In conclusion, it has been shown that a crude calculation based on the Green's function formalism of pseudolocalized vibrations does yield two localized vibrational frequencies which have the qualitative features of the experimental results.

In the paper immediately following this one, we discuss the electron-lattice coupling, which we then use to analyze the details of the vibronic spectrum. Finally, we indicate how, in principle, the results of this analysis can be connected to the vibrational problem discussed in this paper. We defer, until the end of the next paper, a comparison of the results of the present vibronic spectra and those observed in other systems.

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Rare-Earth Ions in the Alkali Halides. III. Electron-Lattice Coupling and the Details of the Vibronic Spectra

W. E. BRON AND MAX WAGNER*
IBM Watson Research Center, Yorktown Heights, New York

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Electron-lattice interaction is discussed for the case of rare-earth ions in the alkali halides. A selection rule is derived to show that for the present defect electronic transitions can be coupled only to vibrational modes of A_1 symmetry. Under the assumption of electrostatic coupling between the electron and the lattice vibrations, a coupling function is derived which is proportional to the projection of the field of the electron undergoing a transition on to the eigenvectors of the vibrations. It is further shown that this coupling function can be determined from the details of the structural form of the vibronic spectra. A number of other features of the vibronic spectra are accounted for through the properties of Franck-Condon integrals.

INTRODUCTION

In this paper, which is the third in the series on rare-earth ions in the alkali halides, we deal with the coupling of electronic transitions to the pseudolocalized lattice vibrations analyzed in the second paper in the series. [The first paper (marked I) has appeared previously[1] and the second (marked II) immediately precedes this one.[2]]

We show that selection rules exist which govern the coupling of electronic transitions to lattice vibrations. For the important case of an electrostatic coupling a more explicit discussion of the electron-lattice interaction is given. It is shown that for a center with inversion symmetry the coupling has no dipolar term; thus for ions whose electronic wave functions do not overlap the nearest lattice neighbors (e.g., rare-earth (R.E.) ions) the coupling can at best be quadrupolic. This restricted coupling makes it possible to obtain very sharp vibronic spectral lines. It also makes it possible to define a coupling function, which, in principle, can be obtained experimentally from the structural form of the vibronic line spectra. Finally, the details of the spectra are accounted for in terms of the properties of Franck-Condon integrals.

EXPERIMENTAL RESULTS

The experimental methods have already been described. We refer the reader to Refs. 1 and 2.

Many details of the vibronic spectra have already been given in Ref. 2. Figure 1 shows a representative vibronic spectra as observed on the lowest energy emission band in Yb^{2+}:KI at 10°K. This figure shows the general result, that any one vibronic series does not consist of a single set of equally spaced lines. Each major spacing contains a number of lines with a minor interval which is again approximately constant. Here, we adopt the notation given in Ref. 2, and assign ω_1 to the frequency difference in the major interval, and ω_2 to that of the minor interval. Similarly, $m(0,1,2,\cdots)$ refers to an index which counts the lines of the major interval and $n(0,1,2,\cdots)$ to that of the minor interval. The minor interval is specifically enumerated in Fig. 1 for $m=5$ and is easily discernible for other m values. This figure also shows the general result that the sharp-line vibronic spectra is found on the high-energy side of the broad emission bands. The converse is observed on absorption bands where the sharp vibronic lines are observed to be displaced asymmetrically against the low-energy side of the broad-band background.

Measurements have been made of the integrated intensities of the lines of the main (ω_1) vibronic series observed in the emission spectra of the Eu^{2+}-doped alkali halides. Table I lists the lines of the lowest energy

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* Present address: Institut für Theoretische und Angewandte Physik der Technische Hochschule, Stuttgart, Germany.

[1] W. E. Bron and W. R. Heller, Phys. Rev. **136**, A1433 (1964).

[2] M. Wagner and W. E. Bron, preceding paper, Phys. Rev. **139**, A223 (1965).

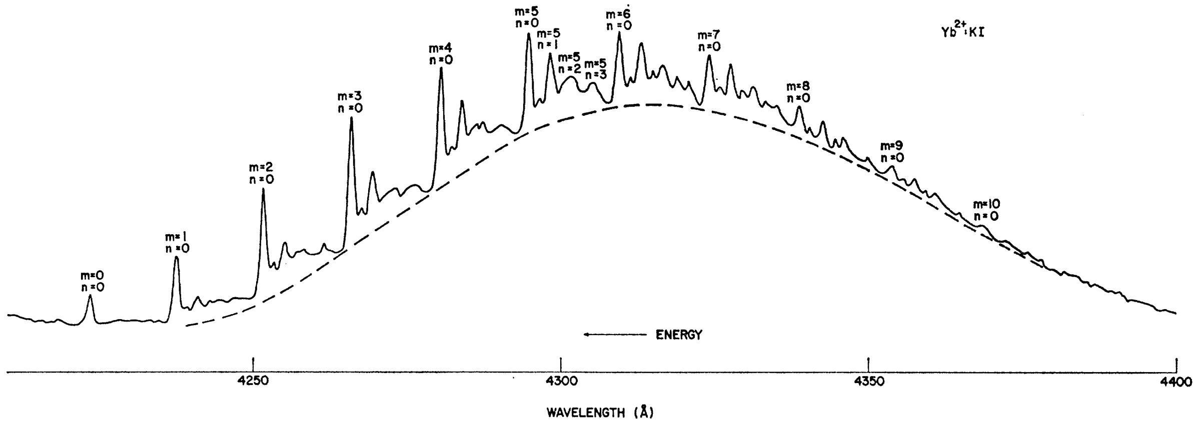

FIG. 1. Major and minor vibronic intervals observed on the lowest energy emission band of Yb^{2+}:KI at 10°K. Shown as a dashed line is the graphically obtained background intensity used to determine the integrated intensities and half-widths of the vibronic lines.

emission band and their corresponding integrated intensities normalized to the intensity of the $m=0$ line. The integrated intensity and the half-widths of the lines of the minor (ω_2) vibronic series were also determined. Those are listed in Table II for the lines $m=0$, $n=1, 2, 3$, observed on the lowest energy absorption band of Sm^{2+}:KCl. The half-width of the lines of a major (ω_1) vibronic series could not be determined. The half-widths of the lines of these series, which are observed to be inherently narrower than those of the minor vibronic series, were distorted through instrument broadening.

TABLE I. Normalized integrated intensities of the ω_1 vibronic series on the lowest energy emission band of Eu^{2+}-doped alkali halides.

Sample	m	ν (cm^{-1})	Normalized integrated intensities
Eu^{2+}:NaCl	0	23 674	1.0
	1	465	1.3
	2	261	0.5
	3	080	0.3
Eu^{2+}:KCl	0	24 342	1.0
	1	146	1.3
	2	23 964	0.7
	3	788	0.3
Eu^{2+}:RbCl	0	24 536	1.0
	1	352	1.5
	2	170	1.2
	3	23 987	0.5
Eu^{2+}:KBr	0	24 333	1.0
	1	225	1.9
	2	119	1.9
	3	015	0.7
	4	23 906	0.3
	5	804	0.2
Eu^{2+}:KI	0	23 750	1.0
	1	671	6.7
	2	593	11.7
	3	514	21.7
	4	435	23.3
	5	356	28.3
	6	277	22.3
	7	199	18.3
	8	120	10.0
	9	041	5.0

In determining the integrated intensities and half-widths given in Tables I and II, the following method was adopted to subtract the broad background. As will be shown in a later section of the discussion, the broad background originates primarily from lattice vibrations of A_1 symmetry which extend over a frequency range which is large compared to those which give rise to the sharp vibronic lines. Examples of such broad frequency distributions can be seen in Fig. 8 of Ref. 2 near ω equal 2 and 3×10^{-13} sec^{-1}. Since, as will also be shown, the sharp vibronic lines should be asymmetrically displaced against the high-energy side of the broad background in the emission spectra (and conversely in the absorption spectra) the low-energy side is essentially representative of the broad background. We have graphically reflected the low-energy side to the high-energy side, under the reasonable assumption that the broad background is symmetric about the maximum of the band. We illustrate this procedure with the dashed line in Fig. 1. We estimate that this approximation of the background leads to errors in the integrated intensities and in the half-width which do not exceed 10 to 15%.

DISCUSSION

In the discussion, which is to follow, we investigate in Sec. I the symmetry properties of electron-lattice

TABLE II. Half-widths of spectral lines of a vibronic series with ω_2 frequency as observed in the absorption spectrum of Sm^{2+}:KCl at 10°K.

$m=0$ n	λ (Å)	ν (cm^{-1})	Half-width (cm^{-1})
1	6366.7	15 707	7±2
2	6356.5	15 732	18±2
3	6344.4	15 762	26±4

coupling. This is done to determine the selection rule, already indicated in Ref. 2, that only vibrational modes of A_1 symmetry can be coupled to electronic transitions. In Sec. II, we investigate, in some detail, the case of electrostatic coupling, and indicate how this leads to an electron-lattice coupling function which can, in principle, be determined from the integrated intensities of the lines of the vibronic spectra. The latter, together with other features of the structural form of the vibronic spectra, is discussed in Sec. III.

I. Coupling Selection Rules

It is well known from the theory of the Jahn-Teller[3] effect for molecules that an electronic state of given symmetry can only couple to selected modes which obey certain symmetry requirements. Naturally, this is also true for the electron-lattice coupling.

Here we are concerned with selection rules which govern the coupling of electronic transitions between states of opposite parity to lattice vibrations. As will be shown below, a measure for the first-order coupling of an electronic transition to lattice vibrations is given by the displacement $\alpha_{\mu\mathbf{m}}{}^i$ of the lattice equilibrium. Hence one has to project $\alpha_{\mu\mathbf{m}}{}^i$ onto the orthonormal set of eigenvectors $\zeta_{\mu\mathbf{m}}{}^i$ [see Eq. (11) of Ref. 2] to get the displacement of the single normal coordinates, $q(\kappa)$

$$q'(\kappa)-q(\kappa)=\alpha(\kappa)\,, \tag{1a}$$

where

$$\alpha(\kappa)=\textstyle\sum_{\mathbf{m}\mu i}\alpha_{\mu\mathbf{m}}{}^i\zeta_{\mu\mathbf{m}}{}^i(\kappa)\,. \tag{1b}$$

We continue the notation established in Ref. 2. Accordingly, $\mathbf{m}$ is the position of the mth unit cell in the Bravais lattice, $\boldsymbol{\mu}$ the position of the ions within the cell, $i(i=1, 2, 3)$ the ith Cartesian component, κ is the index for the vibrational modes of the disturbed lattice, and $\zeta_{\mu\mathbf{m}}{}^i(\kappa)$ are the orthonormal eigenvectors of Eq. (11) in Ref. 2.

There is also a second-order coupling due to the change in the spring constants during the electronic transition. Therefore the eigensolutions of Eq. (8) of Ref. 2 are different for the two electronic states and there is not even an exact one-to-one correspondence between single eigenvectors of the two sets, i.e., there is no exact diagonal coupling. But, as will be shown by one of us (M.W.),[4] for a strongly localized disturbance there is an approximate one-to-one correspondence between single eigenvectors for the pseudolocalized and localized modes as well as for the unlocalized ones. One finally arrives at the very helpful concept that the *phonon modes are changed only in their equilibrium position*, whereas the local modes change also their frequency during the transition. Drastic deviations from this approximation are not to be expected in real crystals. For alkali halide host lattices we may even neglect any second-order coupling since, as is shown in Table III, Ref. 2, absorption and emission exhibit essentially the same vibrational frequencies.

The total Hamiltonian of the electron-lattice system is

$$H_t=H_{\mathrm{el}}(x)+H_{\mathrm{nucl}}(X)+U(x,X)\,, \tag{2}$$

where H_{el}, the purely electronic part, is a function of the electron coordinates; H_{nucl}, the purely nuclear part, is a function of the nuclear coordinates; and U is the total interaction potential which is a function of all electron and nuclear coordinates. In the present context, x, X are to stand for Cartesian coordinates. The total Hamiltonian H_t must be invariant under any operation R of the point group of the defect, i.e., under any operation of the group of V [the matrix of the disturbance, see Eq. (9) of Ref. 2]. Since $H_{\mathrm{el}}+H_{\mathrm{nucl}}$ is itself invariant, we must have that

$$RU(x,X)=U(x,X)\,. \tag{2a}$$

The interaction potential $U(x,X)$ can be developed into a power series in X

$$\begin{aligned}U(x,X)=U(x)&+\textstyle\sum_{\mathbf{m}\mu i}U_{\mu\mathbf{m}}{}^i(x)X_i\\&+\textstyle\sum_{\mathbf{m}\mu i,\mathbf{n}\nu j}U_{\mu\nu,\mathbf{mn}}{}^{ij}X_iX_j+\cdots\,.\end{aligned} \tag{3}$$

If we chose the normal coordinates $q(\kappa,s_\kappa)$ to belong to an irreducible representation κ of V (s_κ denotes the different degenerate coordinate within the representation κ) then we may rewrite (3)

$$U(x,X)=U(x)+\textstyle\sum_{\kappa,s_\kappa}U_{\kappa,s_\kappa}(x)q(\kappa,s_\kappa)+\cdots \tag{4}$$

which we have carried out to only the linear term, since for the case under study we are neglecting second-order coupling. Because of the harmonic approximation in the nuclear part of the Hamiltonian we need, at any rate, not go beyond the second order. From the fundamental theorem of algebra we have that (2a) must be valid for each power in q itself; thus $U(x)$ transforms according to the unit representation, whereas $U_{\kappa,s_\kappa}(x)$ must be a basis for the representation κ in x space. Similar, although more complicated, rules are easily derived for the higher terms in (4).

Employing the zero-order Born-Oppenheimer approximation[5] the vibrational equation reads

$$\begin{aligned}\{H_{\mathrm{nucl}}(X)+\langle\psi_n{}^0(x)|U(x,X)|\psi_n{}^0(x)\rangle\}\Phi_m{}^n(X)&\\=E_{mn}\Phi_m{}^n(X)\,,&\end{aligned} \tag{5}$$

where $\psi_n{}^0(x)$ is the zero-order Born-Oppenheimer wave function of the electron in the state n and $\Phi_m{}^n(X)$ the nuclear wave function for the state m. The effect of the linear potential in (5) is thus

$$\textstyle\sum_{\kappa,s_\kappa}\langle\psi_n{}^0(x)|U_{\kappa,s_\kappa}(x)|\psi_n{}^0(x)\rangle q_{\kappa,s_\kappa} \tag{6}$$

and it is this term which defines the equilibrium of the lattice oscillators for the electronic state n. (The

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[3] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[4] M. Wagner (to be published).

[5] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

similar term arising from the term which is second order in q_κ defines the effect of the electronic state on the frequency of the oscillator.) Now, as is well-known from standard group theory,[6] the matrix elements $\langle n|U_{\kappa,s_\kappa}|n\rangle$ do not vanish only if the symmetric product of the irreducible representation $\psi_n{}^0(x)$ with itself contains the irreducible representation $U_{\kappa,s_\kappa}(x)$. Thus we have the *coupling selection rule*:

> The electronic wave function of a vibronic system is coupled only to those normal coordinates q_{κ,s_κ} whose representation is contained in the symmetric product $[\psi_n{}^0\times\psi_n{}^0]$.

This rule has its most simple form, if the electronic function is nondegenerate. In this case the direct product is the unit representation, whence all nondegenerate electronic wave functions are coupled only to those modes which leave the symmetry of the defect unchanged. Consequently, for a defect whose symmetry group has only one-dimensional irreducible representations, all electronic states can couple only to the modes of the unit representation, and if one of them has a large local amplitude, all $\psi_n{}^0$ are mainly coupled to this mode. The divalent rare-earth ions in alkali halides, for which the symmetry is C_{2v},[1,2] belong to this class of defects. Therefore all electronic states of this defect couple to only A_1 modes.

In the case of degenerate electronic functions the symmetric product $[\psi_n\times\psi_n]$ contains in general, apart from the unit representation, also other representations. Because there is now also a coupling to modes which destroy the initial symmetry, the electronic levels will not remain degenerate and a Jahn-Teller splitting of the states can be expected. It is because of this complication that defects of lower symmetry are more easily tractable than those of a higher one.

We shall confine ourselves, therefore, to defects with nondegenerate electronic states, i.e., with only one-dimensional irreducible representations. It is to be emphasized, however, that this restriction does not apply to those parts of this study where only the vibrational problem is considered.

It is also to be emphasized that the above selection rules are only valid for the zero-order term in the series (written in shorthand notation)

$$\psi_n(x,X)=\psi_n{}^0(x)+\psi_n{}^1(x)X+\cdots. \tag{7}$$

It is not possible to give such simple selection rules if the electronic wave function depends strongly on the vibrational coordinates X.

II. The Coupling Functions

All vibronic bands with a sequence of sharp lines above (or below) the zero-phonon line can be considered to arise from transitions which are localized at foreign ions in the crystal. This is especially so for the lanthanide and actinide ions, whose electronic wave functions involved in the transition can be given by those of the free ion, rearranged properly in the crystal field. This is certainly true for transitions within the inner f orbitals of the lanthanides and actinides, which have a splitting,[7] due to the static crystal field, of the order of 100 to 1000 cm^{-1}, whereas the ionization potential for an f electron is of the order of at least 10^5 cm^{-1}.[8] Since even for (the lowest) d orbitals the crystal-field splitting is only increased by one order of magnitude, we may suppose that the conclusion drawn here for the f electron holds for the $5d$ electron to a good approximation.

We may assume, therefore, that the zero-order Born-Oppenheimer approximation for the electronic wave functions is well justified to a high degree of accuracy. This approximation seems to hold even for some cases when vibronic structure is no longer present. For instance, in the system KCl:Tl$^+$ even the wave functions of the electrons in the outer shell of Tl$^+$ ($6s^2$ and $6s6p$) can be taken as the ionic ones,[9] although there is already some overlapping with the nearest neighbors.

Naturally, the assumption that the electronic wave functions are given by the static crystal-field calculations[7] is only possible for nondegenerate levels. As has already been mentioned the defect in (R.E.)-doped alkali halides has C_{2v} point symmetry and therefore has only one-dimensional states. We defer the complication of degenerate states for a later study.

With this assumption the practical calculation of any given vibronic band is "reduced" firstly to the calculation of the quantity

$$\langle\psi_f|U_\kappa|\psi_f\rangle-\langle\psi_i|U_\kappa|\psi_i\rangle \tag{8}$$

which gives the displacement α_κ of the oscillator equilibrium between the initial (i) and final (f) states and secondly of the quantity

$$\langle\psi_f|U_{\kappa\kappa}|\psi_f\rangle-\langle\psi_i|U_{\kappa\kappa}|\psi_i\rangle \tag{9}$$

which gives the frequency change. (Here $U_{\kappa\kappa}$ refers to the second-order coupling coefficient.) With these two quantities the vibronic band is readily calculated, as will be shown in Sec. III of the discussion.

But, of course, U_κ and $U_{\kappa\kappa}$ can only be defined if one knows the Cartesian coupling coefficients $U_{\mu\mathrm{m}}{}^i(x)$ and $U_{\mu\nu,\mathrm{mn}}{}^{ij}(x)$ and the solution of the disturbed lattice dynamics. The latter has already been outlined in Ref. 2. But there is no general method of handling the Cartesian coupling $U(x,X)$ in the Schrödinger equation. The procedure depends on the number of electrons which are not included explicitly since it is, of course, impossible to make an exact calculation. It would unduly extend our study to investigate the differ-

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[6] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1958), p. 343 ff.

[7] D. S. McClure, *in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 401.

[8] J. D. Axe and P. P. Sorokin, Phys. Rev. **130**, 945 (1963).

[9] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

ent possibilities of various approximation, which themselves depend heavily on the peculiarities of the particular problem. For ionic crystals the simplest approximation is based on a modified point-ion model[10] which takes into account the polarizability of the lattice ions.

We shall outline this approximation in somewhat more detail. Suppose the impurity ion, which is located at the origin, has s electrons involved in the transition. These electrons located at $\mathbf{r}_s$ have a Coulombic interaction with the lattice point charges $Z_{\mathrm{m}}{}^{\mu}$ at $\mathbf{R}_{\mathrm{m}}{}^{\mu}$, then

$$U(x,X)=\rho e^2\sum_{\mathrm{m}\mu}\sum_{s}\frac{Z_{\mathrm{m}}{}^{\mu}}{|\mathbf{r}_s-\mathbf{R}_{\mathrm{m}}{}^{\mu}|},\qquad(10)$$

where ρ is an effective dielectric constant to account for the polarization of the ions. If the electrons, which are involved in the transition, have much higher average velocity than those of the outer ionic shells of the surrounding lattice (which determine essentially the polarizability), we can employ a second adiabatic approximation[11] and ρ takes the value

$$\rho=\epsilon_\infty$$

(ϵ_∞=refraction index).

In (10) we use the obvious notation

$$r_s=\{x_s,y_s,z_s\}\,,\quad R=\{X,Y,Z\};$$

Eq. (10) can be expanded about the equilibrium positions of the nuclei,

$$U(x,X)\sim e^2\sum_{\mathrm{m}\mu}\sum_{s}\frac{Z_{\mathrm{m}}{}^{\mu}}{|\mathbf{r}_s-\mathbf{R}^{(0)}{}_{\mathrm{m}}{}^{\mu}|}\times\left\{1+\sum_i\frac{(x_s{}^i-X^{(0)}{}_{\mu\mathrm{m}}{}^i)}{|\mathbf{r}_s-\mathbf{R}^{(0)}{}_{\mathrm{m}}{}^{\mu}|^2}\xi_{\mu\mathrm{m}}{}^i+\cdots\right\},\qquad(11)$$

where $\xi_{\mu\mathrm{m}}{}^i$ are Cartesian nuclear displacements from the equilibrium positions $X^{(0)}{}_{\mu\mathrm{m}}{}^i$, which latter we can choose in the most suitable way, e.g., we may choose them as the equilibrium positions of the electronic ground state. In the vibrational equation of motion we have then a linear term of the form

$$\textstyle\sum_{\mathrm{m}\mu} eZ_{\mathrm{m}}{}^{\mu}\xi_{\mu\mathrm{m}}{}^iF_i(\mathbf{R}_{\mathrm{m}}{}^{\mu})\,,\qquad(12)$$

where the integral

$$F_i{}^{(f)}(\mathbf{R})=\int e\psi_f\sum_s\frac{(\mathbf{x}_s{}^i-\mathbf{R}^{(0)i})}{|\mathbf{r}_s-\mathbf{R}|^3}\psi_f{}^*dx_i\qquad(13)$$

is just the ith component of the electric field of the charge distribution $|\psi_f|^2$. $\mathbf{F}^{(f)}(\mathbf{R})$ is a basis of the unit representation in R space if ψ_f is nondegenerate. (Otherwise it belongs to the symmetric product representation $[\psi_f\times\psi_f]$.) We have thus established directly the symmetry property of the matrix $\langle f|U_{\mathrm{m}}{}^{\mu}|f\rangle$ in the special case of a Coulombic interaction.

We assume also that the repulsion potential of the ions is not changed appreciably during an electronic transition. This should be so since both the initial and final electronic state are localized strongly at the foreign atom.

The integral (13) has interesting symmetry aspects. First, we may decompose $F^{(f)}(\mathbf{R})$ into a sum of multipole fields.

$$F^{(f)}(\mathbf{R})=-e\frac{\mathbf{R}}{R^3}-\frac{p^{(f)}}{R^3}+\frac{3(p^{(f)}\cdot\mathbf{R})\mathbf{R}}{R^5}+\cdots,\qquad(13\mathrm{a})$$

where

$$p^{(f)}=\sum_s e\int\psi_f\mathbf{r}_s\psi_f{}^*\prod_s d^3x_s.\qquad(13\mathrm{b})$$

If the electric wave functions ψ_f are strongly localized well within the nearest-neighbor surroundings, the decomposition (13a) is already valid for the nearest neighbors. From (8) through (12) we see that the Cartesian displacement during the electronic transition is proportional to the difference

$$\alpha^{(gf)}{}_{\mu\mathrm{m}}{}^i\propto\rho eZ_{\mathrm{m}}{}^{\mu}[F_i{}^{(f)}(R^{(0)}{}_{\mathrm{m}}{}^{\mu})-F_i{}^{(g)}(R^{(0)}{}_{\mathrm{m}}{}^{\mu})]\xi_{\mu\mathrm{m}}{}^i,\qquad(14\mathrm{a})$$

where we have assumed that the initial state (i) is the electronic ground state (g).

Inserting (13a) into (14) the monopole term cancels, and the coupling is as localized as a dipolic field. But in many cases its localization is even stronger. If the defect has inversion symmetry, the symmetric product is an even representation, whereas the dipole operator r_s is odd, whence (13b) is zero. Therefore, the first nonvanishing term in (14a) is of quadrupolic localization (i.e., it is localized with $1/R^4$).

In our case of (R.E.)$^{2+}$ ions in alkali halide host lattices the symmetry of the defect is C_{2v}. But the parent symmetry is O_h and within an assumed restricted crystal-field approximation the breakdown of the O_h symmetry does not mix different representations of the O_h symmetry.[12] Hence we can to a good approximation ascribe a "parity" to each electronic state in C_{2v} symmetry as well, although there is no inversion symmetry, and consequently the dipole expectation value (16) becomes negligibly small.

Thus for ions whose wave functions are strongly localized, the coupling function $F_i{}^{(f)}R^{(0)}{}_{\mathrm{m}}{}^{\mu}$ is localized with $1/R^4$. Writing (14a) in normal coordinates,

$$\alpha^{(gf)}(\kappa)=\frac{\rho e}{\omega_\kappa}\textstyle\sum_{\mathrm{m}\mu i}Z_{\mathrm{m}}{}^{\mu}\times[F_i{}^{(f)}(R^{(0)}{}_{\mathrm{m}}{}^{\mu})-F_i{}^{(g)}(R^{(0)}{}_{\mathrm{m}}{}^{\mu})]\zeta(\kappa)_{f\mathrm{m}}{}^i,\qquad(14\mathrm{b})$$

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[10] B. S. Gourary and F. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 210.

[11] M. Wagner, Z. Naturforsch. **15a**, 889 (1960).

[12] This is, of course, only true if we restrict the crystal-field approximation to a superposition of electronic wave functions of the same configuration, i.e., of the same parity. Naturally there are also small admixtures from other orbitals, whence the dipole matrix element (16) does not exactly vanish in C_{2v} symmetry. Admixtures from foreign configurations are usually neglected.

where $\zeta(\kappa)_{m\mu}{}^{i}$ are the orthonormal eigenvectors defined in Eq. (11) of Ref. 2. It is clear that F projects most strongly on those eigenvectors ζ_κ which have a large local amplitude, i.e., onto pseudolocalized (or truly localized) modes.

In the region of a strong "scattering" resonance, i.e., where the resonance denominator $[1+\mu_j]$ of Eq. (18) of Ref. 2 becomes very small, the width of the resonance peak spans only a small frequency interval. This can be seen to be the case for the two resonance peaks shown in Fig. 8 of Ref. 2. From Eq. (14b) it is then evident that, if a strongly localized electronic transition is coupled to vibrations (of A_1 character) near a "scattering" resonance, the coupling extends only over a limited frequency range. We may suspect, therefore, that the resultant vibronic spectral lines are sharp. On the other hand, if the wave function of the transition electron overlaps the nearest-neighbor ions, the monopole term in (14b) does not cancel, i.e., $F^{(f)}-F^{(g)}$ may even increase before starting to decrease away from the center. This is the case for the F center in the alkali halides, where the electron is coupled to a frequency range which is extended enough to exhibit only a broad absorption band with no vibrational structure.

The above discussion is limited to the case of first-order coupling. It is possible to treat in a similar way second-order changes, i.e., the changes in the oscillator frequencies, but as experimental evidence shows that these are negligible, we do not write down the respective formula. We turn instead our attention to the details of the vibronic spectra and show that, in principle, the displacement of the equilibrium position of the oscillator κ between the ground electronic state and the final state α^{gf} can be obtained from the spectra.

III. STRUCTURE OF VIBRONIC SPECTRA

The structural form of vibronic spectra has been analyzed by a number of investigators.[13] For the present case of sharp-line vibronic series we use the method recently reported by Wagner.[14] In general, the structural form of the vibronic spectral lines can be accounted for in detail by the properties of Franck-Condon integrals

$$I_{mm'}(\beta_\kappa,\gamma_\kappa)=\int\Phi_m(q_\kappa)\Phi_{m'}(q_\kappa-\alpha_\kappa)dq_\kappa\,, \tag{15}$$

where $\Phi_m(q_\kappa)$ are the eigenfunctions of the lattice oscillator κ, m and m' refer to the quantum number associated with, respectively, the initial and the final state of the oscillator, and α_κ is the equilibrium displacement in the coordinate q_κ due to the electronic transition. [See Eqs. (1a) and (1b).] The purpose of what follows is to compare the structural form of the experimentally observed vibronic lines with that predicted by Eq. (15) and to extract values of α_κ from this data. Therefore, only the results of (15) will be stated; the reader is referred to Wagner's paper[14] for the pertinent derivations. The integration (15) can be written in terms of two parameters β_κ and γ_κ,

$$\beta^2=\omega_\kappa'/\omega_\kappa\,,\quad \gamma^2=\omega_\kappa{}^2\alpha_\kappa{}^2/h\omega_\kappa\,, \tag{16}$$

which are measures of the change in vibrational frequency ω_κ, and the change in the equilibrium displacement. Since the present experiments were carried out near 10°K, absorption and emission transitions can be expected to originate from states with $m=0$. Also, since the vibrational frequencies observed in absorption nearly equal those observed in emission, β^2 is approximately equal to unity. For $\beta^2\approx1$ the probability of a vibrational transition from $m=0$ to $m'=m$ is

$$p_m(\kappa)=(1/m!)[p(\kappa)]^m\,, \tag{17}$$

where $p(\kappa)$ is a coupling function equal to

$$p(\kappa)=2\beta_\kappa{}^2\gamma_\kappa{}^2/(1+\beta_\kappa{}^2)^2\,. \tag{18}$$

The square root of $p_m(\kappa)$ is equal to $I_{0m}(\beta_\kappa,\gamma_\kappa)$ except for a constant factor.

It has already been pointed out that electronic transitions, which are coupled to pseudolocalized vibrations, must be considered as coupled not to one oscillator but to a distribution of lattice oscillators.[15] For a general distribution of oscillators, the functional form of the mth line of the resulting vibronic series can be expressed as

$$f_m(\omega)=\frac{1}{\Delta\omega}\sum_{m_1,m_2}\cdots\prod_\kappa\frac{1}{m_\kappa!}[p(\kappa)]^{m_\kappa}\,, \tag{19}$$

where $m=\sum m_\kappa$ defines the individual members of the vibronic series, and the summation has the additional restriction that $\omega<\sum m_\kappa\,\omega_\kappa<\omega+\Delta\omega$, since $f_m(\omega)$ is the probability per unit frequency.

The integrated intensity of the mth line (as normalized to the zero-quantum line) is given by

$$F_m=\frac{1}{m!}[\sum_\kappa p(\kappa)]^m=\frac{1}{m!}P^m\,, \tag{20}$$

where P is an effective coupling function for the distribution of oscillators. The position of the center of a line is given by

$$\omega_m=m\times[\sum\nolimits_\kappa p(\kappa)\omega_\kappa/P] \tag{21}$$

in agreement with the result that within the harmonic approximation vibronic lines are equally spaced.

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[13] See, for example, M. Lax, J. Chem. Phys. **20**, 1752 (1952); R. Kubo and Y. Toyosawa, Progr. Theoret. Phys. (Kyoto) **13**, 160 (1955); K. K. Rebane and V. V. Kkizhnyakov, Opt. i Spektroskopiya **14**, 362 (1963) [English transl.: Opt. Spectry. (USSR) **14**, 193 (1963)].

[14] M. Wagner, J. Chem. Phys. **41**, 3939 (1965).

[15] An alternative viewpoint, recently given by Wagner, considers pseudolocalized vibrations in terms of metastable states of a localized oscillator. The structural form of vibronic spectra is, however, more easily discussed in terms of sums over a distribution of lattice oscillators. See M. Wagner, Phys. Rev. **136**, B562 (1964).

TABLE III. Normalized integrated intensities of vibronic lines on lowest energy emission band of Eu^{2+}:KI.

m	ν (cm^{-1})	F_m Experimental	F_m Calculated for $P=5$
0	23 750	1.0	1.0
1	671	6.7	5.0
2	593	11.7	12.5
3	514	21.7	20.8
4	435	23.3	26.0
5	356	28.3	26.0
6	277	22.3	21.8
7	199	18.3	15.5
8	120	10.0	9.7
9	041	5.0	5.4

The effective coupling function can be evaluated from the experimental integrated intensities and Eq. (20). Table III shows, for the representative case of the emission to the ground state of Eu^{2+}:KI, that the normalized integrated intensities (F_m) of a large number of lines of a given vibronic set can be fitted by a single value of P. Table IV lists the values of P as determined from the integrated intensities of the lines of the emission data of Eu^{2+} in the various alkali halides as given in Table I.

It follows from Eq. (19) that the functional form of the first phonon line ($m=1$) gives the frequency distribution of P. For certain specific frequency distributions it is possible to determine, in addition, an analytical form for the half-widths of the vibronic lines. For example, a Lorentzian distribution for which

$$\sum_{\kappa} p(\kappa) \rightarrow \int \frac{P_0}{(\omega^2-\omega_0^2)^2+\Gamma^2/4} d(\omega^2) \tag{22}$$

and if the resonance is sharp, i.e., $\Gamma/2 \ll \omega_0^2$, then the functional form of the lines can be written in an approximate form

$$f_m^{(L)}(\omega) = \frac{1}{2\pi m!}\left[\frac{2\pi P_0}{\Gamma}\right]^m \frac{\Gamma_m/\omega_0}{(\omega - m\omega_0)^2 + (\Gamma_m/2\omega_0)^2} \tag{23}$$

and the half-width H_m of a Lorentzian line is given by

$$H_m^{(L)} = m \times \Gamma/\omega_0. \tag{24}$$

In a similar manner the half-width of a Gaussian distribution may be shown to be

$$H_m^{(G)} \propto \sqrt{m}. \tag{25}$$

The observed half-widths as given in Table II of this paper progress nearly proportionally to m, i.e., as would be expected from a Lorentzian distribution. A Lorentzian distribution can in fact be expected on theoretical grounds. In the vicinity of resonance the frequency distribution of the eigenvectors of Eq. (17) of Ref. 2 can be approximated rather well by a Lorentzian distribution. This has been shown in the recent treatment by Wagner[15] of the general problem of scattering resonance and metastable states. Wagner's result depends on the postulate that the amplitude of the local mode decays exponentially with time. The present experimental result would appear to support this postulate. The reader is referred to the paper by Wagner for a more detailed treatment of this point.

Since the distribution of frequencies $\sum_{\kappa} p(\kappa)$ can be determined experimentally from the first phonon line, the coupling function $p(\kappa)$ for the individual oscillators in the distribution can, in principle, also be determined. Then the equilibrium displacements of the individual oscillators α_κ can be obtained through Eqs. (16) and (18). Finally, a comparison of the experimentally determined α_κ can be made with those obtained through Eq. (14a). The latter can be evaluated, in principle, if the wave functions of the electronic states are known together with the values of the vibrational eigenvectors obtained from the formalism of Ref. 2. Thus Eq. (14a) defines the link between the details of the vibronic spectra and the results of the vibrational analysis.

It is possible to account for a number of other features of the vibronic spectra. For example, if the electronic transition is coupled to a second set of oscillators with a Lorentzian distribution $\sum_{\kappa} q(\kappa)$, then the functional form of the lines of the vibronic spectra becomes

$$f_{mn}^{(L)}(\omega) = \frac{1}{2\pi m!n!}\left[\frac{2\pi P_0}{\Gamma_1}\right]^m \left[\frac{2\pi q_0}{\Gamma_2}\right]^n \left[\frac{\Gamma_1 m}{\omega_0'} + \frac{\Gamma_2 n}{\omega_0''}\right] \times \left\{(\omega - m\omega_0' - n\omega_0'')^2 + \left[\frac{\Gamma_1 m}{2\omega_0'} + \frac{\Gamma_2 n}{2\omega_0''}\right]^2\right\}^{-1}, \tag{26}$$

where m, p_0, and the subscript 1 refer to the first set of oscillators, and n, q_0, and the subscript 2 to the second set. ω_0' and ω_0'' are the centers of the distributions $\sum_{\kappa} p(\kappa)$ and $\sum_{\kappa} q(\kappa)$. If the lines of the second distribution are sufficiently narrow and if $\omega_0'' < \omega_0'$, then one observes in addition to the lines of the first set defined by

$$f_{m,0}(\omega) \quad m=0, 1, 2\cdots \tag{27}$$

a second set of lines, between the lines of the first set, defined by

$$f_{mn}(\omega) \quad n=1, 2, 3\cdots; \tag{28}$$

the number of lines observable in the n series depends on ω_0''/ω_0' and the inherent half-width of the second distribution. The formulation (26) therefore accounts

TABLE IV. Effective coupling function P for ω_1 vibronic series on the lowest energy emission band of Eu^{2+}-doped alkali halides.

Sample	P
Eu^{2+}:NaCl	1.1
Eu^{2+}:KCl	1.1
Eu^{2+}:RbCl	1.5
Eu^{2+}:Br	1.9
Eu^{2+}:KI	5.0

for the observation of the ω_2 frequency as a minor vibrational interval in the vibronic spectra.

The electronic transition can also be coupled to a frequency distribution which is broad. Such distributions can be understood from those parts of the solutions of the vibrational problem that are not localized, e.g., those solutions for which the resonance is not sharp (see Fig. 8, Ref. 2). If a coupling exists to a narrow distribution $\sum_\kappa p(\kappa)$ and to a broad distribution $\sum_\kappa q(\kappa)$ such that the lines of the broad series overlap strongly, then the combined spectrum contains the sharp series of lines of Eq. (27) [and that of Eq. (28) if ω_2 is also present] superimposed on a continuous background. This is so, providing ω_κ is considerably smaller than the frequency extent of the continuous background. The center of the continuous background is given by

$$\bar{\omega}_{\text{cont}}=\sum_\kappa p(\kappa)\omega_\kappa+C\sum_\kappa q(\kappa)\omega_\kappa\,, \tag{29}$$

where C is a constant equal to

$$C=\frac{\exp[\sum_\kappa q(\kappa)]}{\{\exp[\sum_\kappa q(\kappa)]\}-1}\,. \tag{30}$$

$\sum_\kappa p(\kappa)\omega_\kappa$ is just the center of the sequence $f_{m,0}$. From (29) it is obvious, therefore, that for small ω_κ the set $f_{m,0}$ is displaced asymmetrically against the low-energy side of the continuous background of absorption bands. This can be seen to hold true in Fig. 1 of Ref. 2. The reverse is predicted in the emission spectra, as is indeed observable in Figs. 2–4 of Ref. 2.

SUMMARY AND CONCLUSIONS

In this paper we have shown that electronic transitions between one-dimensional states can be coupled only to normal mode vibrations of the unit representation, i.e., for C_{2v} symmetry only to A_1 modes. From an analysis of the special case of an electron-lattice coupling through electrostatic interaction, we have defined a coupling function which is proportional to the projection of the field of the electron, undergoing the transition, onto the eigenvectors of the lattice vibrations. We have also shown that the coupling function can be determined experimentally from the details of the functional form of the vibronic spectra, and further, that a number of other features of the vibronic spectra can be accounted for in terms of the properties of Franck-Condon integrals.

Some concluding remarks are perhaps in order on a comparison of the vibronic spectra observed in the present work and those observed by others. For example, in a recent case[16] one observes a coupling of electronic transitions not to the states of a localized vibrational oscillator as observed here, but to certain lattice phonons. In some cases both localized and lattice vibrations appear in the vibronic spectra. For example, in Sm^{2+}:KCl we find pseudolocalized vibrations coupled to $4f^6\rightarrow 4f^5 5d$ transitions. However, we observe apparent coupling of lattice vibrations to $4f^6\rightarrow 4f^6$ transitions (these latter results have not been included in the present paper). Loudon[17] has recently shown from symmetry arguments that certain simple defects and phonon symmetries could lead to the simultaneous observation of both types of vibrations.

Without, however, going into the details of the group theoretic properties, it is possible to make a number of preliminary observations as to the factors which govern the various types of vibrational coupling.

The general problem of electron-lattice coupling can be characterized by the strength of the dynamical lattice distortion (change in mass or spring constants, or both) and the strength of the coupling of the electronic transition to the lattice vibrations. Using these parameters we may distinguish four extreme cases.

A. Small Lattice Distortion, Weak Electron-Lattice Coupling

An example of such a system is Pr^{3+} in a $LaCl_3$ crystal.[16] Here, because the distortion is so small, one can apply first-order perturbation theory, which yields the restriction to one-phonon processes and vibronic selection rules to special points of the Brillouin zone.[18] The spectrum consists of a strong electronic line ("zero-phonon line") and a vibronic line for each involved frequency.[16]

B. Large Lattice Distortion, Strong Coupling

This is the case treated in detail in this and the preceding paper. Other examples are rare-earth ions in certain alkaline-earth halides which exhibit line structure, and also the F center with no line structure in its broad band. The number of the involved lattice quanta is often of the order of 10.

C. Small Lattice Distortion, Strong Electron-Lattice Coupling

Because of the localized nature of the coupling and the nonlocalized properties of phonons, a broad frequency region is involved and the first "phonon line" should be a reproduction of those parts of the frequency distribution of the ideal lattice which from symmetry considerations can be coupled to the electronic transition. Apparently the spectra of Sm^{2+}:CaF_2 reported by Wood and Kaiser[19] belong to this class. The exciton bands of the alkali halides[20] and the localized excitons of halogen ions in alkali halides[21] appear to be other examples.

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D. Large Lattice Distortion, Weak Coupling

Here the phonon solutions are strongly altered near the defect and there is the possibility of localized modes with a sharp frequency outside the bands and of scattering resonances with strongly increased local amplitudes. Thus, electronic transitions of proper symmetry types can couple to narrow frequency regions. But because of the weak coupling we may expect only a limited line structure above the zero-phonon line.

On the other hand, some cases such as M and R centers[22] and NO_2^- molecules[23] in alkali halides, as well as the $4f^n \rightarrow 4f^n$ transitions of Sm^{2+} in the alkali halides are not as easily classified. These defects are complex and should cause considerable local distortion. They should belong to either the case B or D. Yet the vibronic structures in parts of their spectra appear to represent coupling to certain singular points in the phonon distribution. It is possible that in these cases coupling to localized vibrations is forbidden by symmetry considerations. We intend to subject these cases to further study.

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Paramagnetic Relaxation of Some Rare-Earth Ions in Diamagnetic Crystals[*]

Chao-Yuan Huang[†]

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

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The pulsed-saturation method at 8.9 kMc/sec was used to measure the spin-lattice relaxation rate T_1^{-1} for Eu^{2+}, Ho^{2+}, and Tm^{2+} in CaF_2, for Yb^{3+} in yttrium gallium garnet, yttrium aluminum garnet, and lutetium gallium garnet; for Nd^{3+} in yttrium gallium garnet and yttrium aluminum garnet; and for Sm^{3+} in lanthanum ethyl sulphate at low temperatures. The experimental data in most cases are in satisfactory agreement with the theoretical predictions based on the combined Van Vleck–Orbach theory. Besides the expected conventional processes, a process $T_1^{-1} \propto T^5$ was observed for Eu^{2+} in CaF_2 in the temperature range $15°K < 30°K$. Furthermore, a pronounced anisotropy in T_1 (a factor ~ 6) for Sm^{3+} in lanthanum ethyl sulphate was found both experimentally and theoretically.

I. INTRODUCTION

It has been shown by Heitler and Teller,[1] Fierz,[2] Kronig,[3] Van Vleck[4] and others that the dominant spin-lattice interaction is through the thermal modulation of the Stark field. According to them the energy transfer between the spin system and the lattice vibration gives rise to two processes: (1) a one-phonon process in which a phonon is absorbed or emitted accompanied by a quantum jump of a spin between two Zeeman levels; (2) a two-phonon process in which a phonon is scattered by a spin and another phonon with different energy is emitted accompanied by a quantum jump of spin. Theoretically, it is found that the former predominates at low temperatures.

Before 1961, no detailed theory for the rare earths had existed. This problem was first attacked by Orbach[5] who uses a simple orbit-lattice interaction to estimate the spin-lattice relaxation time.

Since the divalent rare-earth ion in CaF_2 is surrounded by eight F ions sitting at the eight corners of a cube and the trivalent rare-earth ion in the garnet occupies the site surrounded by eight oxygen ions situated at the corners of a distorted cube,[6] the orbit-lattice interaction for an XY_8 molecular cluster is computed in Sec. II, based on the normal coordinates calculated by Huang and Inoue.[7] In order to facilitate the calculation of the spin-lattice relaxation time for Sm^{3+} in lanthanum ethyl sulphate, denoted LES, Orbach's phenomenological orbit-lattice interaction is criticized and improved. The formulas for calculating the spin-lattice relaxation times are also given in this section. The experimental results

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[†] Present address: Research Institute for Advanced Studies, Baltimore, Maryland.

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