

is obtained by using only the diffusion coefficients at the highest temperature for all the isotopes and employing Zener's theory as was suggested by the work of Nowick.⁴ The values of H and D_0 thus calculated yield excellent agreement with the experimental results for cadmium and indium but significant deviations are seen for tin and antimony. Moreover, they do not reproduce the experimental correlation between H and D_0 which is shown in Fig. 7. Perhaps this discrepancy results from our use of a constant value of ν . It should be noted that Zener's theory shows better agreement with experiment for smaller values of Z where the activation energies predicted by the screening theory deviate appreciably and the situation is reversed for cases of larger Z . It may

be that an appreciable portion of the free energy is expended in the changing of configurations other than the straining of the lattice (e.g., the redistribution of the electronic charge) when a relatively large number of extra electrons are attached to the impurity atoms, and that the assumption of Zener's theory is thus violated.

The negative values for the entropy of activation, which were implied by the old data and have been subject to much theoretical speculation, are not observed in the present work and their notion, in all probability, must be discarded for the case of dilute chemical diffusion in f.c.c. metals.

The authors wish to express their gratitude to Dr. F. Seitz and Dr. D. Lazarus for many helpful discussions.

PHYSICAL REVIEW

VOLUME 96, NUMBER 3

NOVEMBER 1, 1954

Shapes of Absorption and Emission Lines of Impurities in Solids*

D. L. DEXTER

Institute of Optics, University of Rochester, Rochester, New York, and Solid State Division, Naval Research Laboratory, Washington, D. C.

(Received June 28, 1954)

Existing treatments of band shapes in solids, for the simplest impurity centers, predict Gaussian shape functions. These treatments assume for simplicity that the electronic matrix element is independent of the nuclear wave functions, and that the energy width of the band is negligible compared with the energy of the mid-point of the band. We estimate here the expected magnitude of the effect of correcting these assumptions in typical cases, and find that the emission or absorption band may deviate from a Gaussian by twenty percent or more on the wings.

ABSORPTION and emission spectra are not generally of a simple shape for several possible reasons. In the simplest case, where only a single initial electronic state and a single final electronic state can contribute to the line, where the environment of all the centers is identical, where the transition is far from resonance with the host lattice, and where the configurational coordinate curve for the final electronic state is sufficiently displaced from that for the initial state, an approximate calculation leads to a Gaussian shape function for the absorption or emission spectrum.¹⁻⁴ This result depends on the Born-Oppenheimer approximation and on the assumption that the electronic transition probability is independent of the nuclear wave functions, i.e., the wave functions for the lattice vibrations. This assumption is generally made in three parts: (1) the wave function of only one electron is changed during the transition, (2) the electronic matrix element for this one electron is independent of the nuclear wave functions, and (3) the width of the

band is negligible as compared with the energy of its mid-point. On configurational coordinate diagrams these assumptions are equivalent to assuming that the electronic transition probability is independent of the configurational coordinate, so that line shapes are determined solely by the geometry of the energy curves.

The purpose of this note is to point out the influence of these approximations upon the calculated line shape. For simplicity and ease of presentation the description will be given in terms of the usual configurational coordinate model (in which the important coordinate is presumably the position of the nearest ions).

In case the ground and excited states are influenced by about the same relative amount⁵ by the lattice oscillations, as may be true in a system such as KCl:Ti where both ground and excited state wave functions are relatively compressed, the electronic momentum matrix element is given by

$$\langle \mathbf{p} \rangle = \langle \mathbf{p} \rangle_0 (1 - \Delta R/R), \quad (1)$$

where R is any characteristic length in the wave functions of the center. As the neighbors of the center move and cause a change in the wave function, i.e., in R ,

⁵ By the phrase "the same relative amount" we mean the equality of the logarithmic differentials of the damping lengths of the two wave functions.

* Research supported in part by U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

¹ M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).

² F. E. Williams and M. H. Hebb, *Phys. Rev.* **84**, 1181 (1951).

³ R. C. O'Rourke, *Phys. Rev.* **91**, 265 (1953).

⁴ C. C. Klick, *Phys. Rev.* **85**, 154 (1952).

they also change the energy of the transition between these electronic states by an amount proportional to R^{-2} . Thus the square of the matrix element, which determines transition probabilities, is

$$\langle \mathbf{p} \rangle^2 = \langle \mathbf{p} \rangle_0^2 (1 + \Delta E/E). \quad (2)$$

In the event that the excited state wave function is so diffuse that it is relatively uninfluenced by the vibrations of the nearest neighbors, as is probably the case with the F center, for example, most of the variation in the matrix element will occur because of variations in the ground-state wave function. For the sake of definiteness, let us consider transitions between a $1s$ and a $2p$ state, for which the momentum matrix element is proportional to

$$(a\alpha)^3/(a+\alpha)^4,$$

where α and a are the damping lengths in the exponentials of the $1s$ and $2p$ wave functions, respectively. Expanding, we find

$$\langle \mathbf{p} \rangle = \langle \mathbf{p} \rangle_0 \left\{ 1 + \Delta\alpha \left(\frac{3}{2\alpha} - \frac{4}{a+\alpha} \right) \right\}. \quad (3)$$

As the neighbors move and cause a change in the $1s$ wave function, its energy likewise changes, and the change in the energy of the transition is $\Delta E = -(2/\alpha)\Delta\alpha|E_{1s}|$, and thus the square of the matrix element is given by

$$\langle \mathbf{p} \rangle^2 = \langle \mathbf{p} \rangle_0^2 \left\{ 1 - \frac{\Delta E}{E} \left[\frac{E}{|E_{1s}|} \left(\frac{3}{2} - \frac{4}{1+a/\alpha} \right) \right] \right\}. \quad (4)$$

The quantity in square brackets is of the order of plus or minus one-tenth; in the case of an isolated atom, the ratio a/α is 2, $|E/E_{1s}|$ is $\frac{3}{4}$, and the coefficient of $\Delta E/E$ is $-\frac{1}{8}$. In actual cases the ratios a/α and $|E/E_{1s}|$ will not be exactly 2 and $\frac{3}{4}$; for the F center in NaCl perhaps better values are 1.5 and 0.8,⁶ so that the coefficient of $\Delta E/E$ is $+0.08$.

An absorption band arises from a summation of the

⁶ D. L. Dexter, Phys. Rev. **83**, 435 (1951).

contributions from one electronic transition and all possible nuclear transitions. Since the integrated absorption cross section for each individual absorption line is proportional to $\langle \mathbf{p} \rangle^2/E$, the absorption band will not in general be a Gaussian $G(E)$, but rather a function of the form

$$\sigma(E) = E^n G(E), \quad (5)$$

where n may take different values in the various cases mentioned above. For a system such as that discussed in leading to Eq. (2), n will have the value zero because of the cancellation of the effects arising from the magnitude of the matrix element and the energy. In the case of Eq. (4), however, n has the value

$$-1 - \frac{E}{|E_{1s}|} \left(\frac{3}{2} - \frac{4}{1+a/\alpha} \right),$$

or about -1.1 and -0.9 for the two models mentioned after Eq. (4). Thus it appears that at least a small amount of long-wavelength tail on the absorption band may usually be expected.

In emission, on the other hand, the exponent n must be increased by two in each case, because of the $\langle \mathbf{p} \rangle^2 E$ dependence of the spontaneous emission probability. (In referring to the emission band shape we shall mean the *number* of photons, rather than the energy, emitted as a function of energy.) Thus for the case treated first, an E^2 factor modifies the Gaussian, and for the other two cases, an approximately linear factor. (It is interesting to note that an approximate mirror-image relation exists between emission and absorption in the latter two cases.)

In typical impurity centers the half-width of a band may be one-tenth of the energy of its mid-point, so that the emission or absorption band may deviate from a Gaussian by twenty percent or more on the wings. This circumstance makes the common practice of analyzing these spectra into sums of Gaussians of questionable significance.

The writer is indebted to Dr. C. C. Klick for interesting discussions on this material.