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Oscillator strengths of defects in insulators: The generalization of Smakula's equation (*)

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Abstract. — A generalization of Smakula's equation is developed for the case of defect absorption in host materials with weak absorption but rapidly varying refractive index. As an example the generalization is applied to the $\alpha$ and $\beta$ bands in ionic crystals. In the case of additively-colored KI it is found that the ratio of oscillator strengths is $f_\beta/f_\alpha \approx 0.6$. This result is in qualitative disagreement with the commonly accepted theoretical treatment which for NaCl predicts $f_\beta/f_\alpha \approx 2$. Possible reasons for this disagreement are discussed.

1. Introduction. — Smakula's [1] celebrated relation for the strength of a defect's optical absorption has formed the basis of quantitative absorption studies for fifty years. In the commonly used Mollwo-Roos [2] form, Smakula's equation states that for defects with oscillator strength $f$ and density $\rho$ in a host medium of refractive index $n_0$

$$\rho f = \frac{9}{4 \pi} \frac{mc}{e^2 \hbar} \frac{n_0}{(n_0^2 + 2)^2} \mu_{\text{max}} \Gamma,$$

where $\mu_{\text{max}}$ and $\Gamma$ are the maximum absorption coefficient and the full width at half maximum of the defect's absorption band, respectively.

This relation was originally deduced for a dilute solution of absorbing species in a transparent medium with constant refractive index on the assumption that the absorption is Lorentzian and that the field at the absorbing centre is the Lorentz local field. A less restrictive derivative leads to the more modern form [3, 4]

$$\rho f = \frac{mc}{2 \pi^2 e^2 \hbar} n_0 \left( \frac{\varepsilon_0}{\varepsilon_{\text{eff}}} \right)^2 \int \mu(E) \, dE,$$

where $(\varepsilon_{\text{eff}}/\varepsilon_0)$ is the ratio of the effective field at the absorbing defect to the average field in the medium and no assumption is made about the absorption band shape.

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In many current studies, two of the key assumptions made above do not hold:

1) The host medium is often not completely transparent, and

2) The refractive index of the host is not constant over the defect's absorption band.

Examples of both of these conditions occur for defect or perturbed-exciton absorptions just to the long-wavelength side of the fundamental absorption of the host medium.

In the present paper we generalize Smakula's equation by relaxing these assumptions and we apply the results to the $\alpha$- and $\beta$-band absorptions in the alkali halides as an example.

2. Generalization of Smakula's equation. — In essence Smakula's equation is a partial $f$ sum rule. However, care is necessary in its generalization because the $f$ sum rule can be written in several equivalent forms when the sum over the entire spectrum is taken [5]. The forms of interest here are for the imaginary part of the dielectric function, $\varepsilon_2$,

$$\int_0^\infty \omega \varepsilon_2(\omega) \, d\omega = 2 \pi^2 Ne^2/m$$

and for the imaginary part of the refractive index, $\kappa(\omega)$,

$$\int_0^\infty \omega \kappa(\omega) \, d\omega = \pi^2 Ne^2/m,$$
While $\varepsilon_2(\omega)$ and $\kappa(\omega)$ obey these very similar sum rules over the whole spectrum, their partial sum over a finite-energy interval differ markedly. (For an example, see Ref. [5].) This difference is obvious if one recalls that $\varepsilon_2(\omega) = 2\varepsilon(\omega)\kappa(\omega)$. Physically it can be seen from the fact that $\varepsilon_2(\omega)$ is a measure of heat generation, while $\kappa(\omega)$ is related to the decrease in amplitude of the transmitted light wave.

In the present context the quantity of interest is the dipole oscillator strength which is directly related to the polarizability and hence to $\varepsilon_2$. Thus, eq. (3) is the appropriate form of the sum to consider over the finite-energy interval $a \leq \omega \leq b$. This leads to

$$fn = \frac{m}{2\pi^2 e^2} \int_a^b \omega \varepsilon_2(\omega) d\omega \tag{5$$

$$= \frac{m}{2\pi^2 e^2} \int_a^b \omega n(\omega) \kappa(\omega) d\omega, \tag{5b}$$

where $f$ is the oscillator strength; that is, the fraction of electrons effective for absorption in the frequency range $a \leq \omega \leq b$.

In optical experiments $\kappa(\omega)$, not $\varepsilon_2(\omega)$, is generally measured so that there is a temptation to define the oscillator strength from eq. (4) rather than eq. (3) to avoid having to have a knowledge of $n(\omega)$. However, this is incorrect because it leads to the omission of the factor of $n(\omega)$ found in the second form of eq. (5).

The importance of this factor is illustrated in figure 1 which shows the absorption of a model system consisting of a single strong Lorentz oscillator representing the host material and a weaker oscillator representing the imperfection — the latter was chosen to have an oscillator strength $10^{-4}$ times that of the host corresponding to the case of a dilute imperfection. The parameters were chosen so that the host refractive index, $n_0(\omega)$, is approximately 1.5 over most of the region of transparency, but rises rapidly just below the host absorption frequency, $\omega_{\text{host}}$. The imperfection absorption frequency was varied over the ranges $0.3 \omega_{\text{host}} \leq \omega \leq 0.9 \omega_{\text{host}}$. Despite the fact that the oscillator strength of the imperfection remained a constant, the imperfection absorption band appears to become weaker and very distorted as it approaches the tail of the host absorption. Qualitatively this can be viewed as a result of the shielding of the imperfection by the polarizable host (1). The factor $n(\omega)$ in eq. (5b) compensates the absorption spectrum as measured by $\kappa(\omega)$ for this shielding. The importance of refractive index variation for the intrinsic absorption of a semiconductor was noted previously by Dexter [5a].

(1) Detailed considerations show that a compensatory increase in the host absorption occurs in another spectral region so that the $f$ sum rule for $\kappa(\omega)$ over the entire spectrum (eq. (4)) remains valid when both host and imperfection spectra are included in the summation.

In the defect problem the quantity of primary interest is the change in oscillator strength introduced by an imperfection. The resulting partial $f$ sum for the defect can be derived in an approximate form by taking differentials of eq. (5) or without approximation by applying superconvergence techniques [6] to the function $\varepsilon_0^{1/2}(\omega) \kappa^{1/2}(\omega) - \varepsilon_2(\omega)$, where $\varepsilon_0(\omega)$ is the dielectric function of the unperturbed host and $\varepsilon(\omega)$ is the dielectric function of the host material with defects. The result is:

$$\rho f = \frac{m}{2\pi^2 e^2} \left( \frac{\varepsilon_0}{\varepsilon_{\text{eff}}} \right)^2 \times$$

$$\times \int \omega [n_0(\omega) \Delta \kappa(\omega) + \Delta n(\omega) \varepsilon_0(\omega)] d\omega, \tag{6}$$

where $\Delta n$ and $\Delta \kappa$ are the changes in the real and imaginary parts of the dielectric function caused by the defects. Here $n_0(\omega)$ and $\varepsilon_0(\omega)$ are the real and imaginary parts of the refractive index of the unperturbed host crystal.

In eq. (6) the ratio of the average field in the medium, $\varepsilon_0$, to the effective field at the centre, $\varepsilon_{\text{eff}}$, has been included to take into account the possibility that the local field acting on the defect may differ from the
average field in the medium [3]. In this case the oscillator strength is that which the defect would exhibit in free space.

For a host substance which is only weakly absorbing in the range \( a \leq \omega \leq b \) this expression reduces to

\[
\rho_f = \frac{m}{\pi^2 e^2} \left( \frac{\varepsilon_0}{\varepsilon_{\text{eff}}} \right)^2 \int_a^b \omega n_0(\omega) \Delta \chi(\omega) \, d\omega, \tag{7}
\]

where \( \Delta \chi \) is just the defect-induced change in absorption. In the event \( n_0(\omega) \) is a constant, this reduces to eq. (2) since \( \mu(\omega) = 2 \omega \chi(\omega)/c \).

In transmission experiments, eq. (7) is generally a sufficient approximation to eq. (6) since \( \chi_0(\omega) \) must be small in order that transmission is possible in the first place. The opposite, of course, holds in a highly absorbing region where the second term of eq. (6) dominates the oscillator strength.

3. An example: the \( \alpha \)- and \( \beta \)-bands. — As an example of the case of the present formalism, the generalized Smakula's equation was applied to the spectra of the \( \alpha \)- and \( \beta \)-bands [7] in KI. The observed spectra of an additively colored sample measured at liquid nitrogen temperature are shown in figure 2.

In order to calculate the oscillator strength it is necessary to know the value of the refractive index well into the ultraviolet. A number of measurements [8] of \( n(\omega) \) have been made, but these have been generally limited to near room temperature and extend only into the low-energy U.V. A dispersion-theory parametrization of the room-temperature index has been made by Ramachandran [9] on the assumption that the first peak of the crystal's fundamental absorption lies at \( \lambda = 2.190 \) Å at room temperature. As the temperature is lowered, this peak shifts towards blue reaching \( \lambda \approx 2.120 \) Å at 77 K. Since the behaviour of the index in the \( \beta \)-band region is strongly dependent on the position of the first exciton line, a fitting of \( n(\omega) \) with a dispersion formula with \( \lambda_0 \approx 2.120 \) Å was employed to estimate \( n(\omega) \) in the tail of the fundamental for use with the present 77 K spectra. While this estimate is subject to considerable uncertainty, it was found that the strength of the \( \alpha \)- and \( \beta \)-bands relative to one another is rather insensitive to the approximation used for \( n(\omega) \).

As a check on the background subtractions and the model of the \( \beta \)-band as an F centre-related absorption, the ratio of the number of F centres after and before the bleach, \( N_F/N_{F,0} \), was calculated from eq. (7) for both the F- and \( \beta \)-band absorption. The results are:

\[
\begin{align*}
N_F & = 0.22, & N_F & = 0.25 .
\end{align*}
\]

The 12% difference between these two F-band conversion ratios is well within experimental and computational error.

The oscillator strength of the \( \alpha \)- and \( \beta \)-bands relative to the F-band was found by a similar calculation using eq. (7) on the assumption that \( \varepsilon_{\text{eff}} \) was the same for all bands. The results are:

\[
\frac{f_\alpha}{\Sigma f_F} = 0.20 \quad \text{and} \quad \frac{f_\beta}{\Sigma f_F} \approx 1.4 ,
\]

where \( \Sigma f_F \) is the total F centre absorption including both the F-band and its high-energy tail (presumably the K-band). The ratio of the strengths of the \( \alpha \)- and \( \beta \)-bands is thus:

\[
\frac{f_\alpha}{f_\beta} \approx 0.64 .
\]

If it is assumed that \( \Sigma f \) is of the order of unity (or \( \approx 1.1 \) if transfer of core oscillator strength is included [4]) we conclude that \( f_\alpha \approx 1.0 \) while \( f_\beta \approx 1.5 \).

These figures are surprising in two regards. First, they are in conflict with the calculations of Dexter [10] who found for NaCl that \( f_\alpha = 1.89 \) and \( f_\beta = 0.612 \). Or, more to the point, that \( f_\alpha f_\beta \approx 3 \). (The possibility of the existence of this disagreement was first noted by Seitz [11] from a comparison of the \( \alpha \)- and \( \beta \)-band peak heights before and after bleaching.)
Secondly, a $\beta$-band strength much greater than unity is in conflict with the accepted $\beta$-band model since only one electron is involved. This conflict could be accounted for by assuming that the value of $\kappa_{\text{eff}}$ for the $\beta$-band transition is greater than that for the $F$-band. However, it seems reasonable to assume that $\kappa_{\text{eff}}$ for both the $\alpha$- and $\beta$-bands is the same so that the ratio $f_{\text{sum}}$ would remain unchanged in conflict with Dexter's result.

The theoretical prediction that the $\alpha$-band should be stronger than the $\beta$-band arises from a simple exclusion-principle argument and the model for the $\alpha$- and $\beta$-bands. The $\alpha$-band is believed to be a perturbed exciton in which an electron is excited from the halogen-ion valence band to an $F$-centre-like state at a halogen-ion vacancy. Similarly, the $\beta$-band is believed to involve the transition of a valence electron to an $F'$ centre-like state. In the former case — the $\alpha$-band absorption — both spin-up and spin-down electrons can make transitions from a halogen ion into the vacancy. However, in the case of the $\beta$-band the Pauli principle allows transitions of only half the halogen ion electrons to the final $F'$-centre-like state because one state is already occupied by the $F$ centre electron.

A possible resolution of this apparent conflict is that there is a spin-orbit splitting of the Greek bands so that only the lowest transitions are detectable. In KI the spin-orbit splitting of the exciton is $0.9$ eV which is roughly 1.5 times the separation of the $\alpha$-band from the fundamental. Thus, if the $\alpha$-bands were split by a similar amount, the higher energy transitions would lie under the fundamental and not be included in our $f$ sum.

The possibility that such a splitting occurs in the $\beta$-band has been raised by a calculation of Fuchs [12] who finds a number of transitions lying beneath the fundamental absorption band.

An experimental test of this conjectured explanation should be possible through a quantitative study of the oscillator strengths of the $\alpha$- and $\beta$-bands in ionic systems with small spin-orbit interactions such as the fluorides or chlorides.

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Note added in proof. — The considerations given here also apply to the analysis of magneto-optical studies in which finite-energy moments of the circular dichroism are employed [13]. Here the variation of the refractive index should be included when calculating the line shape function, $f_{\text{sum}}(E)$. This effect should be significant for the $\alpha$- and $\beta$-bands as well as the higher energy absorptions of the various U centres.

DISCUSSION

Question. — W. A. SIBLEY.

It appears your calculation would also be valid for two overlapping absorption bands when one band is considerably more intense than the other. Is this correct and if so what would the intensity ratio have to be in order for the effect to be measurable?

Reply. — D. Y. SMITH.

In principle that is correct and we have demonstrated the effect in some model calculations. However, for one defect band to have a significant effect on another it would have to produce a significant change in the refractive index of the host material. With the usual defect concentrations of one part in $10^4$ or less, the effect is unobservable for practical purposes. However, it should be seen in the effect of one host absorption on another host absorption.

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