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Institut de Physique, Université de Neuchâtel

Antiresonance in Vibronic Absorption Spectra of a Two-Impurity System

By

T. IIDA¹⁾ and M. AEGERTER

Antiresonance effect is studied in a system composed of two-impurity centers in a crystal; one has a broad absorption band while the other has sharp phonon-line structure in its absorption spectrum when no interaction occurs between the two defects. A general expression of the change in the absorption spectrum due to interaction between them is given. The antiresonance effect on a sharp zero-phonon line is investigated in detail and the favourable conditions for the observation of such an effect are also discussed.

Nous avons étudié des phénomènes d'antirésonance apparaissant dans des cristaux contenant deux centres d'impuretés différentes. Le premier possède une large bande d'absorption optique tandis que le second présente une structure de raies phononiques étroites, lorsqu'il n'existe aucune interaction entre les défauts. Nous donnons une expression générale pour les changements apparaissant dans les spectres d'absorption causés par une interaction entre ces défauts et discutons plus particulièrement l'effet d'interférence entre la bande large et la raie étroite sans phonon. Les conditions favorables pour l'observation d'un tel effet sont également discutées.

1. Introduction

The optical absorption spectra of rare gases have very characteristic "antiresonance" lineshapes. They come from interference effects between discrete autoionized states and ionized continua. The theoretical investigation of this effect has been done by Fano [1].

Optical spectra having similar characteristics have also been found in solid state physics. Well-known examples of this effect can be observed in the absorption spectra of excitonic transitions overlapped by the continuum of band-to-band transitions [2 to 4] or in the case of a sharp transition of an impurity center overlapped by band-to-band transitions of the host crystal [5, 6]. The theory of the latter effect has been studied by Shibata and Toyozawa [5]. They have reformulated Fano's theory with a method useful for the application to problems in solid state physics and have obtained more general formula than that given by Fano. We shall use the same method in this paper.

The interference effect between a sharp transition and a broad vibronic band has been first investigated by Sturge et al. [7] in the case of the absorption spectrum of an impurity center in a crystal. In this paper we present a more general and detailed study of a similar effect in a system composed of two-impurity centers in a crystal. We assume that, in the absence of interaction between two centers, a center "A" has a broad absorption band due to rather strong electron-phonon interaction, while for the other center "B", the elec-

¹⁾ On leave from Osaka City University, Osaka, Japan.

tron-phonon interaction is so weak that a sharp zero-phonon line and its associated many-phonon lines can be observed. The interference effect on the zero-phonon line will be discussed in detail for two illustrative cases where the broadening of the absorption band of center A is attributed to the interaction with either acoustic or optical phonons.

Two parameters are introduced to discuss the favorable conditions for the observation of the sharp antiresonance. One is the ratio of the dipole matrix element of center B to that of center A. The other is, in the first case, the ratio of the strength of the interaction between the two centers to the half-width of the absorption band of center A, and in the second case, it is the ratio of the strength of the interaction between the two centers to an optical phonon energy.

Examples of sharp antiresonance spectra are calculated for various values of these parameters.

Sharp antiresonances have been observed by Taylor [8] in the absorption spectra of X-rayed calcium fluoride crystals doped with rare-earth ions. He proposed that the antiresonances come probably from the interaction between the rare-earth ion and a neighboring color center. The rare-earth ions have very weak sharp absorption lines which are superimposed on the broad absorption band of the color center. This system, therefore, appears as a typical example for the model discussed in this paper. However, a direct comparison between theory and experimental results will not be carried out in this paper.

In Section 2 we discuss how to describe a two-center vibronic system and derive a general expression of the absorption lineshape. In Section 3 we apply the general formula to simple cases and discuss the favorable conditions for the observation of sharp antiresonance. Several examples of calculated lineshapes are also presented.

2. Formulation

2.1 Vibronic states of a two-impurity system

Let us consider the vibronic states of two-impurity centers A and B interacting with each other in a crystal. The Hamiltonian of the system is assumed to have the form

$$\mathcal{H} = h_a(Q) + h_b(Q) + \mathcal{H}_l + V_{ab}, \quad (1)$$

where $h_a(Q)$ and $h_b(Q)$ are respectively the electronic Hamiltonians of centers A and B which depend on vibrational normal coordinates Q_j , \mathcal{H}_l is the Hamiltonian of the lattice, V_{ab} an interaction between the electrons of the two centers.

We expand $h_n(Q)$ ($n = a, b$) in a Taylor series about a suitable equilibrium configuration of the lattice. By retaining linear terms only, we can rewrite the Hamiltonian as

$$\left. \begin{aligned} \mathcal{H} &= \mathcal{H}_0 + V_{ab}, \\ \mathcal{H}_0 &= \sum_{n=a,b} (h_n - \sum_j u_{nj} Q_j) + \mathcal{H}_l, \end{aligned} \right\} \quad (2)$$

where h_n is the Q -independent zero-th order term of $h_n(Q)$. We shall treat V_{ab} as a perturbation to \mathcal{H}_0 . For simplicity, the eigenstates of h_n are assumed to be non-degenerate. We denote the ground state of $h_a + h_b$ by a real function Φ_0 , and the two lower excited states with energy $\hbar\omega_a$ and $\hbar\omega_b$ by real functions Φ_a and Φ_b ; Φ_a (or Φ_b) corresponds to center A (or B) in its lowest excited state and center B (or A) in its ground state. Having assumed the non-degeneracy of the

electronic states, we can use the Born-Oppenheimer approximation and then the vibrational states of the lattice are determined within the first approximation by the following equations

$$\mathcal{H}_1 \chi_{0p}(Q) = E_{0p} \chi_{0p}(Q)$$

for the ground state and

$$\left(\mathcal{H}_1 + \hbar\omega_n - \sum_j \bar{u}_{nj} Q_j \right) \chi_{np}(Q) = E_{np} \chi_{np}(Q); \quad n = a, b$$

for the excited states, where $\bar{u}_{nj} = \langle \Phi_n | u_{nj} | \Phi_n \rangle$; the equilibrium configuration of the lattice for the ground state is chosen as the origin in Q -space. Then the eigenfunctions and eigenvalues of \mathcal{H}_0 can be written as

$$E_{0p} = \sum_j p_j \hbar\omega_j, \quad \psi_{0p} = \Phi_0 \chi_{0p}(Q) = \Phi_0 \prod_j \chi_{0p_j}(Q_j) \quad (3a)$$

and

$$\left. \begin{aligned} E_{np} &= \sum_j (p_j - S_{nj}) \hbar\omega_j + \hbar\omega_n, \\ \psi_{np} &= \Phi_n \chi_{np}(Q) = \Phi_n \prod_j \chi_{np_j}(Q_j); \quad n = a, b, \end{aligned} \right\} \quad (3b)$$

where the zero-point energy is eliminated. $S_{nj} = (\bar{u}_{nj}^2 / 2\omega_j^2) / \hbar\omega_j$ and $\sum_j S_{nj} \hbar\omega_j$ is the lattice relaxation energy, χ_{0p_j} is a harmonic oscillator wave function, and χ_{np_j} is a displaced one whose equilibrium position is given by $\bar{u}_{nj} / \omega_j^2$.

2.2 Absorption lineshape

The optical absorption lineshape can be expressed at zero temperature as [5]

$$I(\omega) = \frac{1}{\pi} \text{Im} \langle \psi_{00} | DGD | \psi_{00} \rangle \quad (4)$$

apart from the unimportant constant factor; $\hbar\omega$ is the photon energy and G is the Green function defined as

$$G(Z) = \frac{1}{Z - H}; \quad Z = \hbar\omega - i\hbar\gamma, \quad (5)$$

where $\hbar\gamma$ is a sufficiently small positive number. The operator H is the Hamiltonian corresponding to the excited state:

$$\begin{aligned} H &= H_0 + H', \\ H_0 &= \sum_p E_{ap} P_{ap} + \sum_{p'} E_{bp'} P_{bp'}, \\ H' &= \sum_{p,p'} (P_{ap} V_{ab} P_{bp'} + P_{bp'} V_{ab} P_{ap}), \end{aligned}$$

where P_{ap} and $P_{bp'}$ are projection operators on the spaces of ψ_{ap} and $\psi_{bp'}$, respectively. The operator D is the relevant electric dipole moment given by

$$D = \sum_p P_{ap} d P_{00} + \sum_{p'} P_{bp'} d P_{00} + (\text{hermitian conjugate}), \quad (6)$$

where P_{00} is the projection operator on the state ψ_{00} and d the electric dipole moment operator. After some algebra the absorption lineshape (4) is given by

$$I(\omega) = \frac{1}{\pi} \text{Im} \sum_p d_a^2 |\langle \chi_{ap} | \chi_{00} \rangle|^2 \left\langle \psi_{ap} \left| \frac{1}{Z - H_0} \right| \psi_{ap} \right\rangle + (\mathbf{L}^\dagger + i\mathbf{M}^\dagger) \mathbf{G}_b (\mathbf{L} + i\mathbf{M}), \quad (7)$$

where d_n ($n = a, b$) is the dipole matrix element and T stands for the transpose of real vectors \mathbf{L} and \mathbf{M} providing V_{ab} is a real operator. The p -th elements of these vectors are written explicitly as

$$L_p = d_b \langle \chi_{bp} | \chi_{00} \rangle + d_a (\hbar V) \operatorname{Re} F_p(\omega) \quad (8a)$$

and

$$M_p = d_a (\hbar V) \operatorname{Im} F_p(\omega), \quad (8b)$$

where $\hbar V = \langle \Phi_a | V_{ab} | \Phi_b \rangle$ and

$$F_p(\omega) = \sum_{p'} \frac{\langle \chi_{bp} | \chi_{ap'} \rangle \langle \chi_{ap'} | \chi_{00} \rangle}{\hbar\omega - E_{ap'} - i\hbar\gamma}. \quad (8c)$$

The matrix \mathbf{G}_b satisfies the relation

$$\mathbf{G}_b = \mathbf{G}_b^{(0)} + \mathbf{G}_b^{(0)} (\Delta + i\mathbf{\Gamma}) \mathbf{G}_b \quad (9)$$

and pp' elements of $\mathbf{G}_b^{(0)}$, Δ , and $\mathbf{\Gamma}$ are given as

$$G_{b,pp'}^{(0)} = \left\langle \psi_{bp} \left| \frac{1}{Z - H_0} \right| \psi_{bp'} \right\rangle, \quad (10)$$

$$\Delta_{pp'} = (\hbar V)^2 \operatorname{Re} F_{pp'}(\omega), \quad (11a)$$

$$\Gamma_{pp'} = (\hbar V)^2 \operatorname{Im} F_{pp'}(\omega) \quad (11b)$$

with

$$F_{pp'} = \sum_{p''} \frac{\langle \chi_{bp} | \chi_{ap''} \rangle \langle \chi_{ap''} | \chi_{bp'} \rangle}{\hbar\omega - E_{ap''} - i\hbar\gamma}. \quad (11c)$$

The first term of (7) represents the direct transitions from the ground state to the states in which center A is in its unperturbed excited state. The interference effect is included in the second term.

We have assumed the validity of the Born-Oppenheimer approximation and retained only harmonic terms in the vibrational potential. Within these approximations, the vibronic levels are stationary states. Real crystals, however, cannot be accurately described within these approximations. We therefore assume that in the expressions (8) and (11) γ is a finite small positive number instead of an infinitesimally small number.

If the electron-phonon interaction of center B is weak enough so that S_{bj} can be regarded as practically negligible, the electric dipole moment given in (6) reduces to

$$D = \sum_p P_{ap} dP_{00} + P_{b0} dP_{00} + (\text{hermitian conjugate}) \quad (12)$$

since $\langle \chi_{bp} | \chi_{00} \rangle = 0$ for $p \neq 0$. This will be a reasonable approximation to calculate the change of the shape of the sharp zero-phonon line of center B. In this case, equation (9) has a diagonal form which can be solved exactly with respect to \mathbf{G}_b . Furthermore the very sharp line means that the zero-phonon state of center B is relatively well defined. Then we have

$$G_{b,00} = \frac{1}{\hbar\omega - E_{b0} - \Delta_0 - i\Gamma_0}, \quad (13)$$

where $\Delta_0 \equiv \Delta_{00}$ and $\Gamma_0 \equiv \Gamma_{00}$ are respectively the energy shift and the broadening of the zero-phonon line of center B due to the interaction with the many-

phonon states of center A. Substituting (13) into (7), we obtain

$$I(\omega) = \frac{d_a^2}{\pi} \text{Im } F(\omega) + \frac{1}{\pi} \frac{M_0^2 q^2 - 1 + 2q\varepsilon}{\Gamma_0 (\varepsilon^2 + 1)}, \tag{14}$$

where

$$F(\omega) = \sum_p \frac{|\langle \chi_{ap} | \chi_{00} \rangle|^2}{\hbar\omega - E_{ap} - i\hbar\gamma}, \tag{15}$$

$$q = \frac{L_0}{M_0}, \tag{16a}$$

and

$$\varepsilon = \frac{\hbar\omega - E_{b0} - \Delta_0}{\Gamma_0}. \tag{16b}$$

If the interaction between the two centers (and therefore Γ_0) is sufficiently small, the linewidth of the function $(q^2 - 1 + 2q\varepsilon)/(\varepsilon^2 + 1)$ will be so small that L_0 , M_0 , Δ_0 , and Γ_0 may be regarded as independent of ω within the interesting region. Then the second term of (14) gives a set of asymmetric Lorentzian shapes corresponding to various values of q . From (8), (11), and (15), we have the following useful relations:

$$L_0 = d_b + d_a(\hbar V) \text{Re } F(\omega), \quad M_0 = d_a(\hbar V) \text{Im } F(\omega), \tag{17a}$$

$$\Delta_0 = (\hbar V)^2 \text{Re } F(\omega), \quad \text{and} \quad \Gamma_0 = (\hbar V)^2 \text{Im } F(\omega). \tag{17b}$$

With these relations (14) becomes much simpler

$$I(\omega) = \frac{d_a^2}{\pi} \text{Im } F(\omega) \frac{(\varepsilon + q)^2}{\varepsilon^2 + 1} \tag{18}$$

with

$$q = \frac{d_b \hbar V}{d_a \Gamma_0} + \frac{\Delta_0}{\Gamma_0}. \tag{19}$$

The expression (18) has the same form as those given in [1, 5, 7]. The factor $(\varepsilon + q)^2/(\varepsilon^2 + 1)$ gives a characteristic lineshape superimposed on the broad absorption band of center A. This factor is plotted in Fig. 1 for different constant values of q [1].

Let us briefly discuss the more general case where the vibrational states χ_{00} and χ_{bp} are centered at different origins. In this case, equation (9) may be formally solved with respect to G_b as discussed by Toyozawa [2]. Introducing a trans-

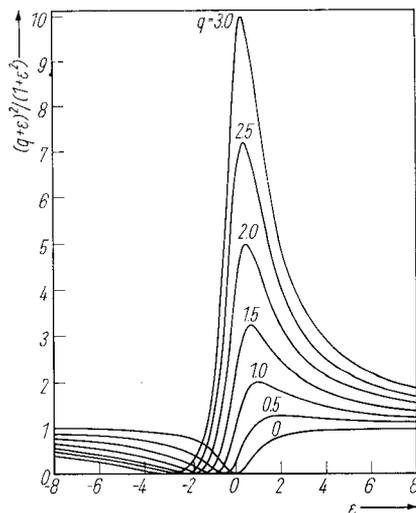


Fig. 1. Lineshapes of $(\varepsilon + q)^2/(\varepsilon^2 + 1)$ given by Fano [1] for various values of q (reverse the scale of abscissas for negative q)

formation matrix \mathbf{A} which diagonalizes the matrix $[(\mathbf{G}_b^{(0)})^{-1} - \mathbf{A} - i\mathbf{\Gamma}]$, we may write the p -th diagonal element as

$$\{A[(\mathbf{G}_b^{(0)})^{-1} - \mathbf{A} - i\mathbf{\Gamma}]\mathbf{A}^{-1}\}_{pp} = \hbar\omega - E'_{bp} - \Delta'_p - i\Gamma'_p,$$

where the p -th element is numbered such that E'_{bp} becomes E_{bp} when $V \rightarrow 0$. Since the quantities with primes are all renormalized ones, all orders of the interaction are taken into account. Using the result of the diagonalization, equation (7) can be written in the following form after straightforward calculation:

$$I(\omega) = \frac{1}{\pi} \text{Im } F(\omega) + \frac{1}{\pi} \sum_p \frac{M_p'^2 q_p'^2 - 1 + 2q_p' \epsilon_p'}{\Gamma_p'^2 + 1},$$

where $q_p' = L_p'/M_p'$ and $\epsilon_p' = (\hbar\omega - E'_{bp} - \Delta'_p)/\Gamma_p'$; L_p' and M_p' are the p -th elements of \mathbf{AL} and \mathbf{AM} , respectively. If the quantities q_p' , M_p' , Δ'_p , and Γ_p' can be regarded as independent of ω over a sufficient region near $\omega = (E_{bp} + \Delta_p)/\hbar$, the second term shows that the absorption spectrum can be decomposed into a number of asymmetric Lorentzian lines each one corresponding to the p -th phonon line of center B.

3. Calculation and Discussion

Let us carry out more detailed calculations of the lineshape (18) for the two particular cases where the broadening of the absorption band of center A is caused by interaction with either acoustic phonons or optical phonons, and then discuss what are the favorable conditions for the observation of the sharp anti-resonance. What we must do now is to calculate the function $F(\omega)$ given by (15). This can be readily done following Davidov [9] if true localized modes are not considered. In this case, the overlap integral of the two harmonic oscillator wave functions with different equilibrium positions can be approximated as follows:

$$\langle \chi_{a p_j} | \chi_{00} \rangle \begin{cases} = 1 - \frac{1}{2} S_{a_j} & \text{if } p_j = 0, \\ = -(S_{a_j})^{1/2} & \text{if } p_j = 1. \end{cases}$$

When p_j is larger than unity the integral tends to zero more rapidly than N^{-1} . Since N is the total number of degrees of freedom of the lattice, it is sufficient to only retain terms up to the order N^{-1} . Within this approximation, the function F can be transformed into

$$F(\omega) = \frac{i}{\hbar} e^{-S} \int_0^\infty \exp \left[i \left(\omega_a - \sum_j S_{a_j} \omega_j + i\gamma - \omega \right) t + S(t) \right] dt, \quad (20)$$

where $S = \sum_j S_{a_j}$ and $S(t) = \sum_j S_{a_j} e^{i\omega_j t}$. In the first case we take into account the interaction with acoustic phonons for which $\omega_j \leq \omega_0$. If $(\sum_j S_{a_j} \omega_j^2)/2 > \omega_0^2$ is also satisfied, the integral can be approximately calculated:

$$F(\omega) = \frac{i}{\hbar} \sqrt{\frac{\pi}{2}} \frac{1}{W} [1 - \varphi(z)] e^{z^2}, \quad (21)$$

where $W = \left(\sum_j S_{aj}\omega_j^2\right)^{1/2}$, $z = [\gamma - i(\omega_a - \omega)]/(2)^{1/2} W$, and $\varphi(z)$ is the Gaussian error function

$$\varphi(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy.$$

Near the frequency ω_a or $|z| < 1$, $\varphi(z)$ can be approximated as $\varphi(z) \approx 2z/\sqrt{\pi}$, then we have

$$F(\omega) = \frac{i}{\hbar} \sqrt{\frac{\pi}{2}} \frac{1}{W} \left[1 - i \frac{(\omega - \omega_a)}{\sqrt{\pi/2} W} \right] e^{-[(\omega - \omega_a)^2/2W^2]} \tag{22}$$

assuming $W \gg \gamma$. Inserting the imaginary part of (22) into (18), we obtain the absorption spectrum

$$I(\xi) = \frac{d_a^2}{\hbar W} \frac{e^{-(1/2)\xi^2}}{\sqrt{2\pi}} \frac{(q + \varepsilon)^2}{\varepsilon^2 + 1}, \tag{23}$$

where $\xi = (\omega - \omega_a)/W$ and $\exp[-(1/2)\xi^2]/(2\pi)^{1/2}$ is a normalized Gaussian curve with a peak at $\xi = 0$ ($\omega = \omega_a$) and a half-width of 1. From (17b) and (22), we obtain

$$\Delta_0^* = \frac{\Delta_0}{\hbar W} = \left(\frac{V}{W}\right)^2 \xi e^{-(1/2)\xi^2} \tag{24a}$$

and

$$\Gamma_0^* = \frac{\Gamma_0}{\hbar W} = \left(\frac{V}{W}\right)^2 \sqrt{\frac{\pi}{2}} e^{-(1/2)\xi^2}. \tag{24b}$$

Here Δ_0^* and Γ_0^* represent respectively the energy shift and the broadening versus ξ . The quantities q and ε are written as

$$q = \sqrt{\frac{2}{\pi}} (\xi + \alpha e^{(1/2)\xi^2}) \tag{25}$$

and

$$\varepsilon = \frac{(\xi - \xi_b - \Delta_0^*)}{\Gamma_0^*}, \tag{26}$$

where $\alpha = (d_b/d_a) (W/V)$ and $\xi_b = (\omega_b - \omega_a)/W$.

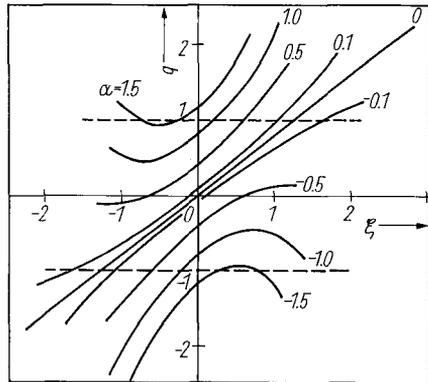


Fig. 2. Behavior of the parameter q given by (25) for various values of α

On the basis of the above calculations let us discuss the favorable conditions for the observation of sharp antiresonance within the half-width, $|\xi| < 1$, of the absorption band of center A. The ε -dependence of the function $(\varepsilon + q)^2/(\varepsilon^2 + 1)$ given in Fig. 1 shows that each line consists of an asymmetric curve with a peak and a dip, i.e., an antiresonance. The dip area gets larger with decreasing $|q|$ -values and in the range of $|q| < 1$ the dip area becomes larger than that of the peak; the complete antiresonance occurs for $q = 0$. As Shibata and Toyozawa [5], we regard the condition $|q| < 1$ as the criterion for sharp antiresonance. The behavior of q given by (25) is shown in Fig. 2 for different values of α and can be roughly summarized as follows: the criterion is satisfied in the range $|\alpha| \lesssim 1.5$, that is, $0 \lesssim \alpha \lesssim 1.5$ for the low-energy side with respect to the center of the absorption band and $-1.5 \lesssim \alpha \lesssim 0$ for the high-energy side.

In the vicinity of the center of the broad absorption band, the $|q|$ -value decreases with $|\alpha|$ and $|\alpha| \approx 0$ gives the smallest value for $|q|$. For higher or lower energies but within the half-width, $|\alpha| \approx 0.5$ gives smaller values for $|q|$ than $\alpha \approx 0$.

In order to have the value of $|q|$ sufficiently close to zero, $|d_b/d_a|$ or $|W/V|$ must be small enough. The small value of $|W/V|$ leads to an increase of the broadening Γ_0^* as shown by (24b). Too large broadening will make the observation of the antiresonance very difficult and is unfavorable for the assumption that q , Δ_0^* , and Γ_0^* can be regarded as constant in the interesting energy range. Therefore, $|d_b/d_a|$ should be ≈ 0 in order to realize the condition $|\alpha| \approx 0$; this means that the electric dipole transition of center B should be quite weak or forbidden in the absence of the interaction with center A.

There is another restriction on the magnitudes of Γ_0^* which gives a lower limit to it. The broadening $\Gamma_0^* \hbar W$ must be at least as large as the experimental resolution, which is of the order of 10^{-4} eV in usual case. If we tentatively assume a linewidth $\hbar W$ of the order of 10^{-1} eV, we may put a lower limit of Γ_0^* as $\Gamma_0^* \gtrsim 10^{-3}$. Then, from (24b), the lower limit of $(V/W)^2$ is given as $(V/W)^2 \gtrsim 10^{-3}$ in the range of $|\xi| < 1$ (half-width), since the order of magnitude of $(\pi/2)^{1/2} \times \exp(-\xi^2/2)$ is unity in this range. This means that an interaction much

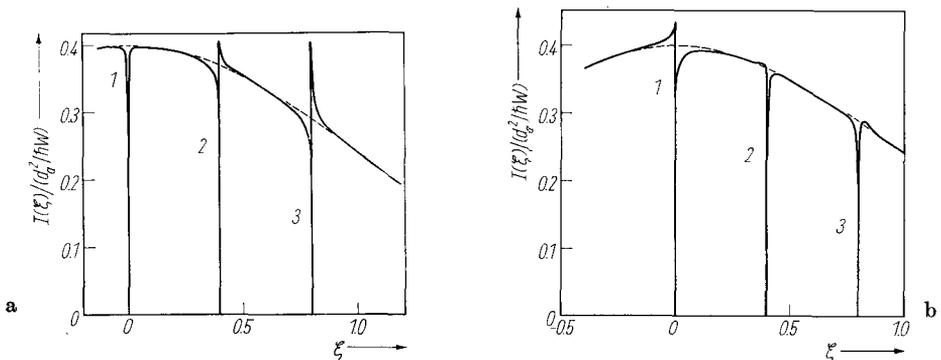


Fig. 3. a) Calculated antiresonance lineshapes given by (23) providing $(V/W)^2 = 10^{-3}$ for $\alpha = 0$, ($|d_b/d_a| = 0$). (1) $\xi_b = 0$, $q = 0$; (2) $\xi_b = 0.4$, $q = 0.319$; (3) $\xi_b = 0.8$, $q = 0.638$. b) Same as Fig. 3a, for $\alpha = -0.5$, ($|d_b/d_a| \approx 0.016$). (1) $\xi_b = 0$, $q = -0.399$; (2) $\xi_b = 0.4$, $q = -0.113$; (3) $\xi_b = 0.8$, $q = +0.089$

smaller than the half-width will be unfavorable for the observation of antiresonance. From the definition of α and under the above condition, the ratio $|d_b/d_a|$ should be larger than $\approx 10^{-2}$, in order to realize the situation $|\alpha| \approx 0.5$.

We can then conclude that the favorable condition for the observation of the antiresonance is that the interaction between two centers should not be too small compared with the half-width of the broad band; moreover $|d_b/d_a|$ should be sufficiently small in the vicinity of the center of absorption band while for higher or lower energies but within the half-width this ratio should not be too small.

Typical examples of absorption spectra are shown in Fig. 3, which are calculated for $\xi_b = 0, 0.4,$ and 0.8 in the cases of a) $\alpha = 0$ and b) $\alpha = -0.5$, providing $(V/W)^2 = 0.001$. We can observe that for $\xi_b = 0, \alpha = 0$ gives sharper antiresonance than $\alpha = -0.5$ and for $\xi_b = 0.4$ and $0.8, \alpha = -0.5$ gives sharper antiresonances than $\alpha = 0$.

In the range far away from the center of absorption band of center A, $|\omega - \omega_a| \gg W \gg \gamma$, the integral (20) becomes

$$F(\omega) = \frac{i}{\hbar} \frac{\gamma - i(\omega - \omega_a)}{(\omega - \omega_a)^2 + \gamma^2}.$$

Substituting the real and imaginary parts of this expression into (19), we obtain

$$q = \left(\frac{\omega - \omega_a}{\gamma} \right) \left(\frac{d_b}{d_a} \frac{\omega - \omega_a}{V} + 1 \right).$$

This shows that $|q|$ is much larger than unity except when (d_b/d_a) is infinitely close to $V/(\omega_a - \omega)$ so that $[(d_b/d_a)(\omega - \omega_a)/V + 1] \ll 1$. Such an exceptional case could seldom be expected and sharp antiresonances will scarcely occur in this range.

In the second case, we take into account the interaction with phonons which belong to one of optical branches. Usually the dispersion of the optical phonon frequencies is very small, so that we may put approximately $\omega_j = \omega_0$. In this case the integral (24) is easily calculated:

$$F(\eta) = \frac{1}{\hbar\omega_0} \sum_{p=0}^{\infty} \frac{e^{-S} (S)^p}{p!} \frac{(\eta + S - p) + i\delta}{(\eta + S - p)^2 + \delta^2}, \quad (27)$$

where $\eta = (\omega - \omega_a)/\omega_0$ and $\delta = \gamma/\omega_0$. Substituting real and imaginary parts of (27) into (17) and (18), we have

$$I(\eta) = \frac{d_a^2}{\pi\hbar\omega_0} f_i(\eta) \frac{(\epsilon + q)^2}{\epsilon^2 + 1}, \quad (28)$$

$$A_0^* = \frac{A_0}{\hbar\omega_0} = \left(\frac{V}{\omega_0} \right)^2 f_r(\eta), \quad (29a)$$

and

$$I_0^* = \frac{I_0}{\hbar\omega_0} = \left(\frac{V}{\omega_0} \right)^2 f_i(\eta), \quad (29b)$$

where $f_r(\eta)$ and $f_i(\eta)$ are the real and imaginary parts of $\hbar\omega_0 F(\eta)$. In this case the energy shift and the broadening are proportional to the square of the ratio of the two-center interaction to the optical phonon energy. Other important quantities are given as

$$q = \frac{\beta + f_r(\eta)}{f_i(\eta)} \quad (30)$$

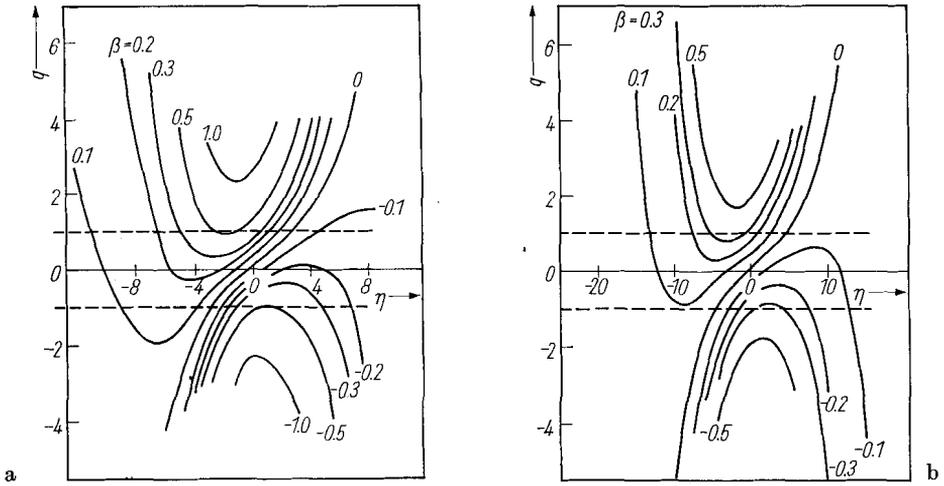


Fig. 4. a) Behavior of the parameter q given by (30) for various values of β in the case of $S = 5$. b) Same as Fig. 4a, in the case of $S = 15$

and

$$\varepsilon = \frac{\eta - \eta_b - \Delta_0^*}{\Gamma_0^*}, \tag{31}$$

where $\beta = (d_b/d_a) (\omega_b/V)$ and $\eta_b = (\omega_b - \omega_a)/\omega_0$. In (28), the function $(d_a/\hbar\omega_0) f_i(\eta)$ is the absorption spectrum of center A in the absence of the interaction with center B; it is composed of a set of Lorentzian phonon lines with a half-width δ . The dashed lines in Fig. 5 and 6 show the absorption spectrum for $\delta = 1$, where the intensities have been normalized by $(d_a^2/\pi\hbar\omega_0)$.

The energy dependence of q given by (30) is plotted in Fig. 4 for various values of β in the cases of a) $S = 5$ and b) $S = 15$; too small values of S might

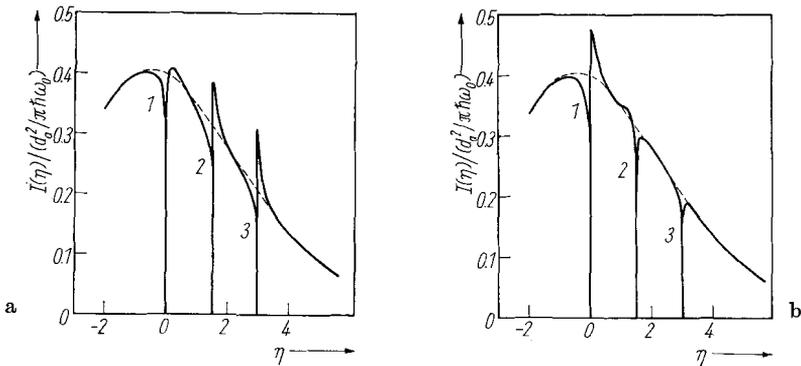


Fig. 5. a) Calculated antiresonance lineshapes given by (28) providing $(V/\omega_0)^2 = 0.05$ for $S = 5, \beta = 0, (|d_b/d_a| = 0)$. (1) $\eta_b = 0, q = +0.074$; (2) $\eta_b = 1.5, q = +0.488$; (3) $\eta_b = 3, q = 1.078$. b) Same as Fig. 5a, for $S = 5, \beta = -0.2, (|d_b/d_a| \approx 0.045)$. (1) $\eta_b = 0, q = -0.419$; (2) $\eta_b = 1.5, q = -0.133$; (3) $\eta_b = 3, q = +0.107$

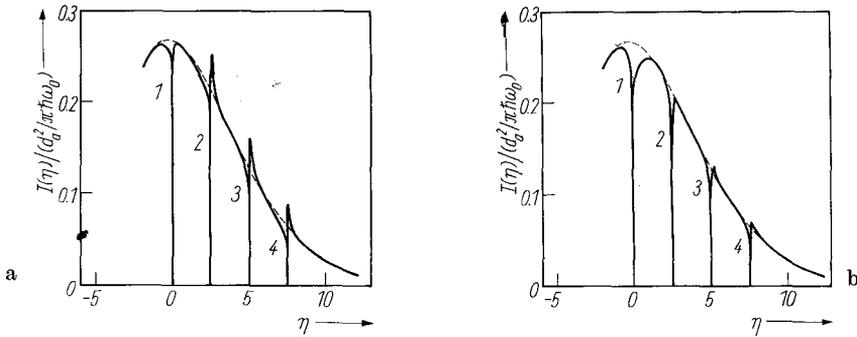


Fig. 6. a) Calculated antiresonance lineshapes given by (28) providing $(V/\omega_0)^2 = 0.1$, for $S = 15$, $\beta = 0$, $(|d_b/d_a| = 0)$. (1) $\eta_b = 0$, $q = +0.052$; (2) $\eta_b = 2.5$, $q = +0.535$; (3) $\eta_b = 5$, $q = +1.153$; (4) $\eta_b = 7.5$, $q = 2.203$. b) Same as Fig. 6a for $S = 15$, $\beta = -0.1$, $(|d_b/d_a| \approx 0.032)$. (1) $\eta_b = 0$, $q = -0.323$; (2) $\eta_b = 2.5$, $q = +0.066$; (3) $\eta_b = 5$, $q = +0.390$; (4) $\eta_b = 7.5$, $q = 0.643$

be unfavorable for the observation of antiresonance because they give narrow linewidths. It can be seen from Fig. 4 that the criterion $|q| < 1$ is satisfied in the range of $|\beta| \lesssim 0.5$ for $S = 5$ and $|\beta| \lesssim 0.3$ for $S = 15$, i.e., in more detailed, $0 \lesssim \beta \lesssim 0.5$ and $0 \leq \beta \leq 0.3$ for the low-energy side with respect to the center of the broad band and $-0.5 \gtrsim \beta \gtrsim 0$ and $-0.3 \gtrsim \beta \gtrsim 0$ for the high-energy side. In the vicinity of the center of the absorption band, $|q|$ decreases with decreasing $|\beta|$; a favorable condition for the sharp antiresonance is then $|\beta| \approx 0$. For higher or lower energies but within the half-width, $|\beta| \approx 0.2$ and $|\beta| \approx 0.1$ give smaller values of $|q|$ in the cases of $S = 5$ and 15 , respectively.

As in the first case, owing to the existence of an upper limit of I_0^* , the situation $|\beta| \approx 0$ is realized when $|d_b/d_a| \approx 0$, that is, when the electronic dipole transition of center B is very weak or forbidden in the absence of the interaction with center A.

If we assume $h\omega_0 \approx 10^{-2}$ eV and therefore $I_0^* \gtrsim 10^{-2}$, the lower limit of $(V/\omega_0)^2$ is given by substituting the values of $f_i(\eta)$ in Fig. 5 and 6 into (29b); except in the vicinity of the center of absorption band we have $(V/\omega_0)^2 \gtrsim 10^{-2}$ for $S = 5$ and $(V/\omega_0)^2 \gtrsim 10^{-1}$ for $S = 15$. Under these conditions $|d_b/d_a| \gtrsim 10^{-2}$ must be satisfied in both cases in order to realize the situations $|\beta| \approx 0.2$ for $S = 5$ and $|\beta| \approx 0.1$ for $S = 15$.

The above discussion leads us to the same conclusion as in the first case concerning the favorable condition for the observation of sharp antiresonance except that in this case the interaction of two centers is compared with the optical phonon energy instead of the half-width.

Typical examples of the sharp antiresonance spectra are calculated for $\eta_b = 0, 1.5, \text{ and } 3$ in the case of $S = 5$ providing $(V/\omega_0)^2 = 0.05$ and for $\eta_b = 0, 2.5, 5, \text{ and } 7.5$ in the case of $S = 15$ providing $(V/\omega_0)^2 = 0.1$. They are plotted in Fig. 5 and 6. We see that in both figures the sharp antiresonances for $\eta_b = 0$ occur when $|\beta| = 0$, while those for $\eta_b = 1.5$ and 3 in the case of $S = 5$ and those for $\eta_b = 2.5, 5, \text{ and } 7.5$ in the case of $S = 15$ occur when $\beta = -0.2$ and $\beta = -0.1$, respectively. This is consistent with the above discussion.

Taylor [8] has measured the absorption spectra of rare-earth ions in calcium fluoride irradiated with X-rays and has observed sharp antiresonance lines

superimposed upon a broad background absorption due to a color center. The positions of these lines coincide with those of very weak absorption lines of the rare-earth ions; for example, in X-irradiated $\text{CaF}_2:\text{Dy}^{3+}$ the line is observed at 2.76 eV, which corresponds to the transition ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$ of Dy^{3+} at ≈ 2.77 eV. Although these sharp antiresonances have been observed at rather high temperatures, they may be still regarded as good examples of the antiresonances discussed above.

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References

- [1] U. FANO, Phys. Rev. **124**, 1866 (1961).
U. FANO and J. W. COOPER, Phys. Rev. **137**, A1364 (1965).
- [2] Y. TOYOZAWA, Progr. theor. Phys. (Kyoto) **20**, 53 (1958); J. Phys. Chem. Solids **25**, 59 (1964).
- [3] J. J. HOPFIELD, J. Phys. Chem. Solids **22**, 63 (1961).
J. C. PHILLIPS, Phys. Rev. **136**, A1705 (1964).
K. P. JAIN, Phys. Rev. **139**, A544 (1965).
J. HERMASON and J. C. PHILLIPS, Phys. Rev. **150**, 652 (1966).
J. HERMASON, Phys. Rev. **150**, 660 (1966).
- [4] Y. TOYOZAWA, M. INOUE, T. INUI, M. OKAZAKI, and E. HANAMURA, J. Phys. Soc. Japan **22**, 1337 (1967).
M. OKAZAKI, M. INOUE, Y. TOYOZAWA, T. INUI, and E. HANAMURA, J. Phys. Soc. Japan **22**, 1349 (1967).
- [5] A. SHIBATANI and Y. TOYOZAWA, J. Phys. Soc. Japan **25**, 335 (1968).
- [6] E. S. PYSH, S. A. RICE, and J. JORTNER, Phys. Rev. Letters **15**, 289 (1965).
- [7] M. D. STURGE, H. J. GUGGENHEIM, and M. H. L. PRYCE, Phys. Rev. **2**, 2459 (1970).
- [8] M. J. TAYLOR, Phys. Rev. Letters **23**, 405 (1969).
- [9] A. S. DAVIDOV, Theory of Molecular Excitons, Plenum Press, New York/London 1971.

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