Vibrationally induced electronic transitions in crystals of magnetic compounds. I, Effects of vibrations on the crystal field line spectra

Vibrationally Induced Electronic Transitions in Crystals of Magnetic Compounds

I. Effects of Vibrations on the Crystal Field Line Spectra

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Abstract: Effects of the lattice vibration on the LAPORTE forbidden inner shell transitions of the transition metal ions are discussed. The oscillating electric field caused by the optical modes of vibration is taken as the perturbation which gives rise to the mixing of the states with opposite parity to the unperturbed states. It is shown that the frequency distribution of the optical modes is reflected in the line spectra of the optical absorption through the mixed intermediate states.

§ 1. Introduction

The general aspects of the electronic spectra of transition metal ions in crystals are well accounted for by the so-called ligand field theory[1][2]. Though the electric dipole transition is involved in the majority of the absorption spectra, direct inner shell transitions, $d \to d$ and $f \to f$ are forbidden in the free ion. This prohibition is removed by the mixing of states with opposite parity. Such mixing is induced by absence of a centre of symmetry of the ligand field and by destruction of the centre of symmetry by vibrations. In fact, remarkable increase in the absorption intensities is observed by substitutions of the ligands which remove the centre of symmetry of the ligand field. The effect of vibrations has been investigated by several authors for crystals in which a complex as MX_6, M being a metallic ion and X the ligand, can be treated as an independent unit to a good approximation[3][4][5]. In this case the mixing is brought about by odd parity modes of the molecular normal vibration of the complex.

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In many of the crystals, however, there can exist no such localized mode and we have to deal with the vibration of the whole crystal[5]. Since the crystals concerned are mostly ionic, the lattice vibration generally gives rise to electric polarization which creates oscillating electric field in the crystal. Although the field must be of complicated space dependence, we shall pick up, as a first approximation, its uniform part acting on one of the metallic ions as the perturbation responsible for the mixing of the states with odd parity.

As a result of the electronic transition, equilibrium distances between the ion and its surroundings will change in general. This occurs when the level distance depends upon the crystal field strength[6]. In this case, the vibrational states after the transition are different from those before it, and the excited ion may be treated as an impurity atom inserted in the perfect lattice as far as the vibrations are concerned[7]. The absorption spectra for such transitions are observed as broad bands as the result of exciting various vibrations[8][9]. In this paper, however, we shall treat only the case of no change in equilibrium distances of the ions.

In general, the electronic excitation may also propagate over the whole crystal and we will have an exciton band composed of the various states of the wave-like propagation. In the following, however, we shall restrict our discussion only to the electronic excitation localized in an ion.

§ 2. Interaction of localized electrons with optical vibrations

It is well known that a running (itinerant) electron in an ionic crystal interacts mainly with the optical longitudinal waves. This interaction has been discussed in great detail[10]. For our purpose, however, we have to deal with the local field acting on the electrons bound in a cation. This gives a very complicated problem, because there can be polarization due to the deformation of the ions in addition to that due to their displacement and these two effects couple with each other through electrostatic force as well as the repulsion arising from the overlap of the ion clouds[11][12][13][14].

In order to take account of these circumstances, MOTT[12] introduced a parameter γ, and expressed the force acting on an ion by

$$F = E + \frac{4\pi}{3}\gamma P \tag{1}$$

instead of the usual expression for the Lorentz field ($\gamma = 1$). The relation between the electric field E and the electric polarization P is given by simple macroscopic calculation as

$$E = \begin{cases} 0 & \text{for transverse waves} \\ -4\pi P & \text{for longitudinal waves .} \end{cases} \tag{2}$$

Combining (1) and (2) we get

$$F = \begin{cases} \dfrac{4\pi}{3}\gamma P & \text{for transverse waves} \\ -\dfrac{8\pi}{3} P \left(1 + \dfrac{1-\gamma}{2}\right) & \text{for longitudinal waves .} \end{cases} \tag{3}$$

We shall adopt this force, which is not a pure electric field but involves other effects, as the perturbation giving rise to the mixing of the intermediate states with opposite parity.

Now, let the displacement of the n-th ion in the l-th unit cell be denoted by $u_n(l)$. Then it will be expressed as a superposition of the crystal normal modes as

$$ u_n(l) = \sum_{ks} \frac{1}{\sqrt{2 M \omega_{ks}}} \left[a_{ks}\, c_n(k, s) \exp(i\, k\, R_l) + a_{ks}^*\, c_n^*(k, s) \exp(-i\, k\, R_l) \right] , $$

where a_{ks}^* and a_{ks} denote the creation and annihilation operators of the phonon with the wave vector k and the type specified by the subscript s, and M is the mass of a unit cell.

For brevity, we shall restrict the following discussion to the optical vibration of a diatomic lattice with ionic charge $\pm Z e$. Then the relative displacement of a couple of ions in the l-th cell will be given by

$$ u(l) = \sum_{k, s} \frac{1}{\sqrt{2 M \omega_{ks}}} \left[a_{ks}\, c(k, s) \exp(i\, k\, R_l) + a_{ks}^*\, c^*(k, s) \exp(-i\, k\, R_l) \right] . \qquad (4) $$

For vibrations of long wave lengths, the magnitude x of the relative displacement is connected with those of the each ion by

$$ x_1 = \frac{m_2}{m_1 + m_2}\, x , \qquad x_2 = \frac{m_1}{m_1 + m_2}\, x . $$

These relations, together with the normalization condition of the normal coordinates, give the value of $c(k, s)$ as

$$ \left| c(k, s) \right| \simeq \left[\frac{M}{N} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \right]^{1/2} , \qquad (5) $$

where N is the number of unit cells in the crystal. We can, therefore, write the relative displacement vector as

$$ u(l) = \sum_{k, s} \frac{\varepsilon_{ks}}{\sqrt{2 N \mu \omega_{ks}}} \left[a_{ks} \exp(i\, k\, R_l) + a_{ks}^* \exp(-i\, k\, R_l) \right] , \qquad (6) $$

where ε_{ks} stands for the unit vector in the direction of the relevant vibration and μ is the reduced mass of the pair of ions, i.e.

$$ \mu \equiv m_1 m_2 / (m_1 + m_2) . \qquad (7) $$

If we neglect the deformation of ions, the polarization P would be given by $P = NZ e\, u$. The deformation, or the polarization of each ion, will be taken into account by multiplying a factor σ to the above expression. This factor, however, is not the same for transverse and longitudinal waves. According to the calculation by YAMASHITA and KUROSAWA[11] for NaCl, the factor is almost unity for transverse waves of long wave-lengths but is equal to 0,45 for the longitudinal waves. We shall, therefore, leave the factors σ_t and σ_l as parameters to be adjusted in comparison with experiments. Then, using the expression (3) for the force F, we can obtain the

interaction energy of the electrons localized at the lattice site $R_l = 0$ with the optical vibrations as

$$
\left.
\begin{aligned}
H' = - \boldsymbol{F} \cdot \boldsymbol{p} = &- \frac{4\,\pi}{3}\,\sigma_t\,\gamma \sum_{\boldsymbol{k}} \sqrt{\frac{N\,Z^2\,e^2}{2\,\mu\,\omega_{\boldsymbol{k}t}}}\, (a_{\boldsymbol{k}t} + a^{*}_{\boldsymbol{k}t})\, \boldsymbol{\varepsilon}_{\boldsymbol{k}t} \cdot \boldsymbol{p} \\
&- \frac{4\,\pi}{3}\,\sigma_t\,\gamma \sum_{\boldsymbol{k}} \sqrt{\frac{N\,Z^2\,e^2}{2\,\mu\,\omega_{\boldsymbol{k}t'}}}\, (a_{\boldsymbol{k}t'} + a^{*}_{\boldsymbol{k}t'})\, \boldsymbol{\varepsilon}_{\boldsymbol{k}t'} \cdot \boldsymbol{p} \\
&+ \frac{8\,\pi}{3}\,\sigma_l\Big(1 + \frac{1-\gamma}{2}\Big) \sum_{\boldsymbol{k}} \sqrt{\frac{N\,Z^2\,e^2}{2\,\mu\,\omega_{\boldsymbol{k}l}}}\, (a_{\boldsymbol{k}l} + a^{*}_{\boldsymbol{k}l})\, \boldsymbol{\varepsilon}_{\boldsymbol{k}l} \cdot \boldsymbol{p} \,,
\end{aligned}
\right\}
\tag{8}
$$

where $\boldsymbol{p} = \sum_j e\,\boldsymbol{r}_j$ is the electric dipole moment operator of the electrons concerned, and the subscripts t, t' and l specify the transverse and longitudinal waves respectively.

§ 3. Spectral line shape

We have seen that the interaction between the localized electrons and the optical phonons is expressed in the following form:

$$
H' = \sum_{\boldsymbol{k}s} H'_{\boldsymbol{k}s} = \sum_{\boldsymbol{k}s} f(\boldsymbol{k},\,s)\, \boldsymbol{\varepsilon}_{\boldsymbol{k}s} \cdot \boldsymbol{p}(a_{\boldsymbol{k}s} + a^{*}_{\boldsymbol{k}s}) \,.
\tag{9}
$$

The probability of an electric dipole transition of an ion from the electronic ground state $|g\rangle$ to one of the excited states $|e\rangle$ accompanying the creation or annihilation of a phonon $(\boldsymbol{k},\, s)$ is proportional to the absolute square of the following:

$$
\begin{aligned}
T_{\pm}(n_{\boldsymbol{k}s}) \equiv &\sum_{i} \frac{\langle e; n_{\boldsymbol{k}s} \pm 1 \,|\, \boldsymbol{E} \cdot \boldsymbol{p} \,|\, i; n_{\boldsymbol{k}s} \pm 1 \rangle \langle i; n_{\boldsymbol{k}s} \pm 1 \,|\, H'_{\boldsymbol{k}s} \,|\, g; n_{\boldsymbol{k}s} \rangle}{E_i - E_g \pm \hbar\,\omega_{\boldsymbol{k}s}} \\
&+ \sum_{i} \frac{\langle e; n_{\boldsymbol{k}s} \pm 1 \,|\, H'_{\boldsymbol{k}s} \,|\, i; n_{\boldsymbol{k}s} \rangle \langle i; n_{\boldsymbol{k}s} \,|\, \boldsymbol{E} \cdot \boldsymbol{p} \,|\, g; n_{\boldsymbol{k}s} \rangle}{E_i - E_e \mp \hbar\,\omega_{\boldsymbol{k}s}} \\
&= \left.
\begin{aligned}
&\langle n_{\boldsymbol{k}s} + 1 \,|\, a^{*}_{\boldsymbol{k}s} \,|\, n_{\boldsymbol{k}s} \rangle \\
&\langle n_{\boldsymbol{k}s} - 1 \,|\, a_{\boldsymbol{k}s} \,|\, n_{\boldsymbol{k}s} \rangle
\end{aligned}
\right\} f(\boldsymbol{k},\,s) \sum_{i} \left[\frac{\langle e \,|\, \boldsymbol{E} \cdot \boldsymbol{p} \,|\, i \rangle \langle i \,|\, \boldsymbol{\varepsilon}_{\boldsymbol{k}s} \cdot \boldsymbol{p} \,|\, g \rangle}{E_i - E_g \pm \hbar\,\omega_{\boldsymbol{k}s}} \right. \\
&\hspace{5cm} \left. + \frac{\langle e \,|\, \boldsymbol{\varepsilon}_{\boldsymbol{k}s} \cdot \boldsymbol{p} \,|\, i \rangle \langle i \,|\, \boldsymbol{E} \cdot \boldsymbol{p} \,|\, g \rangle}{E_i - E_e \mp \hbar\,\omega_{\boldsymbol{k}s}} \right] \\
&= \left.
\begin{aligned}
&\sqrt{n_{\boldsymbol{k}s} + 1} \\
&\sqrt{n_{\boldsymbol{k}s}}
\end{aligned}
\right\} f(\boldsymbol{k},\,s) \sum_{i} [\text{the same as the above}] \,,
\end{aligned}
$$

where $\boldsymbol{E}$ is the amplitude of the external oscillating electric field $\boldsymbol{E}\cos\omega\,t$ due to the photon.

Now, the term $\hbar\,\omega_{\boldsymbol{k}s}$, being the energy of the created or annihilated phonon, is negligibly small compared with the electronic excitation energies, i.e. $E_i - E_g \gg \hbar\,\omega_{\boldsymbol{k}s}$ and $E_i - E_e \gg \hbar\,\omega_{\boldsymbol{k}s}$. We shall, therefore, omit them in the energy deno-

minators. Furthermore, we may replace $f(\boldsymbol{k}, s)$ by $f(0, s)$ because we are considering only the optical modes of lattice vibrations. Then we can write the above as

$$T_{\pm}(n_{\boldsymbol{k}s}) = \left.\begin{array}{c} \sqrt{n_{\boldsymbol{k}s} + 1} \\ \sqrt{n_{\boldsymbol{k}s}} \end{array}\right\} f(0, s)\, [\boldsymbol{E} \cdot \boldsymbol{A} \cdot \boldsymbol{\varepsilon}_{\boldsymbol{k}s} + \boldsymbol{\varepsilon}_{\boldsymbol{k}s} \cdot \boldsymbol{B} \cdot \boldsymbol{E}]\,,$$

where $\boldsymbol{A}$ and $\boldsymbol{B}$ are second order tensors defined by

$$\boldsymbol{A} \equiv \sum_i \frac{\langle e \,|\, \boldsymbol{p} \,|\, i \rangle \langle i \,|\, \boldsymbol{p} \,|\, g \rangle}{E_i - E_g}\,, \qquad \boldsymbol{B} \equiv \sum_i \frac{\langle e \,|\, \boldsymbol{p} \,|\, i \rangle \langle i \,|\, \boldsymbol{p} \,|\, g \rangle}{E_i - E_e}\,. \tag{10}$$

Then, with the help of the Bose-Einstein distribution function for the phonon number $w(n_{\boldsymbol{k}s})$, we can express the shape function of the electronic absorption $|\,g\,\rangle \to |\,e\,\rangle$ in the following form

$$\begin{aligned}
I(\omega) &= \sum_{\boldsymbol{k},\,s} \sum_{n_{\boldsymbol{k}s}} w(n_{\boldsymbol{k}s})\,[|\,T_{+}(n_{\boldsymbol{k}s})\,|^2\,\delta(\omega - \omega_0 - \omega_{\boldsymbol{k}s}) \\
&\qquad\qquad\qquad\qquad + |\,T_{-}(n_{\boldsymbol{k}s})\,|^2\,\delta(\omega - \omega_0 + \omega_{\boldsymbol{k}s})] \\
&= \sum_s f^2(0, s) \sum_{\boldsymbol{k}} [(\langle n_{\boldsymbol{k}s}\rangle + 1)\,\delta(\omega - \omega_0 - \omega_{\boldsymbol{k}s}) \\
&\qquad + \langle n_{\boldsymbol{k}s}\rangle\,\delta(\omega - \omega_0 + \omega_{\boldsymbol{k}s})]\,|\,\boldsymbol{E} \cdot \boldsymbol{A} \cdot \boldsymbol{\varepsilon}_{\boldsymbol{k}s} + \boldsymbol{\varepsilon}_{\boldsymbol{k}s} \cdot \boldsymbol{B} \cdot \boldsymbol{E}\,|^2\,,
\end{aligned} \tag{11}$$

where $\omega_0 = (E_e - E_g)/\hbar$ and $\langle n_{\boldsymbol{k}s}\rangle$ means the thermal average value of the phonon number before the transition

$$\langle n_{\boldsymbol{k}s}\rangle = \frac{1}{\exp(\hbar\,\omega_{\boldsymbol{k}s}/k\,T) - 1}\,. \tag{12}$$

It will be shown in Appendix that the last factor $|\,\boldsymbol{E} \cdot \boldsymbol{A} \cdot \boldsymbol{\varepsilon}_{\boldsymbol{k}s} + \boldsymbol{\varepsilon}_{\boldsymbol{k}s} \cdot \boldsymbol{B} \cdot \boldsymbol{E}\,|^2$ can be replaced by the one independent of $(\boldsymbol{k}, s)$. Thus we get the following shape function

$$\begin{aligned}
I(\omega) &\propto \sum_s f^2(0, s) \sum_{\boldsymbol{k}} [(\langle n_{\boldsymbol{k}s}\rangle + 1)\,\delta(\omega - \omega_0 - \omega_{\boldsymbol{k}s}) \\
&\qquad\qquad\qquad\qquad + \langle n_{\boldsymbol{k}s}\rangle\,\delta(\omega - \omega_0 + \omega_{\boldsymbol{k}s})] \\
&\propto \frac{1}{\langle\omega_t\rangle}\,\sigma_t^2\,\gamma^2 \sum_{\boldsymbol{k}} [(\langle n_{\boldsymbol{k}t}\rangle + 1)\,\delta(\omega - \omega_0 - \omega_{\boldsymbol{k}t}) \\
&\qquad\qquad\qquad\qquad + \langle n_{\boldsymbol{k}t}\rangle\,\delta(\omega - \omega_0 + \omega_{\boldsymbol{k}t})] \\
&\quad + \frac{2}{\langle\omega_l\rangle}\,\sigma_l^2\Big(1 + \frac{1 - \gamma}{2}\Big)^2 \sum_{\boldsymbol{k}} [(\langle n_{\boldsymbol{k}l}\rangle + 1)\,\delta(\omega - \omega_0 - \omega_{\boldsymbol{k}l}) \\
&\qquad\qquad\qquad\qquad + \langle n_{\boldsymbol{k}l}\rangle\,\delta(\omega - \omega_0 + \omega_{\boldsymbol{k}l})]\,.
\end{aligned} \tag{13}$$

Since $\langle n_{\boldsymbol{k}s}\rangle = 0$ at $0°\,K$, only the transitions with the simultaneous excitation of phonons will be observed, and the spectra reproduce the frequency distribution of the optical branches. With raising temperature, the terms proportional to $\langle n_{\boldsymbol{k}s}\rangle$ increase rapidly, and make the spectral patterns symmetrical with respect to $\omega = \omega_0$.

§ 4. Discussion

We have used several approximations in deriving our result. First, we adopted MOTT's expression (3) as the perturbation to our localized electrons. The parameter γ introduced there is determined for many crystals and is found to be small compared with unity in most cases. These values are, however, obtained in connection with the dielectric properties of the crystals, and it is not confirmed that we can expect the same values of the parameter for such optical properties as treated in the present paper.

We have also made some approximations in deriving the expression of u. These, as well as the above treatment of the forces acting on the electrons, are valid only for long wave-lengths. Therefore, the observed spectral pattern might not reflect the spectra of the optical modes in such high fidelity as expected in our theory. Improvement of the theory in this respect will not be easy, and it must be inevitable to use some other approximations. Furthermore, the effect of the acoustical modes of shorter wave-lengths may not be negligible[14]). Detailed discussions of these difficult problems are, however, not very fruitful in the present stage.

If comparison with experiments would be possible, the most important information will be obtained from the intensity ratio of the bands corresponding to the transverse and longitudinal modes, i.e. the first factors of the two terms in the expression (10). The values of the parameters could be compared with those obtained from the dielectric properties of the crystals. The extension of the present theory to more general polyatomic crystals can be carried through straightforwardly, though we have to introduce some more empirical parameters.

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Appendix

The expression (11) will be written as

$$I(\omega) = \sum_s f^2(0, s) \sum_k \varrho(\omega, \omega_{ks}) \left| E \cdot A \cdot \varepsilon_{ks} + \varepsilon_{ks} \cdot B \cdot E \right|^2 .$$

Now, let us consider a shell in the k-space corresponding to

$$\overline{\omega} - \frac{1}{2} \delta \omega \leqq \omega_{ks} \leqq \overline{\omega} + \frac{1}{2} \delta \omega .$$

Then,

$$J \equiv \sum_k^{shell} \varrho(\omega, \omega_{ks}) \left| E \cdot A \cdot \varepsilon_{ks} + \varepsilon_{ks} \cdot B \cdot E \right|^2$$

$$= \varrho(\omega, \overline{\omega}) \sum_k^{shell} \left| E \cdot A \cdot \varepsilon_{ks} + \varepsilon_{ks} \cdot B \cdot E \right|^2$$

$$= \varrho(\omega, \overline{\omega}) \sum_k^{shell} \left[(\varepsilon_{ks} \cdot A^* \cdot E)(E \cdot A \cdot \varepsilon_{ks}) + (\varepsilon_{ks} \cdot A^* \cdot E)(\varepsilon_{ks} \cdot B \cdot E) + \cdots \right]$$

$$= \varrho(\omega, \overline{\omega}) \sum_{\lambda, \mu} \left[(A^* \cdot E)_\lambda (E \cdot A)_\mu + (A \cdot E)_\lambda (B \cdot E)_\mu + \cdots \right] \sum_k^{shell} \varepsilon_{ks}^\lambda \varepsilon_{ks}^\mu ,$$

where λ and μ stand for x, y, z which are taken to agree with the directions of the principal axes of the k-space. In the last factor, the summand may be replaced by the average value over the energy shell:

$$\sum_k^{shell} \varepsilon_{ks}^\lambda \varepsilon_{ks}^\mu = \sum_k^{shell} \langle \varepsilon_{ks}^\lambda \varepsilon_{ks}^\mu \rangle .$$

Then, for an *isotropic* crystal, we have

$$\langle \varepsilon_{ks}^\lambda \varepsilon_{ks}^\mu \rangle = \delta_{\lambda\mu} \langle \varepsilon_{ks}^\lambda \varepsilon_{ks}^\lambda \rangle = \frac{1}{3} \delta_{\lambda\mu} \langle \varepsilon_{ks} \cdot \varepsilon_{ks} \rangle = \frac{1}{3} \delta_{\lambda\mu} .$$

Substituting this in the above, we get

$$J = \frac{1}{3} \varrho(\omega, \overline{\omega}) \sum_\lambda \left[(A^* E)_\lambda (E A)_\lambda + \cdots \right] \sum_k^{shell} 1$$

$$= \varrho(\omega, \overline{\omega}) \left(\sum_k^{shell} 1 \right) \text{(factor independent of } k, s)$$

$$= \sum_k^{shell} \varrho(\omega, \omega_{ks}) \times \text{(factor independent of } k, s) .$$

Hence

$$I(\omega) = \sum_s f^2(0, s) \sum_k \varrho(\omega, \omega_{ks}) \times \text{(factor independent of } k, s) .$$