2$, $\sum_k B_k^2$, $\sum_k A_k^2 B_k$, and $\sum_k B_k^3$. If vibrations of only one symmetry were involved, the A and B coefficients would now be overdetermined, but the symmetry of most defects is such that many symmetries are involved so that these five relations are not enough to uniquely determine all the A 's and B 's.

The problems are reduced somewhat because, although all modes have nonzero B values, most have zero A values. Those modes with a nonzero A value can be determined by symmetry arguments. This point has been discussed by Henry *et al.*²⁸ If the symmetrized product of the representation appropriate to either the electronic ground or excited state contains the representation to which a certain vibration belongs, then $A \neq 0$ for this vibration. Accordingly, we find that of the eight modes interacting with the M center only one, the totally symmetric one, has a nonzero A ; of the twenty modes interacting with the F center six (one from the totally symmetric representation, two from the E_g representation, and three from the T_{2g} representation) have a nonzero A , etc. In view of this qualitative distinction between those vibrations which do and those which do not have a zero A value, we shall attempt to treat the data as if vibrations of only two

²⁹ *American Institute of Physics Handbook*, edited by D. R. Gray (McGraw-Hill Book Company, Inc., New York, 1963), Sec. 4, p. 58.

³⁰ A. Gold and T. H. Keil, *Phys. Status Solidi* **13**, 175 (1966).

types existed, one an "even" vibration with A_E^2 and B_E values which are sums of the A^2 and B values for all of the "even" modes, and the other an "odd" vibration with $A_0=0$ and a B_0 value which is a sum of the B values for all of the "odd" modes. This procedure is strictly valid only if one even and one odd mode dominate the interaction, but the precision of the measurements is too low to decide differently. It is a unique property of the third moment that it contains a term proportional to $\sum_k A_k^2 B_k$, which equals $A_E^2 B_E$ in our approximation. The large size of this term makes possible a separate determination of B_E and B_0 . For some of the bands our data are so limited that we are unable to distinguish between B_E and B_0 . In this case we fit the data with a single B parameter which is the sum of B_E and B_0 .

PERTURBATION CALCULATIONS

The second analytical technique that we shall employ, which is especially useful if fine structure in bands is to be investigated, involves a determination of the vibrational wave functions associated with the electronic excited state in terms of the vibrational wave function associated with the electronic ground state and H' by means of a perturbation approach. Ideally, once these wave functions are found, a complete reconstruction of all of the details of a band can be made. Usually, because of the complexity involved, we are limited to small perturbations of the vibrational wave functions, to calculations which are appropriate to 0°K , and to vibrations of only one symmetry.

We will write the total vibrational wave function associated with the electronic ground state $\Phi_g^{n_i, n_j, \dots} = \prod_i \varphi_i^{n_i}$, where $\varphi_i^{n_i}$ is the wave function describing the normal coordinate x_i , n_i is the quantum number of this mode, and the product is taken over all N modes of the lattice. These modes are normalized and orthogonal. At 0°K the only state occupied is $\Phi_g^0 = \prod_i \varphi_i^0$. The total vibrational wave function associated with the electronic excited state, $\Phi_e^{n_i, n_j, \dots}$, can be formally expanded in terms of the $\varphi_i^{n_i}$ of the electronic ground state. For example, the vibrational ground state is

$$\begin{aligned} \Phi_e^0 = S\Phi_g^0 [1 + \sum_i J_{ij} \varphi_i^1 / \varphi_i^0 + \sum_{ij} J_{ij} \varphi_i^1 \varphi_j^1 / \varphi_i^0 \varphi_j^0 \\ + \sum_{ijk} J_{ijk} \varphi_i^1 \varphi_j^1 \varphi_k^1 / \varphi_i^0 \varphi_j^0 \varphi_k^0 + \dots], \quad (8) \end{aligned}$$

where S is a normalization constant. The strength of the zero-phonon line at 0°K , given by the square of the overlap integral of Φ_e^0 and Φ_g^0 , is equal to S^2 . In this expansion products of the form $\varphi_i^n \varphi_i^m / \varphi_i^0 \varphi_i^0$, where all of the subscripts are the same, are to be replaced by $\varphi_i^{n+m} / \varphi_i^0$ and signify that the i th mode is in the $n+m$ vibrational state.

The wave functions Φ_g are solutions to $H\Phi_g = E\Phi_g$ using the unperturbed vibrational Hamiltonian H while

Φ_e are solutions using $H+H'$. By substituting into this equation, Eqs. (2) and (3) for H' , and Eq. (8) for Φ_g^0 , we obtain an infinite set of recursion relations involving the J coefficients and the parameters in H' . These can be solved easily when H' is especially simple. For example, if $B=C=D=0$, etc., Eq. (2) simplifies to $H' = \hbar\omega_D A (N\omega_D)^{-1/2} \sum_i \omega_i^{1/2} (a_i^\dagger + a_i)$, and it can be shown that the parameters in Eq. (8) above are given by $J_i = -A (\omega_D / N\omega_i)^{1/2}$, $J_{ij} = J_i J_j / (2!)^{1/2}$, $J_{ijk} = J_i J_j J_k / (3!)^{1/2}$, etc., and $S^2 = \exp(-3A^2/2)$. For small A , $S^2 \approx 1 - 3A^2/2$. The exponential decrease in S^2 as A^2 increases can be attributed to the $(n!)^{1/2}$ factor appearing in the denominator of the J coefficients. Once the J coefficients are determined, the strength of transitions between any two vibrational states of the electronic ground and excited states can be evaluated by calculating the overlap integrals. The over-all band shape can be then determined by taking into consideration all such terms. Visscher³¹ has performed calculations to determine the line shape expected for a related situation—the Mössbauer line of a defect with similar coupling parameters, coupled to a Debye distribution of phonons. We have calculated the line shape expected at 0°K , using the somewhat more realistic phonon spectrum for KCl calculated by Karo and Hardy³² and a value of 1.7 for A^2 . With this value of A^2 , the line shape is similar to that of the R_2 band. A comparison, shown in Fig. 3, will be referred to later in the discussion of the zero-phonon line.

Another simple case of special interest to us occurs when all of the coefficients in H' are zero except B . Then Eq. (2) simplifies to $H' = \hbar B / N [\sum_i \omega_i^{1/2} (a_i^\dagger + a_i)]^2$, and all of the J coefficients in Eq. (8) with an odd number of subscripts are zero. If B is small it can be shown that S^2 , the zero-phonon-line strength at 0°K , is given by $S^2 \approx 1 - B^2/2$, that $J_{ij} \approx -B(\omega_i \omega_j)^{1/2} / N(\omega_i + \omega_j)$, and that all higher-order J coefficients are negligible. As B^2 approaches the value 1, this approximate expression for S^2 no longer holds both because the higher-order J coefficients rapidly increase in magnitude and, in addition, because the J_{ij} coefficients themselves become more complicated, including terms in B^2 , etc. Thus, when A and B are small, S^2 depends on each of them in qualitatively the same way, i.e., as $1 - 3A^2/2$ and $1 - B^2/2$, but when $B \rightarrow 1$ a difference shows up that is caused by the more complicated nature of the $J(B)$ coefficients. Approximate calculations carried out by us show that this difference causes S^2 and, therefore, the zero-phonon-line strength to approach zero much more rapidly than exponentially as B^2 increases in the neighborhood of one.

As an example of the rapid drop in S^2 when B^2 is approximately 1, consider the case of a defect governed by a single vibrational mode. A simple configurational-coordinate diagram is applicable, and B is proportional

³¹ W. M. Visscher, Ann. Phys. (N. Y.) **9**, 194 (1960).

³² A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

TABLE I. Coupling parameters, Debye temperatures, and zero-phonon line strengths for the aggregate bands in KCl.

Band	Derived from moments				Derived from peak position and width				
	Θ_D (°K)	A^2	B_E	B_0	HW_0' (eV)	$\Theta_{D'}$ (°K)	$A^{2'}$	B'	$S^{2'}$
F^a	189	21	+0.13	-0.6	0.163	189	24	-0.7	10^{-16}
R_1	0.086	190	6.7	...	4×10^{-5}
R_2	0.054	217	2.0	+0.5	5×10^{-2}
M	210	2.6	0	-0.7	0.058	197	2.1	-0.5	2×10^{-2}
N_1	0.062	217	2.7	...	2×10^{-2}
N_2	0.058	164	4.1	-0.9	2×10^{-3}

* The values of Θ_D , $\Theta_{D'}$, and HW_0' for the F band are those of Konitzer and Markham.

to the difference in curvature between the excited- and ground-state curves. One easily sees that when B is negative and sufficiently large the curvature of the upper state is reversed so that no bound vibrational state exists. $S^2=0$ for this situation. The critical value of B^2 is $\frac{1}{4}$.

The calculation of the J coefficients and S^2 becomes even more complicated in more realistic situations, i.e., when both the A and B parameters are nonzero, when several A and B parameters corresponding to different symmetries are involved, or when the C , D , etc. terms in H' must also be considered. It appears that under these conditions the conclusions of the last few paragraphs are still applicable, i.e., if any of the parameters in H' other than A is approximately equal to 1 or more, S^2 will be very small.

SPIN-ORBIT AND JAHN-TELLER EFFECTS

Much of the work done on broad absorption bands due to defects has concentrated on the F center. This is unfortunate, because due to its high symmetry, the F center is in some ways more complicated than most other centers. Its first excited state, for instance, is orbitally degenerate. The degeneracy can be removed and transitions involving this state can be split by perturbations of various kinds which are not important for nondegenerate states. Spin-orbit coupling, the Jahn-Teller effect, and random crystalline strains are three examples of such perturbations. Spin-orbit coupling, an important source of broadening for the F band in heavy alkali halides like the cesium salts, has only a small effect in the lighter salts like KCl.³³ Moran has shown³⁴ that the Jahn-Teller splitting of the F band is also large for the cesium halides due to distortions of E_g and T_{2g} symmetry. If spin-orbit coupling is small, as in KCl, the Jahn-Teller splitting is reduced somewhat since then only T_{2g} modes cause a splitting—the E_g modes contributing to a normal broadened line shape.

Longuet-Higgins *et al.*¹⁹ have discussed the line broadening expected from transitions between states, one of which is a Jahn-Teller split multiplet. They show that in absorption a splitting or gross broadening develops when the degenerate state is the upper one, but that

only a mild distortion of the line shape occurs when the situation is reversed. Thus, transitions from the doublet ground state of the R center, for instance, will not be broadened or split unless the excited state is also a multiplet.

Henry, Schnatterly, and Slichter²³ have included spin-orbit and Jahn-Teller effects in a moments analysis. Within the approximations of their theory the moments of an absorption band which terminates on a degenerate state can be separated into a part solely due to spin-orbit coupling (which is insignificant for F centers in KCl) and the rest, solely due to lattice distortions. The part due to lattice distortions is essentially the same as that calculated above by us except that all coupling parameters other than the A 's were assumed to be equal to zero. The Jahn-Teller (JT) effect manifests itself in the nonzero A values for the E_g and T_{2g} vibrations. If these A values are large, the second moment and half-width of the line, which according to Eq. (5) depend upon $\sum_k A_k^2$, should be large. Schnatterly³⁵ has shown that these vibrations are important for the F center. Thus in a family of related centers like the F and F -aggregate centers one would expect those bands whose transitions terminate on degenerate levels to be significantly broader than the rest.

There is a certain amount of evidence demonstrating this. Table I lists the half-widths at 0°K for the F and various aggregate bands. Those bands that correspond to transitions terminating on nondegenerate excited states, i.e., M , and (according to Silsbee³⁶) N_1 , N_2 , and R_2 , have equal half-widths within 10%, indicating approximately equal coupling to the phonons. The R_1 band, which has a doubly degenerate excited state,³⁶ and the F band, with its triply degenerate excited state, are broader by about 50 and 150%, respectively. Other evidence involves the A center,³⁷ an F center whose symmetry has been lowered and description modified by the presence of an adjacent foreign alkali ion. Under these conditions the triply degenerate excited state of the F center splits into a doubly degenerate and a nondegenerate state corresponding to the F_B and F_A bands, respectively. The F_A band, unaffected by the JT

³³ S. E. Schnatterly, Phys. Rev. **140**, A1364 (1965).

³⁶ R. H. Silsbee, Phys. Rev. **138**, A180 (1965).

³⁷ K. Kojima, N. Nishimaki, and T. Kojima, J. Phys. Soc. Japan **18**, 250 (1963).

³³ D. Y. Smith, Phys. Rev. **137**, A574 (1965).

³⁴ P. R. Moran, Phys. Rev. **137**, A1016 (1965).

effect, has a half-width of about 60% of the F band but the F_B band, still degenerate, has a half-width approximately equal to the F bands.

When the moments analysis of Henry *et al.* is extended to include the bilinear coupling parameters B we find that because the electronic excited state is degenerate, a situation which we have previously ignored occurs, i.e., cross terms between modes of different symmetries appear in H' .³⁰ These cross terms can occur between vibrations belonging either to the same representation or to different representations. To each we must associate a new B parameter whose existence will show up as the following modification to the moments given in Eqs. (4)–(6): M_1 is not changed, M_2 is modified by having the new B^2 parameters added to the old B^2 term which appears as a coefficient of U^2 , and M_3 is modified by having the new B^2 added to the old B^2 term which is a coefficient of U and by important changes to the A^2B coefficient of U^2 . To this coefficient must be added terms like $A_k A_j B_{kj}$ where A_k and A_j are the linear coupling parameters for modes of symmetry k and j and B_{kj} is the bilinear cross-coupling parameter between these modes. An important feature of these terms involves the sign of $A_k A_j$ relative to A_j^2 or A_k^2 . For important cases, e.g., when k and j are vibrations from the same two-dimensional representation, $A_j = -A_k$ so that $A_j A_k = -A_j^2$. Because of this sign reversal and if B_{kj} is large enough, the coefficient of U^2 in M_3 may exhibit a different sign for those bands whose transitions terminate upon a degenerate electronic state compared with those which do not.

These complicated discussions are applicable to the F band. The data, however, are insufficient to separate the cross-coupling B parameters from the quadratic ones. In the initial fit of the moments data we shall assume that the cross-coupling B parameters are zero and later discuss the possibility that this is not the case.

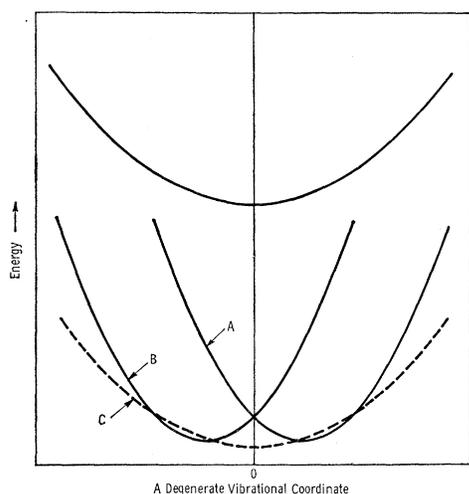


FIG. 1. Configuration-coordinate diagram for a system displaying the Jahn-Teller effect in the electronic ground state.

A situation not covered by Henry *et al.* for which the Jahn-Teller effect is important occurs in absorption for a defect like the R center whose electronic ground state is degenerate. This situation, treated by Longuet-Higgins *et al.*, will be discussed with the aid of the configuration-coordinate diagram shown in Fig. 1. The two solid curves labeled A and B correspond to degenerate electronic states; the coordinate plotted is one of a pair of degenerate vibrational modes. If the other mode were also plotted, the energy diagram (in lowest order) would become a figure of revolution about the vertical axis. The depth of the trough in the lower sheet is proportional to the strength of the electron-lattice coupling. An important feature of the analysis of Longuet-Higgins *et al.* is that for a strong Jahn-Teller effect (the limit which is of interest to us for discussions of the R_2 band³⁶), the lowest-energy vibrational wave functions tend to be concentrated in the vicinity of the trough and have energy levels which are not uniformly spaced but vary approximately as $n(n+1)$, like those of a rotating dumbbell. Because of this property of the ground state the harmonic-lattice approximation made above is violated and the moments analysis and perturbation calculations do not apply unaltered to the various R -center transitions. For most purposes, however, the trough of Fig. 1 can be replaced by a parabola of revolution, indicated by curve C, whose lowest vibrational wave functions approximate to a fair degree those of the trough. The major differences occur on the axis of the figure, but this part of the wave function has little importance when transition probabilities are calculated by performing overlap integrals. A general feature of curve C is that its curvature is less than that of A or B, a property which will be recalled later when we discuss the zero-phonon line of the R_2 band. In our discussion of the moments of the R bands this replacement approximation necessitated by the Jahn-Teller effect in the ground state will be made.

The considerations raised by the Jahn-Teller effect are very complex; the approximations we have had to make because of it place serious limitations upon our attempts to analyze the data. We are indeed fortunate, therefore, to have good measurements of the M band which is a singlet-to-singlet transition and is, therefore, complicated by none of these considerations.

MOMENTS ANALYSIS OF THE DATA

In what follows, the data for the first three moments of the M band given in Figs. 2–4 of paper I will be fitted by various combinations of the function U given in Eq. (7) and its higher powers. First- and second-moment data for the F center are reported by Konitzer and Markham.¹ Third-moment data for the F center can be extracted from the works of Konitzer and Markham and of Schnatterly,³⁵ and are presented in Fig. 2 of this paper. These moment data will also be fitted by the U function and its higher powers. From the co-

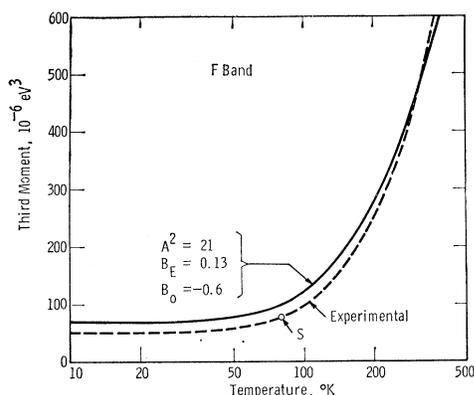


FIG. 2. Third moment of the F band in KCl versus temperature. The experimental curve is constructed from the data of Konitzer and Markham and Schnatterly.

efficients of these terms and the formulas for the moments given in Eqs. (4)–(6) we will attempt to extract unique values for Θ_D and the coupling parameters A , B_E , and B_0 for these bands. We were unable to measure the moments of the remaining bands, but since to a first approximation (exactly for a Gaussian band) the peak position equals the first moment and the half-width equals 2.36 times the square root of the second moment, the data of Figs. 5 and 6 of paper I will be treated as if they were also first- and second-moment data so that approximate information about the coupling parameters for these bands can also be obtained. Because of the lack of moments information, only the A parameter and a single B parameter equal to $B_E + B_0$ will be used to describe them. Hereafter, when we refer to a figure presented in paper I we will prefix the figure number with a I, for example, Fig. I5.

First Moment

According to Eq. (4) the shift in the first moment of a band due to temperature is given by $\Delta M_1 = \frac{3}{4} \hbar \omega_D \times (B_0 + B_E)(U - 1)$, but due to anharmonicities in the crystal that were neglected in our moments analysis, the crystal expands with increasing temperature so as to contribute an additional temperature-dependent shift to the first moment. Jacobs³⁸ has discussed this shift for the F center. To calculate $B_0 + B_E$ we must first subtract from the over-all shift that part due solely to the expansion of the crystal. This can be done if two quantities are known: the thermal-expansion properties of the crystal and the shift in the band due to hydrostatic compression at a constant temperature. Accordingly, we have used the thermal-expansion data for KCl of White³⁹ and the pressure data for the F , M , R_2 , and N_2 bands in KCl of Minomura and Drickamer,⁴⁰

and of Jacobs.³⁸ No pressure data are available for the other bands. The results for the M band are shown in Fig. I2. The dashed line indicates the expected shift in M_1 due solely to the expansion of the lattice. The solid line has been fit to the circled experimental points by the addition to the dashed curve of another term proportional to U with $B_0 + B_E = -1.0$ and $\Theta_D = 210^\circ\text{K}$.

Konitzer and Markham did not report directly upon the temperature dependence of M_1 for the F band, but this information can be obtained from their data. When the appropriate corrections are made for thermal expansion, we find that $B_E + B_0 \approx -0.6$ and $\Theta_D \approx 190^\circ\text{K}$. The same fitting procedure was used with the peak-position data of Fig. I5 (including the M - and F -band data of Konitzer and Markham). The “thermal-expansion” function shown in Fig. I4 describes the frequency shift expected for all of the bands according to a simple model of Jacobs if the shift were due solely to the expansion of the crystal. The pressure data eliminate the need for Jacobs’s model and allow one to construct an “expansion-only” curve for each band which differs from the expansion function shown by a multiplicative constant. When this is done, one finds that the data for each band can be fitted by a sum of the appropriate expansion-only curve and a term proportional to the U function with $\Theta_D' \approx 200^\circ\text{K}$. Typical combination curves of this kind are represented in Fig. I5 by the solid lines. From the fit we conclude that $\Theta_D' \approx 200^\circ\text{K}$ for all of the bands. From the coefficients of U for each band we have calculated the B' values listed in Table I.

These values are called B' instead of B because they have been calculated from the peak position of the band, not its first moment. When a prime is added to any parameter, as in Θ_D' , its signifies that the parameter has been derived from other than moments data and has little theoretical significance unless other information is available to relate the parameter to its unprimed counterpart. The difference between B and B' depends upon the skew of the band. For a Gaussian band $B = B'$; for the M band we can show that $B = B' - 0.5$, i.e., from the first-moment data $B = B_0 + B_E = -1.0$ while from the peak-position data $B' = -0.5$; in the same way we can show that for the F band $B = B' + 0.1$. Other bands which display a skew like any of these bands will have a similar relation between B and B' . Certain evidence suggests that the skew of the R_2 band is like the M bands, so that $B(R_2) \approx 0$, and that the N_2 band is approximately Gaussian, so that $B(N_2) \approx -1$. Since no pressure data are available for the R_1 and N_1 bands our only comment is that if these bands behave under pressure like the others, their B values lie in the range $-0.5 > B > -1$.

Second Moment

In Fig. I6 the half-width data for all of the bands are fitted by the solid lines which represent the function

³⁸ I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

³⁹ G. K. White, Phil. Mag. **6**, 1425 (1961).

⁴⁰ S. Minomura and H. G. Drickamer, J. Chem. Phys. **33**, 290 (1960).

$HW_0' \times U(\Theta_D')$, where HW_0' and Θ_D' are separately chosen for each band to give the best fit at low and intermediate temperatures. These values are tabulated in Table I. The values of A' listed in Table I are calculated from the HW_0' values [Eq. (5)] for the second moment, and the assumption that all bands are Gaussian and all B parameters are zero. Because of these latter approximations the desired A^2 may differ from A'^2 by an amount which we estimate to be of the order of 25%. A systematic deviation of the data from the curves is noticeable in Fig. 16 for several of the bands at high temperatures, but since the uncertainties and scatter in the data are also large at these temperatures, the highest temperature data are shown for only the M band. The deviation from the U function is even more evident for the M band in the plot of its second moment shown in Fig. 13. To fit these data, Θ_L was chosen equal to 210°K and a sum of U and U^2 was taken. The best fit is $\bar{M}_2 = 7.2 \times 10^{-4} (4U/5 + U^2/5)$ eV². Since, according to Eq. (5) of the moment analysis,

$$\bar{M}_2 = (\hbar\omega_D)^2 \left[\frac{3}{4} A^2 U + 27/16 (B_0^2 + B_E^2) U^2 \right],$$

we find $A^2 = 2.6$ and $B_0^2 + B_E^2 = 0.45$ for the M band.

Equation (5) also suggests that if $B_0 + B_E$ is approximately -0.6 for the F band as indicated by its first moment, its contribution to the second moment must be an insignificant part of the large M_2 observed. Because of this no U^2 function should be needed to fit the second moment. In confirmation of this, we can fit the second-moment data of Konitzer and Markham for the F band by using a U function alone with $\Theta_D = 189^\circ\text{K}$ and $A^2 = 21$.

It should be noted that the Θ_D and Θ_D' values used to fit, respectively, the second-moment and half-width data of the M band differ by about 5%. The Θ_D' values shown in Fig. 16 for the other bands are likely to differ from the desired Θ_D by about the same amount. The observed spread among the Θ_D' values, however, is several times this much. This probably reflects a real difference among the centers in the way and extent to which each modifies the phonon spectrum of the unperturbed lattice. The observed order $\Theta_D'(N_2) < \Theta_D'(M) < \Theta_D'(R_2) \approx \Theta_{SH} = 225^\circ\text{K}$ is what one would expect from the theory of McCombie, Matthew, and Murray¹⁵ and the pressure measurements of Minomura and Drickamer⁴⁰ and of Jacobs³⁸ which indicate that the N_2 center is the "softest" and the R_2 the "hardest" of these centers and that the R_2 center is about as "hard" as a normal lattice site.

Third Moment

According to Eq. (6) of the moments analysis,

$$\bar{M}_3 = (\hbar\omega_D)^3 \left[3/5 A^2 + 9/5 (B_0^2 + B_E^2) U + 27/8 A^2 B_E U^2 + 27/8 (B_E^3 + B_0^3) U^3 \right].$$

The third-moment data for the M band are compared in Fig. 14 with four curves which correspond to this ex-

pression with those values used for A^2 and Θ_D which were determined by \bar{M}_2 , i.e., $A^2 = 2.6$ and $\Theta_D = 210^\circ\text{K}$. The (B_E, B_0) values for these curves are $(0, -1.0)$, $(0, -0.67)$, $(-1.0, 0)$, and $(-0.67, 0)$. The fit is poor when $B_0 = 0$ but fair when $B_E = 0$. Superficially the fit could be further improved by modifying the values of A^2 or Θ_D , by allowing the coupling parameters C , D , etc. of Eq. (2) to assume nonzero values, or by including in \bar{M}_3 still higher powers of U . In view of the low precision of the experimental measurements of the third moment, such a procedure would be misleading.

It is a general property of the expressions for the moments that the lower moments can be expressed adequately in terms of a few parameters and the function U alone while the higher moments place more emphasis on the higher-order coupling parameters and require in addition to U many of its higher powers. If C , D , etc., do play an important part in explaining the moments, several difficulties arise. Among these are: One of our original assumptions was that the unperturbed lattice was approximately harmonic, i.e., that no C , D , etc., terms were present in H . If such terms are important in H' , they probably are in H also so that the original assumptions are violated. A second problem has to do with the cross terms in H' , some of which were neglected. This assumption is invalid if the C and higher parameters cannot be ignored.

For these reasons and because of the limited validity of some of the other approximations we have made, no attempt will be made to achieve a better fit of the third-moment data for the M band. The conclusions drawn are that some coupling parameters other than A are large; that B_0 is one of them and is equal to about -0.7 ; and that B_E is small. These conclusions are in approximate agreement with the results drawn for the M band from the first and second moments. The conclusions with respect to B_E and B_0 seem quite reasonable on theoretical grounds. Negative B values are expected as a result of the more diffuse nature of the electronic excited state. The magnitude of B_0 is expected to exceed that of B_E if only on the basis of the large number (7) of symmetry modes contributing to it compared to the single mode contributing to B_E .

Figure 2 shows a similar plot of the third moment of the F band versus temperature. The dashed experimental curve was constructed for the F band from three measurements of other experimenters: (1) the value of \bar{M}_3 measured at 80°K by Schnatterly³⁵ labeled S on Fig. 2; (2) the observation of Konitzer and Markham¹ that the shape of the F band does not change between 10 and 300°K; and (3) the relation given by Konitzer and Markham for the half-width of the F band versus temperature. The accuracy of this curve is probably poor. As an example of this, we have made a crude third-moment determination of the F band from the publishing curve, No. 7, of Konitzer and Markham and

find disagreement by about a factor of 2 with Schnatterly's value.

This discrepancy is illustrative of the precision attainable in moment measurements, i.e., Konitzer and Markham, and Schnatterly differ by about 1% in M_1 , 10% in M_2 , and factor of 2 in M_3 . The F band is especially difficult because of problems associated with the overlapping K band. In spite of these discrepancies the experimental curve of Fig. 2 is assumed to be qualitatively correct.

The solid theoretical curve of Fig. 2 is constructed using the parameters $A^2=21$ and $\Theta_D=189^\circ\text{K}$ determined above from M_2 . The values chosen for B_E and B_0 to fit the curve, i.e., $B_E=+0.13$ and $B_0=-0.6$ are such that $B_0+B_E\approx-0.5$, in agreement with the first-moment measurements, and such that $B_0^2+B_E^2\approx 0.4$, a value too small to be apparent in the second-moment data. If the values of B_0 and B_E used in the theoretical curve were interchanged, the new curve would be shifted completely off of the graph of Fig. 2. Thus, as in the case of the M band, a reasonably good fit to all of the available data occurs if unique values are chosen for Θ_D , A^2 , B_0 , and B_E and all other parameters are set equal to zero. The entirely different dependence of M_3 for the F and M bands can be traced to the large positive term in M_3 (for the F band) which contains the product A^2B_E . This term dominates the other terms in M_3 for the F band because A^2 is so large. The positive value indicated for B_E is unusual; it may result somehow from the contributions to B_E of those modes which are involved in the Jahn-Teller effect. An alternate explanation for the positive A^2B_E term may be found in the discussion presented above of the bilinear cross-coupling parameters B_{jk} . They are not zero for the F band, but cause new coefficients to be added to A^2B_E of the form $A_jA_kB_{jk}$. If these terms dominate in the third moment, A_jA_k as well as B_{jk} may be negative giving a positive coefficient $A_jA_kB_{jk}$ which would explain the observed sign. The data is unable to resolve these possibilities. In any case, the Jahn-Teller effect appears to be intimately involved in the explanation of the third moment of the F band.

Zero-Phonon Line

Among the aggregate bands, the R_2 band is anomalous because of its structure and the unusual shift of its peak position with temperature, which is shown in Fig. 15. Both of these features suggest a low value of B . We would like to make third-moment determinations to confirm this, but because of the strong overlap of the different bands we cannot do so. We choose instead to make an arbitrary assumption about the coupling parameters, calculate a theoretical line shape, and compare it with the observed shape to see if it agrees well enough to confirm the choice of parameters. If the A 's and B 's are completely unknown this is an extremely

long process. Keil⁴¹ has outlined a procedure for especially simple cases, i.e., for either $A=0$ or $B=0$ and for vibrations of only one symmetry and one frequency. We chose to perform the calculations at $T=0^\circ$, assume that all $B=0$, explore values of A^2 near the value of 2.0 suggested by the half-width of the R_2 band, assume that vibrations of only one symmetry are important, and use the phonon distribution calculated for KCl by Karo and Hardy³² instead of a Debye distribution. Karo and Hardy's function differs from the Debye distribution by the absence of a discontinuity at ω_D and by the presence of structure at lower frequencies. The application to the R_2 band of this distribution function, which is appropriate for the unperturbed lattice, is provisionally justified by the good agreement of the Θ_D' value (217°K) found for the R_2 band from the half-width data and Θ_{SH} (225°K).

The calculation of the band shape is performed by the perturbation method discussed in the theory section above. The value of A^2 used to derive the curves shown in Fig. 3 is 1.7. The contributions to the band shape due to one-phonon, two-phonon, etc. transitions are shown in Fig. 3 by the dashed lines. The sum of these is the solid line which is to be compared with the experimental broken line of Fitchen *et al.*²⁷ The areas under the solid and broken curves have been adjusted to be approximately the same. The calculated fractional strength of the zero-phonon line is 0.08 while the observed value is 0.02. When selection rules which govern the zero-phonon line are considered,³⁶ the calculated value must be reduced into somewhat better agreement with the observed value. The selection rule we refer to forbids the R_2 band transition to occur for certain

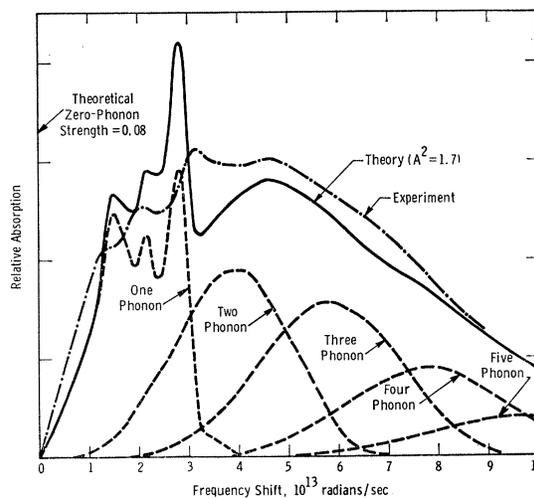


Fig. 3. Shape of the R_2 band in KCl at 0°K . The experimental curve is from Fitchen *et al.* The theory curve is calculated from perturbation theory and the phonon distribution of Karo and Hardy. The contributions to it from the production of one, two, etc. phonons are shown by the dashed curves.

⁴¹ T. H. Keil, Phys. Rev. **140**, A601 (1965).

polarizations of light unless phonons are also created (or destroyed). Our theory has ignored such selection rules and thus predicts a zero-phonon line which is too large.

The crude agreement of the calculated shape of the R_2 band and the strength of its zero-phonon line with observed values are taken as evidence supporting the assumption that $B \approx 0$. Nonzero B values tend to reduce the zero-phonon line and smear out the structure of the band. Part of the deviations observed between the experimental and theoretical curves of Fig. 3 may be due to deficiencies in Karo and Hardy's calculations. A check of their distribution function can be carried out for KBr (but not KCl) by comparing it with the results of neutron-diffraction experiments of Woods *et al.*⁴² The comparison shows deviations of about the magnitude seen in Fig. 3. Any remaining deviations can be blamed on the approximations made by us that the phonon spectrum has the frequency spread of the unperturbed lattice, and that the Jahn-Teller effect in the ground state can be adequately handled by the replacement approximation we have introduced.

Attempts can obviously be made to match the peaks and bumps in the theoretical and experimental curves of Fig. 3. This is equivalent to the efforts of Pierce¹³ to match the experimental R_2 band absorption peaks with singular points in the dispersion curves calculated by Karo and Hardy, except that our procedure excludes from consideration many of these points which do not show up as peaks in the theoretical density-of-states curve. Neither procedure gives a very convincing match, illustrating the need for more reliable density-of-states curves.

The reasonable agreement of Fig. 3 does not rule out a small value for B . Other observations, for example, of the thermal broadening of the zero-phonon line²⁷ also suggest that B , although small, is not zero. Therefore, the results of theories which ignore B , such as that of Fitchen *et al.*²⁷ dealing with the temperature-dependent strength of the zero-phonon line, should be in only approximate agreement with their data. Specifically, their experimental Θ_D' value of 170°K for the R_2 band is probably no more significant than our value of 217°K since both determinations assume that $B=0$ (and ignore the Jahn-Teller effect).

Table I shows estimated values of $S^{2'}$, the strength of the zero-phonon line at 0°K, for the various bands calculated from $A^{2'}$ when all B 's are assumed equal to zero. The values of $S^{2'}$ imply that the zero-phonon line should be seen for all of the bands except the F and, possibly, the R_1 band. The fact that, to the contrary, none are observed for the R_1 , M , N_1 , or N_2 bands is consistent with the values of B implied by the moments

data and the arguments presented in the theory section which conclude that no zero-phonon line should be evident for such large B values.

We believe that the unique nature of the R_2 band, which is related to its low B value, derives from the properties of its degenerate ground state. As explained above, the degeneracy of the electronic ground state causes its vibrational wave functions to be unusually spread out. If the vibrational wave functions for the electronic excited state are also quite extended, which appears to be the normal situation judging from the negative sign of B for all of the other bands, B will be small for the R_2 band and the overlap integral contributing to the zero-phonon strength of the R_2 band will be large.

CONCLUSIONS

The shape of the aggregate bands is governed by interactions with phonons of a wide band of frequencies. Their distribution can, for most purposes, be adequately approximated by a Debye distribution whose characteristic frequency is close to that of the unperturbed crystal, but varies slightly from band to band. This variation is of the nature expected from the theory of McCombie, Matthew, and Murray and from experimental determinations of the "softness" of the different centers.

The characteristics of the bands are dominated by the influence of the linear coupling parameter A . The F and R_1 bands, which involve electronically degenerate terminal states, have larger A values than the other bands due to the Jahn-Teller effect. Except for the R_2 band, all of the bands have bilinear coupling parameters B in the range $-0.5 > B > -1.0$. Values of this magnitude are sufficiently large to strongly affect the shape of the bands and the frequency shift of the bands with temperature, and to cause a reduction in the strength of the zero-phonon lines to the extent that they cannot be observed.

For the R_2 band $B \approx 0$. Because of this a large zero-phonon line and other structure which is probably related to peaks in the density of phonon states can be observed. This unusually low value of B is probably associated with modification of the ground state brought about by the Jahn-Teller effect.

In those cases where the experimental information is most complete, i.e., the F and M bands, it is necessary to include vibrational modes of at least two different symmetries, "odd" and "even," to fit the data. For these bands it is found that $|B_0/B_E| > 1$.

ACKNOWLEDGMENT

The author wishes to express his thanks to Dr. J. Murphy for his many suggestions offered during the course of this work.

⁴² A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, *Phys. Rev.* **131**, 1025 (1963).