

Width of the Narrow "No-Phonon" Lines in the Optical Spectra of Impurities in Solids

D. E. McCUMBER

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 20 August 1963)

Phonon-impurity interactions responsible for part of the width of the no-phonon components of the sharp-line optical spectra of impurities in crystal lattices can be interpreted physically in terms of the secular-perturbation model proposed for magnetic resonance by Bloembergen, Purcell, and Pound. The low-frequency secular excursions of the impurity energy levels produced by the lattice vibrations appear as a finite linewidth to an experimenter making line-shape measurements over macroscopic time intervals. The total linewidth will of course include additional contributions from the finite impurity-state lifetime implicit in interlevel transitions induced by photons and nonsecular phonons. The theory of the no-phonon components of impurity optical spectra is closely related to the theory of line narrowing in magnetic-resonance spectra.

IN a recent paper¹ a mathematical model, in which phonons were Raman scattered² by the impurity ion, was used to account for the observed temperature dependence of the widths of the sharp "no-phonon" R lines of dilute ruby. Similar linewidth expressions have also been derived by different methods in conjunction with the analysis of phonon-impurity interactions which shift the impurity energy but which do not mix the impurity states.³ In this paper we wish to report that the physical processes relevant to the linewidth expressions are the same as those which contribute to a physically appealing line-broadening mechanism proposed for magnetic-resonance lines by Bloembergen, Purcell, and Pound.^{4,5} Those authors reasoned that the low-frequency secular excursions of the impurity energy levels which result from random local magnetic or crystal fields appear as a finite linewidth Γ to an experimenter making line-shape measurements over macroscopic time intervals. Secular excursions are "low frequency" in the required sense if their angular frequencies ω are less than or comparable to the linewidth Γ .⁶

Assuming that the mean-square excursions at different frequencies $|\omega| \leq \frac{1}{2}\Gamma$ add to give the total mean-square secular excursion, Bloembergen *et al.* proposed in essence that

$$\Gamma = \left[\pi \int_{-\Gamma/2}^{\Gamma/2} \frac{d\omega}{2\pi} \gamma(\omega) \right]^{1/2}, \quad (1)$$

where $\gamma(\omega)$ is the power spectrum^{7,8} in the relevant ensemble of the instantaneous-frequency-excursion operator $\Delta\Omega(t)$. If $\hbar\Omega(t)$ is an operator measuring the

"instantaneous energy separation" of the two impurity levels responsible for the observed spectral line and if the relevant system ensemble is implicit in the expectation value $\langle \dots \rangle$, then $\Delta\Omega(t) = \Omega(t) - \langle \Omega(t) \rangle$ and

$$\gamma(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [\Delta\Omega(t), \Delta\Omega(0)]_+ \rangle. \quad (2)$$

The physical and mathematical assumptions underlying Eq. (1) have been discussed in detail by Anderson.⁶

To establish the connection between our results and Eq. (1), it is useful to rewrite that equation in a slightly different form. Squaring Eq. (1) and dividing the result by Γ , we obtain

$$\Gamma = \frac{\pi}{\Gamma} \int_{-\Gamma/2}^{\Gamma/2} \frac{d\omega}{2\pi} \gamma(\omega) \quad (3)$$

$$\approx \frac{1}{2}\gamma(0), \quad (4)$$

where the approximation (4) is valid if $\gamma(\omega)$ varies slowly over the interval $|\omega| \leq \frac{1}{2}\Gamma$. In a sense, the limiting expression (4) is equally as fundamental as Eq. (1), because the assumption that $\gamma(\omega)$ varies slowly in the interval $|\omega| \lesssim \Gamma$ is implicit in a meaningful picture of the spectrum as a sharp no-phonon Lorentz line of width Γ superposed upon a slowly varying background.

For the sharp-line optical spectra of present interest Γ is much less than typical phonon frequencies, and the approximation (4) is very good. Our Raman-scattering expressions for Γ are in fact those appropriate to the approximation (4).^{1,3}

To demonstrate this fact, we consider a simple system in which a single isolated impurity has only two internal states characterized by the "spin" quantum numbers $S_z = \pm \frac{1}{2}$ and in which the phonon-impurity interactions *shift* the impurity energy levels but do not *mix* the impurity states:

$$H = \mathcal{E}S_z + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} (a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \frac{1}{2}) + (S_z + \frac{1}{2}) [\alpha_1 A_1 + \alpha_2 (A_2)^2]. \quad (5)$$

¹ D. E. McCumber and M. D. Sturge, *J. Appl. Phys.* **34**, 1682 (1963).

² I. Waller, *Z. Physik* **79**, 370 (1932); M. Fierz, *Physica* **5**, 433 (1938); J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

³ D. E. McCumber, *J. Math. Phys.* (to be published).

⁴ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

⁵ N. Bloembergen, *Nuclear Magnetic Relaxation* (W. A. Benjamin, Inc., New York, 1961), Eq. (2.54).

⁶ P. W. Anderson, *J. Phys. Soc. Japan* **9**, 316 (1954).

⁷ N. Wiener, *Acta Math.* **55**, 117 (1930); S. O. Rice, *Bell System Tech. J.* **23**, 282 (1944); **24**, 46 (1945).

⁸ N. Bloembergen, *Ref. 5*, pp. 83-85.

Here \mathcal{E} measures the energy separation of the unperturbed impurity levels, the operators $\{a_q, a_q^\dagger\}$ characterize the phonon modes of the lattice, the (α_1, α_2) are real coupling constants, the phonon operators (A_1, A_2) are linear functions of the $\{a_q, a_q^\dagger\}$ and characterize the lattice distortions relevant to the phonon-impurity coupling. The annihilation-creation operators $\{a_q, a_q^\dagger\}$ satisfy the familiar commutation relations

$$[a_q, a_{q'}] = [a_q^\dagger, a_{q'}^\dagger] = 0, \quad [a_q, a_{q'}^\dagger] = \delta(\mathbf{q}, \mathbf{q}'). \quad (6)$$

For definiteness we define

$$A_j = \sum_q [C_{jq} a_q^\dagger + C_{jq}^* a_q], \quad j=1 \text{ and } 2, \quad (7)$$

where the C_{jq} are dimensionless numerical coefficients.

Hamiltonians of the type (5) have been considered in detail in a previous paper.³ If we assume that the phonon excitations are initially described by a temperature T , we may use results from that paper to compute to the lowest nonvanishing order the width Γ of the no-phonon line in the $S_z = -\frac{1}{2} \rightarrow +\frac{1}{2}$ absorption spectrum of the operators $S_\pm = S_x \pm iS_y$. The result is

$$\Gamma = \lim_{\omega \rightarrow 0} \frac{kT}{\hbar\omega} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [\Delta\Omega(t), \Delta\Omega(0)]_- \rangle_{T, S_z = -1/2}, \quad (8)$$

where the expectation value refers to a temperature- T phonon ensemble appropriate to $S_z = -\frac{1}{2}$. For the system (5) the energy separation operator $\hbar\Omega(t)$ relevant to Eqs. (2) and (8) is

$$\hbar\Omega(t) = \mathcal{E} + \alpha_1 A_1(t) + \alpha_2 [A_2(t)]^2, \quad (9)$$

where $A_j(t) = \exp(iHt/\hbar) A_j \exp(-iHt/\hbar)$ in the Heisenberg picture. Using the operator (9) in Eq. (8), we find that in detail

$$\Gamma = 4\alpha_2^2 \int_0^\infty \frac{d\omega}{2\pi} [\rho_2(\omega)]^2 n(\omega) [1+n(\omega)] / \hbar^2. \quad (10)$$

The corresponding frequency of the no-phonon line is

$$\bar{\omega} = \frac{\mathcal{E}}{\hbar} - \frac{1}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \left\{ \frac{\alpha_1^2 \rho_1(\omega)}{\hbar\omega} - \alpha_2 \rho_2(\omega) [1+2n(\omega)] \right\}. \quad (11)$$

In these equations $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$, and $\rho_j(\omega)$ for $j=1$ and 2 is the *effective* density of phonon states. For $\omega > 0$

$$\rho_j(\omega) = 2\pi \sum_q |C_{jq}|^2 \delta(\omega - \omega_q) \equiv -\rho_j(-\omega). \quad (12)$$

Clearly $\rho(\omega)$ is the real density of phonon states weighted by the coupling coefficient C_{jq} . The temperature dependence of expressions (10) and (11) is contained solely in the function $n(\omega)$.

When used in Eq. (2) with an impurity-ground-state thermal-phonon ensemble, the operator (9) gives the

frequency-deviation power spectrum

$$\begin{aligned} \hbar^2 \gamma(\omega) = & \alpha_1^2 \rho_1(|\omega|) [1+2n(|\omega|)] + 2\alpha_2^2 \int_0^\infty \frac{d\bar{\omega}}{2\pi} \rho_2(\bar{\omega}) \\ & \times \{ [1+n(\omega)] \{ n(\bar{\omega} + |\omega|) \rho_2(\bar{\omega} + |\omega|) \\ & + n(\bar{\omega} - |\omega|) \rho_2(\bar{\omega} - |\omega|) \} \\ & + n(\bar{\omega}) \{ [1+n(\bar{\omega} + |\omega|)] \rho_2(\bar{\omega} + |\omega|) \\ & + [1+n(\bar{\omega} - |\omega|)] \rho_2(\bar{\omega} - |\omega|) \} \}. \quad (13) \end{aligned}$$

As $\omega \rightarrow 0$,

$$\frac{1}{2} \gamma(\omega) \rightarrow 4\alpha_2^2 \int_0^\infty \frac{d\bar{\omega}}{2\pi} [\rho_2(\bar{\omega})]^2 n(\bar{\omega}) [1+n(\bar{\omega})] / \hbar^2, \quad (14)$$

which limiting expression is identical with that for Γ in Eq. (10). Its form can also be identified with the Raman-scattering linewidth expression in Ref. 1. It is interesting to note that the linear-coupling $\alpha_1 A_1$ term of (5) does not contribute to the linewidth. In the model of Eqs. (1) and (4) this is primarily because the low-frequency (secular) region $|\omega| \leq \frac{1}{2}\Gamma$ occupies a negligible volume of phonon phase space:

$$\rho_1(\omega) [1+n(\omega)] \rightarrow 0$$

as $\omega \rightarrow 0$.

The equality of the linewidth expressions (10) and (14) could have been anticipated from expressions (4) and (8) if we had used general properties of operator expectation values for thermal ensembles.⁹ In particular, if the expectation value in the definition (2) of $\gamma(\omega)$ refers to the temperature- T phonon ensemble appropriate to $S_z = -\frac{1}{2}$, then

$$\begin{aligned} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [\Delta\Omega(t), \Delta\Omega(0)]_- \rangle_{T, S_z = -1/2} \\ = \gamma(\omega) \tanh \frac{\hbar\omega}{2kT}. \quad (15) \end{aligned}$$

Using this equality with Eq. (8), we find that $\Gamma = \frac{1}{2} \gamma(0)$ as in Eq. (4).

The theory of the vibrational structure and of the no-phonon line in optical transitions in isolated impurities is closely tied to the theory of exchange narrowing in magnetic-resonance spectroscopy and to the theory of the pressure narrowing of Doppler broadening in gas-discharge spectra.^{4,6,10} The first few moments of the complete optical line—that is, the no-phonon line plus its vibrational structure—are considerably dif-

⁹ L. Landau, Zh. Eksperim. i Teor. Fiz. **34**, 262 (1958) [translation: Soviet Phys.—JETP **7**, 182 (1959)]; P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

¹⁰ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948); P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953); R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

ferent from the moments relevant to the no-phonon line alone.^{1,3,11} The no-phonon line is therefore a "narrowed" line in the sense that its width is less than is predicted by the second moment of the complete line.¹² In the physical picture of Bloembergen, Purcell, and Pound, implicit in Eq. (1), we would attribute this narrowing to the fact that very rapid perturbations in the energy separation $\hbar\Omega(t)$ "average out" in the time required for their measurement and do not contribute to the width of the no-phonon line. One should not infer from this, however, that the high-frequency perturbations do not modify the observed spectrum. It is

¹¹ A. Kiel in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 417; R. H. Silsbee, *Phys. Rev.* **128**, 1726 (1962) and **129**, 2835 (1963).

¹² J. H. Van Vleck, *Phys. Rev.* **55**, 924 (1939); M. Lax, *J. Chem. Phys.* **20**, 1752 (1952); M. Lax and E. Burstein, *Phys. Rev.* **100**, 592 (1955); H. Gummel and M. Lax, *Ann. Phys. (Paris)* **2**, 28 (1957).

clear from the study of optical sharp-line spectra that they do indeed make themselves felt. They generate the vibrational structure which accompanies the no-phonon line, and they concurrently modify the integrated intensity of the no-phonon line.³

In summary, we have indicated that a simple secular-perturbation model can be used to interpret physically the results of a linewidth calculation describing the effects of phonon interactions on the spectra of isolated impurities in solids. The linewidth components considered give only a part of the total linewidth. One must, of course, include additional contributions such as those relevant to the finite lifetimes implicit in the interlevel transitions induced by photons and nonsecular phonons. It is clear from a general analysis that the theory of the structure of sharp-line optical spectra parallels that extensively developed for magnetic-resonance spectra.

Deuteron Intrabond Motion and Ferroelectricity in KD_2PO_4 †

HENRY B. SILSBEE AND EDWIN A. UEHLING
University of Washington, Seattle, Washington

AND

V. HUGO SCHMIDT
Valparaiso University, Valparaiso, Indiana

(Received 26 August 1963)

The Slater theory of the ferroelectric phase transition in KH_2PO_4 type crystals as modified by Takagi and extended by Senko is examined again in the light of recent measurements of parameters made on KD_2PO_4 . Making full use of the measurements, and assigning an appropriate numerical value to one adjustable parameter which is not independently measured, the theory gives a nearly correct description of the shape of the spontaneous polarization curve. Also the value obtained for the Curie constant is probably satisfactory in view of limitations of the model and uncertainty of the high-temperature experimental data. The theory fails, however, in at least one important respect; the transition entropy is overestimated. This and other discrepancies are discussed briefly.

I. INTRODUCTION

A POSSIBLE connection between the measured activation energy of deuterons jumping between two off-center equilibrium positions in the hydrogen bond of KD_2PO_4 , and a particular model of the ferroelectric phase transition in these crystals has been noted.¹ The model used is the one described by Slater² and modified by Takagi,³ the principal feature of which is the short-range ordering of the hydrogen positions. The measured activation energy has been identified¹ with the energy of one of the hydrogen configurations.

An extension of the theory was subsequently made by Senko,⁴ who did not, however, make use of the measured activation energy as a basis for a numerical test of the theory. The essential feature of his modification is the introduction of long-range polarization forces. The result is a theory containing both long-range and short-range forces of certain specified types, some of which are capable of independent measurement.

It is the purpose of this paper to review this theory and to describe pertinent features of the experimental data which tend to provide a justification of it. As we show, all of the important experimental parameters can be unambiguously determined, in part by experiments which are not directly related to specific ferro-

† Research supported by the National Science Foundation and by the U. S. Army Research Office Durham, South Carolina.

¹ V. H. Schmidt and E. A. Uehling, *Phys. Rev.* **126**, 477 (1962).

² J. C. Slater, *J. Chem. Phys.* **9**, 16 (1941).

³ Y. Takagi, *J. Phys. Soc. Japan* **3**, 271, 273 (1948).

⁴ M. E. Senko, *Phys. Rev.* **121**, 1599 (1961).