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ZERO-PHONON TRANSITIONS AND VIBRATIONAL STRUCTURE

par A. E. HUGHES (1)


Abstract. — This paper reviews some of the progress made during the last few years in understanding and exploiting the vibrational structure observed at low temperatures in the optical spectra of colour centres. The discussion refers particularly to $F$ aggregate centres in the alkali halides. A short theoretical introduction to the physical reasons for the appearance of this structure is given in terms of a simple model, followed by a description of the results of two main types of experiment and their interpretation. These are: 1) the analysis of phonon-assisted structure in terms of the vibrational modes of a crystal containing a point defect and 2) the investigation of the structure of colour centres using uniaxial stress splitting of the zero-phonon lines. The results of both these classes of experiment will be used to discuss the isotope shifts observed for zero-phonon and phonon-assisted transitions in LiF and LiF.

Résumé. — On passe en revue certains progrès faits ces dernières années dans la compréhension et l'emploi des structures vibratonnelles observées, à basse température, dans les spectres optiques des centres colorés.

La discussion porte en particulier sur les centres complexes des halogénures alcalins. On donne, en admettant un modèle simple, une courte introduction théorique aux raisons physiques qui font apparaître cette structure, puis on décrit les résultats de deux types principaux d'expériences et leur interprétation.

Ce sont : 1) l'analyse d'une structure à phonons, d'après les modes vibrationnelles d'un cristal contenant un défaut ponctuel, et, 2) la recherche de la structure des centres colorés à partir de la décomposition des raies à zéro phonon par tension uniaxiale. Les résultats de ces deux sortes d'expériences servent à discuter les déplacements isotopiques des transitions à zéro phonon et celles où interviennent des phonons dans $\text{LiF}$ et $\text{LiF}$.

1. Introduction. — In the last few years a great deal of attention has been given to the fine structure which appears on some colour centre absorption bands at low temperatures. This structure consists of a sharp « zero-phonon » line on the low energy (long wavelength) side of the band, accompanied by broader phonon-assisted lines extending to higher energies. The width of the zero-phonon line is usually only a few cm$^{-1}$ (see section 2), so that it is potentially valuable as a sensitive probe into the static and dynamic state of the crystal lattice near the defect. Furthermore, the vibrational structure can give information about the vibrational modes which interact with the centre. The first observation of fine structure on a colour centre absorption band was made in 1953 by Delbecq and Pringsheim [1], who found structure on the $R_2$ and $N_1$ bands in LiF. The significance of this structure was not, however, fully appreciated at the time, and although studies of the sharp lines in LiF continued [2], [3] it is only in the last four years that a concerted effort has been made to understand and exploit the phenomenon.

This upsurge in activity follows the work of Fitchen et al. [4], who showed that the sharp structure was not confined to LiF, but also occurred for numerous colour centres in other alkali halides. These authors drew the analogy between sharp optical lines and the Mössbauer effect, which has in many ways influenced the understanding of the phenomenon [5]. The existence of sharp optical lines in solids has, of course, been known for many years in the spectra of rare earth and transition metal impurities, but even in these systems the vibrational structure has only recently become a subject of widespread interest [6].

The purpose of this paper is to describe the various kinds of experiments which have made use of the fine structure of colour centre bands, and to discuss their interpretation and the information which the results provide. It will naturally prove impossible to give a comprehensive review, and the approach will therefore be to select one or two examples from the wealth of available data. The examples chosen will be of experiments on $F$ aggregate centres in the alkali halides, although similar studies have also been made on other ionic crystals, notably MgO [7] and CaF$_2$ [8], and also in diamond [9]. The experiments which will be describ-

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ed fall into two main categories: firstly work on the interaction of the centre with the lattice vibrations, which includes the interpretation of vibrational structure as well as the factors governing the appearance and character of the zero-phonon line, and secondly the investigation of defect structure by studying the zero-phonon line under external perturbations. In the latter case the use of uniaxial stress has proved most fruitful, although magnetic and electric fields have also been tried. Examples from both these categories will be given in sections 2, 3 and 4. In section 5 a description of isotope effects in LiF enriched with $^7$Li and $^6$Li will be given, where information from both the vibrational structure and stress effects are required to interpret the results. Before going on to describe these experiments a simple theoretical model for the optical absorption (or emission) process at a localized defect will be presented, in order to give a quantitative basis for understanding why some bands show structure and others (e.g. the F centre) do not. The results of the analysis will also be useful in providing a background for the sections which follow.

2. The Configuration Coordinate Model. — The physical basis of this model for the description of the optical properties of localized centres in solids has been well documented [10] and is based on the adiabatic Born-Oppenheimer approximation. The model assumes that the electronic states of the centre interact appreciably with only one normal mode of the lattice $Q$, and that in the electronic ground state the equilibrium position of the ions is $Q = 0$. In the excited electronic state the equilibrium position is at $Q = \Delta$, and in general the shape of the potential energy curve differs from that for the ground state. Both curves are assumed to be parabolae i.e. the vibrations are harmonic. The scheme is shown in figure 1.

In the Born-Oppenheimer approximation the wave functions of the system are given by:

- ground electronic state $\Psi_{i,m} = \phi_i(r, Q) \chi_m(Q)$
- excited electronic state $\Psi_{f,n} = \phi_f(r, Q) \chi'_n(Q)$

where $r$ is the electronic coordinate, $m$ and $n$ are vibrational quantum numbers and $\chi_m(Q)$ and $\chi'_n(Q)$ are harmonic oscillator wave functions (Hermite polynomials). The dipole matrix element for an optical transition between the ground and excited states is then given by

$$M = \langle \Psi_{f,n} | \phi_f | \Psi_{i,m} \rangle.$$ 

In the usual Condon approximation the electronic wave functions $\phi_i(r, Q)$ are assumed to be slowly varying functions of $Q$, so that $M$ may be factored into two parts:

$$M = \langle \phi_f | \phi_i \rangle < \chi'_n | \chi_m >.$$ 

The square of the first matrix element determines the overall strength of the transition i.e. the oscillator strength, whilst the band shape is determined by the vibrational overlap matrix element. The probability that the transition takes place between the vibrational levels $m$ and $n$ is thus proportional to $| < \chi'_n | \chi_m > |^2$, and the transition energy is

$$E_1 + (n + \frac{1}{2}) \hbar \omega' - (m + \frac{1}{2}) \hbar \omega$$

(see Fig. 1). The transition $m = n$ involves no net excitation of vibrational quanta, and is thus the zero-phonon line.

If the coupling to mode $Q$ is purely linear then $\omega' = \omega$, and the overlap matrix elements are easily calculated (see for example Kiel [11]). It is simplest to consider first the case at $T = 0$, when the only occupied state is $m = 0$. The probability for a transition involving $n$ vibrational quanta is then given by:

$$P_{n=0} = e^{-S} \frac{S^n}{n!}$$

(1)

where $S = E_2/\hbar \omega$ (see Fig. 1). Equation (1) defines the shape of the absorption band at low temperatures, the shape function $P_{n=0}$ being called the Pekarian [12].

Examples of the shape function for $S = 1$ and $S = 4$ are shown in figure 2. For large values of $S$ the maximum value of $P_{n=0}$ is at $n = S$, in accord with the Franck-Condon principle, and the shape approximates to a Gaussian. Since $P_{n=0}$ is normalized to unity, the transition probability of the zero-phonon line relative to the whole band is $e^{-S}$. The reason for the appearance

![Fig. 1. — Configuration coordinate diagram.](image-url)
of structure on only some bands is now clearly seen: as $S$ increases the zero-phonon probability decreases exponentially, and is only observable in practice for $S \lesssim 6$. The reason the zero-phonon line is seen at all is simply because it is not broadened by coupling to a continuum of normal modes of differing frequencies. This broadens the phonon-assisted peaks $(n \neq 0)$ but not the zero-phonon line. In principle the width of the zero-phonon line at $T = 0$ should be determined only by lifetime broadening, but in practice it is several cm$^{-1}$, about four orders of magnitude larger than a lifetime of $10^{-8}$ s would suggest. This is thought to be caused by random strains of $10^{-10}$ in the lattice, but very little quantitative work has been done on this point.

It follows from equation (1) that $\bar{n} = S$ and $(n - \bar{n})^2 = S$, so that the first moment and width of the band are proportional to $S$ and $\sqrt{S}$ respectively. In fact

$$S = \left( \frac{H_0}{2.36 k_0} \right)^2$$  \hspace{1cm} (2)

where $H_0$ is the band halfwidth at $T = 0$.

The simple single mode picture discussed above may be extended to include all modes if only linear coupling is assumed. The strength of the interaction with mode $Q_i$ of frequency $\omega_i$ is then written $S_i$, and the probability for a transition involving $n_i$ quanta in mode $i$ etc. is then given at $T = 0$ by:

$$P = e^{-S_i} \prod_i \frac{S_i}{n_i!}$$  \hspace{1cm} (3)

the transition being displaced from the zero-phonon line by $\hbar \sum n_i \omega_i$. The zero-phonon probability is thus again of the form $e^{-S}$, where $S = \sum S_i$. By summing equation (3) over all combinations of $n_i$ such that $\sum n_i = n$ it is possible to show that the total probability for all $n$-phonon processes is given by an expression identical to equation (1). Furthermore the first moment of the whole band is given by

$$\frac{\hbar}{\omega} \sum n_i \sum_i n_i \omega_i = Sh \omega$$  \hspace{1cm} (4)

where

$$\omega = \frac{1}{S} \sum S_i \omega_i$$  \hspace{1cm} (5)

The expression for the first moment is thus analogous to that for the single mode case.

When $T > 0$ higher vibrational levels of the ground state become thermally occupied, and the overall band shape becomes modified. In the single mode case the transition probability for the $n$-phonon process then becomes [11]

$$P_n = \left( \frac{m + 1}{m} \right)^{n/2} e^{-S(2m + 1)} I_0[2 S \sqrt{m(m + 1)}]$$  \hspace{1cm} (6)

where $m = (e^{\hbar \omega / kT} - 1)^{-1}$ and $I_0$ is a Bessel function with complex argument. Since $I_0(z) \approx 1 + z^2$, at low temperatures the zero-phonon probability $P_0$ is

$$P_0 = e^{-S \coth(\hbar \omega / 2kT)}$$  \hspace{1cm} (7)

which decreases with increasing temperature.

For interaction with many modes equation (7) may be generalized to

$$P_0 = e^{-S \coth(\hbar \omega / 2kT)}$$  \hspace{1cm} (8)

The dropping of the Bessel function is of greater validity in equation (8) than in (7), because the individual $S_i$ may be made arbitrarily small $(\sim 1/N)$ if the interaction is with non-local modes. If local modes are involved then this is not so and equations (7) and (8) may require modification. This 'Bessel function enhancement' has been discussed for the Mössbauer case by Lax and Waller [13], and hinges on a precise definition of which transitions contribute to the zero-phonon line at elevated temperatures when there is a local or 'Einstein' mode present. Some of the difficulties have been discussed by Silsbee [14].

For a Debye spectrum of coupled modes $S_i \propto 1/\omega_i$ [15], and equation (8) becomes

$$P_0 = e^{-S \left\{ 1 + \frac{2 \pi^2}{3} \left( \frac{T}{\theta_D} \right)^2 \right\}}$$  \hspace{1cm} (9)

Fitchen et al. [4] have plotted log $P_0$ against $T^2$ for the $R_2$ bands in several alkali halides and their results
are shown in figure 3a. It can be seen that the points do lie on a straight line, and the derived values of $\theta_D$ are shown. These are all rather lower than the values from specific heat measurements (e. g. for LiF the specific heat value is $\sim 700 \, \text{OK}$), which is not surprising since the spectrum of coupled modes measured from the one-phonon sideband is clearly not a Debye spectrum. The plot of $\log P_0$ vs. $T^2$ is, in fact, relatively insensitive to the precise form of the spectrum. Kazumata et al. [16] have recently performed a similar analysis on lines in LiF and NaF.

![Figure 3](image)

**Fig. 3.** — The temperature dependence of (a) the relative integrated absorption $I/I_b$ ($= P_0$), and (b) the halfwidth of the zero-phonon line, for $R_2$ bands in the alkali halides. (After Fitchen et al. [4].)

So far only linear coupling has been discussed. Quadratic coupling makes $\omega' \neq \omega$ (see Fig. 1) and also, in the many-mode case, mixes the different $Q_i$. The qualitative effects are easily seen by referring to the single mode picture of figure 1. If $\omega' \neq \omega$ then the various $n \rightarrow n$ transitions, which contribute to the zero-phonon line intensity, occur at slightly different energies for different values of $n$, so that the line becomes broadened and shifted. In the many-mode picture the broadening arises from «Raman» transitions in which a phonon in one mode disappears and a phonon in another mode is created. This description is, of course, somewhat awkward in the single mode case [14]. The shift in the single mode case is given by

$$\Delta E(T) = \hbar (\omega' - \omega) \bar{m}$$

where $\bar{m}$ is defined as before.

The observed temperature dependence of the width of the $R_2$ zero-phonon lines is shown in figure 3b, and shows the form qualitatively expected from the discussion above. For a quantitative discussion of the observed widths the reader is referred to the literature [15]. The quadratic interaction will be discussed further in section 5.

The theory described in this section has emphasized simplicity rather than formal rigour, with a view to providing a background for the following sections. There is a wealth of literature on more formal treatments of this problem and some examples are cited in the references [15], [17].

3. Vibrational Structure. — In the previous section the coupling of a defect to lattice vibrational modes was discussed without particular reference to the types of mode involved. The normal modes of a crystal containing a defect may be divided into three kinds: lattice modes, pseudo-localized or resonant modes, and localized modes. The lattice modes approximate closely to the normal modes of the perfect crystal, and have the same amplitude throughout the whole crystal, except near the defect where there may be some small modification. On the other hand the resonant modes, although not strictly localized since their frequencies lie within the continuum of lattice modes, have a high amplitude near the defect and even a small number or density of resonant modes can give an appreciable contribution to the vibrational structure observed. The truly localized modes have frequencies outside the lattice mode spectrum, and amplitudes which decrease exponentially with distance from the defect. In general if all three types of mode exist for a given defect, then they will all contribute to the observed spectrum, provided certain selection rules are obeyed. These selection rules take on a particularly simple form when the electronic states of the defect are non-degenerate (or Kramers doublets). Since the electronic-vibrational interaction is essentially of the form $\sum q_i Q_i$, where the $q_i$ are electronic operators, it follows that the interaction with $Q_i$ is governed by a matrix element $< \phi | q_i | \phi >$. If $\phi$ is non-degenerate then this matrix element is only non-zero if $q_i$, and hence $Q_i$, belongs to the identity representation ($A_1$) of the point group of the defect. Thus only
modes of $A_1$ symmetry contribute to the vibrational structure. These selection rules have not yet proved of great value in understanding the situation for colour centres, but will be mentioned again later in this section.

Most workers in the field of colour centre zero-phonon lines have also analysed vibrational structure, the most comprehensive studies being those of Pierce [18], [19]. Pierce found that for a wide range of bands in several alkali halides the phonon-assisted peaks could usually be compared with pure lattice modes at the Brillouin zone boundary. The examples discussed in this section will be the $N_1$ and $N_2$ bands in NaCl, which are of interest because they show coupling to two kinds of mode. The $N_1$ band occurs at 8 260 Å with its zero-phonon line at 8 373 Å at 4°K, and has the most complex vibrational structure observed for a colour centre. The structure has been analysed by Pierce [19] and, in higher resolution, by Hughes [20]. Uniaxial stress measurements on the zero-phonon line [20] (see also section 4) show that the defect has monoclinic I symmetry [21] with the optical transition moment directed along a $<112>$ axis. The $N_1$ band is at 8 560 Å, with its zero-phonon line at 8 680 Å. This defect also has monoclinic I symmetry, this time with a $<110>$ transition moment [19]. The two bands are, however, not correlated in intensity. The most probable models for these two centres are the aggregates of 2, 3 and 4 $F$ centres described by Johannson et al [22].

The vibrational structure for the two bands is shown in figure 4, plotted as a function of the vibrational frequency $\omega$. Also shown plotted, curve (b), is the theoretical phonon density of states $N(\omega)$ calculated by Karo and Hardy [23]. It can be seen that peaks 2, 11 for the $N_1$ centre show features which are similar to the sharp peaks and critical points in $N(\omega)$, in particular peak 2 corresponds well to a critical point which is associated with the TA mode at the [100] Brillouin zone boundary. There is not such a good correspondence for the $N_2$ centre, but again the [100] TA mode appears strongly. It is thus tempting to interpret all these peaks as being due to extended lattice modes. However peak 1 for the $N_1$ band and the first peak for the $N_2$ band occur at a frequency where $N(\omega)$ is small, and it is suggested that these peaks are due to resonant modes. It is also possible that the third peak for the $N_2$ band is of this type, as it does not fit in well with $N(\omega)$. It is interesting to note that the frequencies of the resonant modes are virtually identical for the two bands, suggesting that the defects responsible have a rather similar structure.

The values of $S$ may be measured for the $N_1$ and $N_2$ bands from the integrated intensity of the zero-phonon line relative to the whole band, which should be $e^{-S}$ from equation (1). The values found in this way are about 4 for the $N_1$ band [20] and between 2 and 3 for the $N_2$ band [19]. Since these values of $S$ substituted in equation (4) for the centroid of the band yield values for $\bar{\omega}$ close to that observed for the resonant modes, one is led to conclude that the dominant interaction for both $N_1$ and $N_2$ bands is with the resonant modes. The other peaks, resulting from weaker interaction with lattice modes, are then superimposed on a band involving multiphonon processes of the resonant mode frequency. Peak 12 for the $N_1$ band could in fact be the fourth component of this series. This interpretation is thus consistent with the measured values of $S$.

The prominent peak in $N(\omega)$ at $\omega \approx 4 \times 10^{13}$ c/s is not reproduced in either of the observed spectra, but this critical point is not a true Van Hove singularity and has not been identified with any particular features of the dispersion curves. It may be that it is an 'accident' of the particular theoretical model used, or that it is genuine but excluded by a selection rule of the type discussed earlier. The selection rules do give some further information for the two bands discussed here. The [100] TA mode in the alkali halides involves a shearing motion of neighbouring (100) planes, and hence has odd parity about a lattice point [24]. This means that if the $N_1$ and $N_2$ centres have their centre of symmetry on a lattice site, interaction with this mode is forbidden. The appearance of this mode in the spectra thus rules out any model for these defects which has $C_{2h}$ (monoclinic) symmetry, and is centred on a lattice.
It is comforting that neither the $F_2$ nor $F_4$ model [22] falls into this category, and in fact the [100] TA mode has some components of $A_1$ symmetry about the centre of symmetry of these models, which is halfway between two halogen ions along a $<110>$ direction. The $F_3$ [22] model has $C_2$ symmetry so the TA mode is allowed anyway for this case. The selection rules thus do give some extra information about the defect structure for these two centres. When the electronic states are degenerate the selection rules are different, because of the possibility of a Jahn-Teller effect. This point will be briefly discussed in section 4.

The examples of vibrational structure quoted in this section demonstrate quite well the extent to which confident interpretation can be made of the observed spectra. The overall picture at the present time seems to be that in most cases interaction with lattice modes is important, and in some cases, such as the ones described here, resonant modes are observed. No case of a truly localized mode has yet been observed for a colour centre, although internal molecular vibrations are observed for systems such as the NO$^-$ ion in KBr [25]. Many questions, however, remain unanswered, such as the extent to which the observed 'lattice' modes are perturbed by the defect, and these will only be answered when the vibrational modes of these complex defects are better understood.

4. Uniaxial Stress Effects. — The most profitable results for the symmetry and structure of defects using zero-phonon lines have been obtained from uniaxial stress experiments. The splitting of a spectral line associated with a localized centre in a solid is due to the lifting of degeneracy of the centre. This degeneracy can involve both orientational and electronic degeneracy, either separately or together. The theory of uniaxial stress effects has been widely discussed in the literature following the work of Kaplyanskii [21], [26], and it is not proposed to go into details here. The experimental measurements provide the number of components into which the line splits for a given crystallographic direction of stress, the intensity and polarization of the components, and the energy shift of each component. From these the symmetry of the centre and of the electronic states involved in the optical transition can be deduced. The usual experimental procedure is to apply stress along the [100], [111] and [110] axes, and to examine the spectra with light polarized with $E$ parallel ($\pi$) and perpendicular ($\sigma$) to the stress. Under [110] stress the crystal becomes biaxial and there are two independent $\sigma$ patterns, corresponding to light propagating in the [001] and [110] directions. Various experimental arrangements have been used for applying the stress, and descriptions of these may be found in the references [9], [19].

The example described here will be the $R^+$ centre in LiF, which has a zero-phonon line at 4874 Å with a halfwidth at 4 K of 5 cm$^{-1}$. This line has been studied by Hughes and Runciman [27], Farge et al. [28] and Baumann et al. [29], and the defect identified partly on the basis of the stress results. The discussion here will refer to the line in absorption. Figure 5 shows the observed spectra, and the schematic diagrams above each spectrum show the theoretical intensities and polarization for a trigonal $A \rightarrow E$ transition. $L$ denotes the propagation direction of the measuring light.

Each spectrum show the theoretical intensities and polarization expected for an $A \rightarrow E$ transition within a centre of trigonal symmetry. The fit is seen to be excellent, even the '1/6' component in the [111] pattern being detected. The splitting between the two long wavelength components under [110] stress is very small, but a shift between $\pi$ and $\sigma$ components for
L $\parallel [001]$, which is absent for L $\parallel [11\bar{0}]$, indicates the presence of a splitting. The symmetry of the defect and the electronic states are thus uniquely determined from these results. A check on the symmetry assignment may be made by examining the energy shift of each component in the patterns. The perturbation $V$ experienced by the defect due to the stress may be written

$$V = \sum_{i,j} A_{ij} \sigma_{ij}$$

where \{\sigma_{ij}\} is the stress tensor and the $A_{ij}$ are electronic operators. By recasting $V$ into irreducible form it may be shown [30], [31] that the energy shifts of the components in the trigonal $A \rightarrow E$ stress splitting patterns may be expressed in terms of four independent parameters $A_1, A_2, B$ and $C$. The first two describe the removal of orientational degeneracy and the last two the removal of electronic degeneracy. The experimental results are shown in figure 6, the straight lines indicating the theoretical shifts for each line shown on the right hand side of the diagram, with the following values of the parameters (in cm$^{-1}$/kg/mm$^2$):

$$A_1 = 0.35$$
$$A_2 = -0.70$$
$$B = -0.26$$
$$C = -0.25.$$

The consistency of the fit confirms the symmetry assignment, and the linearity of the stress shifts justifies the use of the linear form in equation (11).

This analysis may be carried one stage further, since the $R^+$ line has also been studied in NaF [32]. Equation (11) may be equally well expressed in terms of the strain tensor, in the form

$$V = \sum_{i,j} B_{ij} \epsilon_{ij}.$$  \hspace{1cm} (12)

The $B_{ij}$ parameters are related to the $A_{ij}$ by the elastic constants of the crystal, if we make the assumption that these are unchanged by the presence of the defect. It might then be expected that the $B_{ij}$ would be rather similar for the same centre in different alkali halides. The comparison between the $R^+$ centres in LiF and NaF is shown in table 1, where the elastic constant data is taken from Briscoe and Squire [33] for LiF and Spangenberg and Haussuhl [34] for NaF. It can be seen that there is some correlation, although the agreement is by no means exact. A similar correlation is found for the $N_1$ centres in LiF and NaCl [20], and for the $R$, $R^+$ and $R'$ centres in LiF [35] [36].

<table>
<thead>
<tr>
<th>Strain Parameter</th>
<th>LiF $4,874,\text{Å}$</th>
<th>NaF $5,456,\text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(c_{11} + 2 c_{12}) A_1$</td>
<td>7.5</td>
<td>10.1</td>
</tr>
<tr>
<td>$c_{44} A_2$</td>
<td>-4.6</td>
<td>-3.6</td>
</tr>
<tr>
<td>$(c_{11} - c_{12}) B$</td>
<td>-2.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>$-c_{44} C$</td>
<td>-1.7</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

The absence of stress-induced dichroism in figure 5 shows that the degenerate E state is the excited state rather than the ground state of the $R^+$ centre. This agrees well with the expected electronic states of this centre [32]. If degeneracy occurs in the initial state of a transition, (i.e. ground state in absorption, excited
In addition numerous other lines have been observed and the symmetry of the associated defects determined [27, 19, 37], but no very definite models have been proposed in these cases. It is interesting to note that the only symmetry systems found so far have been [21] rhombic I, rhombic II, monoclinic I, trigonal A → E and tetragonal A → E, and that all these are anisotropic centres. No evidence for the tetrahedral \( N_2 \) centre has been obtained from stress experiments.

Conventional Zeeman and Stark effect experiments on colour centre zero-phonon lines have produced only negative results (*) [35], although the magnetic circular dichroism of the \( R \) centre has been observed by Duval et al. [39]. The negative Zeeman results (in pulsed fields of up to 220 kGs.) are felt to be due to the selection rule \( \Delta M_S = 0 \) appropriate to systems with small spin-orbit coupling [27].

5. Isotope Effects. — Isotope effects on both zero-phonon and phonon-assisted lines have been observed in LiF enriched with \( ^7 \)Li and \( ^6 \)Li by Fetterman and Fitchen [40], Hughes [41] and Durand and Toulouse [42]. Eight zero-phonon lines in all have been measured, the \( R_2, R^+, R', M' \) and \( N_1 \) lines, and three lines at 4747 Å, 5503 Å and 6009 Å due to unidentified defects. All of these lines show isotope shifts of a few \( \text{cm}^{-1} \), the shifts being to the red in \( \text{Li}^6 \text{F} \) relative to \( \text{Li}^7 \text{F} \) in all cases except the \( M' \) line, which shows a blue shift. The author’s results for the \( R_2 \) (3909 Å), \( R^+ \) (4874 Å) and \( N_1 \) (5234 Å) lines are shown in figure 8, and the measured zero-phonon line shifts are listed in table 2. Notice from figure 8 that no measureable isotope shifts are observed for the phonon-assisted peaks of the \( R_2 \) and \( R^+ \) bands, but that peaks B, C, D and E of the \( N_1 \) band show a

![Fig. 7. — Ratio of the intensity of the \( R_2 \) transition in KCl observed for \( E \parallel [110] \) (a) to that observed for \( E \parallel [110] \) (c), under [110] stress at 2 K. The circles are for the \( R_2 \) band and the triangles for the zero-phonon line. (After Silsbee [30].)](image)

Table 2

<table>
<thead>
<tr>
<th>Line</th>
<th>Observed Shift (E)</th>
<th>Calculated Static Shift (E)</th>
<th>Dynamic Shift (E)</th>
<th>Calculated Dynamic Shift (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_2 )</td>
<td>( 3909 ) Å</td>
<td>( -4.4 \pm 0.7 )</td>
<td>( -7.1 \pm 2.8 )</td>
<td>( +2.7 \pm 3.5 )</td>
</tr>
<tr>
<td>( R^+ )</td>
<td>( 4874 ) Å</td>
<td>( -6.8 \pm 0.4 )</td>
<td>( -5.6 \pm 2.0 )</td>
<td>( -1.2 \pm 2.4 )</td>
</tr>
<tr>
<td>( N_1 )</td>
<td>( 5234 ) Å</td>
<td>( -0.4 \pm 0.4 )</td>
<td>( -6.8 \pm 2.5 )</td>
<td>( +6.4 \pm 2.9 )</td>
</tr>
</tbody>
</table>

(*) See, however, the Stark effects reported by Kaplyanskii at this conference.
ZERO-PHONON TRANSITIONS AND VIBRATIONAL STRUCTURE

shift with \( \omega_6 > \omega_7 \). The ratio \( \omega_6/\omega_7 \) for these peaks is about 1.07, close to the value 1.08 expected if only lithium ions participate in the modes concerned. The simple theory of the vibrations of a diatomic lattice suggests that these modes are therefore optical modes at the zone boundary, whilst peaks with \( \omega_6 = \omega_7 \) are zone boundary acoustic modes. This obviously oversimplified picture is reasonably well borne out by comparing the mode frequencies with the calculated dispersion curves for LiF [43].

In order to discuss the isotope shift of the zero-phonon lines it is instructive to consider the energy \( E \) of the zero-phonon transition to be a thermodynamic function of the crystal volume, the mass of the lithium ion \( m \), and the temperature. Simple differentiation then gives:

\[
(\partial E/\partial m)_{P,T} = (\partial E/\partial m)_{V,T} + (\partial E/\partial V)_{m,T} (\partial V/\partial m)_{P,T}.
\]

The measured shift \( (\partial E/\partial m)_{P,T} \) is thus seen to be the sum of two parts. The term \( (\partial E/\partial m)_{V,T} \) represents the dependence of \( E \) on \( m \) at constant volume and temperature, and is related to the interaction between the normal modes and the electronic states. This term is the ‘dynamic shift’. The second term is the ‘static shift’, since it depends on the isotopic volume change of the crystal. The value of \( (\partial E/\partial V)_{m,T} \) may be evaluated from stress experiments, or estimated using the Mollwo-Ivey relation.

Thewlis [44] measured the lattice parameters of Li\(^6\)F and Li\(^7\)F and found a fractional increase for the lighter isotope of \((2.0 \pm 0.5) \times 10^{-4} \) at 25°C. This is a result of the change in the contribution of the zero-point energy to the free energy of the crystal. The increase should be larger at low temperatures where quantum effects become most important, and an estimated value of \((2.5 \pm 0.5) \times 10^{-4} \) at 4°K has been used [41]. It would be desirable to have an actual measurement of the low temperature value. The lineshifts resulting from the isotopic change in volume may now be calculated and these static shifts are given in table 2 for the \( R_2^2 \), \( R^+ \) and \( N_1 \) lines. The difference between the measured shift and the calculated static shift is assumed to be the dynamic shift, and is also shown in table 2.

The dynamic shift is most simply interpreted in terms of the model of section 2. The energy of the zero-phonon line at \( T = 0 \) is, from figure 1,

\[
E = E_1 + \frac{\hbar}{2} (\omega' - \omega).
\]

The static shift is simply the change in the quantity \( (E_1 + E_2) \), and it can be shown both for this and the many-mode case [41] that \( E_2 = S \hbar \omega_0 \) is invariant under isotopic changes. The dynamic shift is thus
entirely due to the quadratic interaction term and is
given by
\[
\delta = \frac{\hbar}{2} (\omega' - \omega)_{\alpha} - \frac{\hbar}{2} (\omega' - \omega)_{\gamma}
\]
(15)

The invariance of SAW is simply a consequence of the fact that this linear interaction energy depends only on force constants and the electronic wave functions of the defect, and not on the ionic masses. From equations 15 and 10 it follows that \(\delta\) is related to the temperature shift \(\Delta E(T)\). When this model is extended to take into account interaction with many modes, it is necessary to make the assumption that the modes important in quadratic coupling are the same as those for linear coupling, in order to relate the dynamic isotope shift to the changes in the vibrational structure. This assumption is one of the weak points in the theory, since it discriminates entirely against odd-parity modes which contribute to the quadratic but not the linear coupling. The dynamic shift \(\delta\) then becomes [41]
\[
\delta = 2 \alpha \left( \frac{x_6 - x_7}{x_6 + x_7} \right)
\]
(16)

where \(x = <\omega^2>/<\omega>\), evaluated for the one-photon side-band, and \(\alpha\) is essentially given by
\[
\alpha = \frac{\hbar}{2} \sum_{\gamma} (\omega'_{\gamma} - \omega_{\gamma}),
\]
(17)

and may be evaluated from \(\Delta E(T)\). It should be remembered that in measuring \(\Delta E(T)\) from the observed temperature shift, allowance must be made for the effects of thermal expansion.

The value of \(\delta\) estimated for the \(N_1\) line is given in table 2. Unfortunately the cumulative error in the result is large, and all that can be said is that the sign and order of magnitude are correct. This limited success is perhaps not surprising in view of the shortcomings of the theory, but does make it difficult to assess whether the ideas involved are adequate to explain the dynamic shift or not. The situation for the only other line which shows a large dynamic shift, the \(M'\) line, is also similarly rather unsatisfactory [40]. Since no vibrational isotope shifts were observed for the \(R_2\) and \(R^+\) lines we expect \(\delta \approx 0\) in these cases, and it can be seen from table 2 that this is so to within experimental error.

The results of work on isotope shifts so far have thus shown that in most cases the static shift is the dominant effect, but that in two cases, the \(N_1\) and \(M'\) lines, there is a large residual dynamic shift. The quantitative evaluation of the dynamic shift from the observed vibrational structure is, however, rather difficult, and involves a large degree of uncertainty.

References
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