Thermal Broadening of the Mössbauer Line and of Narrow-Line Electronic Spectra in Solids*

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The dependence of the lattice vibration Hamiltonian upon the excitation state of an electron or nucleus is examined as a possible source of thermal broadening of narrow-line electronic spectra or Mössbauer spectra in solids. A simple model is proposed to illustrate this mechanism and calculational techniques described to determine the line width appropriate to that model. Application to the Mössbauer problem shows the absence of any observable thermal broadening except in the case of localized modes. The mechanism is consistent with the observed thermal broadening of the narrow lines of ruby, but that specific problem appears to be too complex to permit a detailed test of the theory.

INTRODUCTION

THE recent extensive studies of the narrow-line spectra of solids, both for their own interest and for laser applications, and the discovery of the Mössbauer effect have stimulated an interest in mechanisms for line broadening of such spectra. Markham[1] has reviewed many of the theoretical ideas about thermal broadening, but that review, and the work which it considers, are primarily concerned with lines which are broad compared with the typical lattice vibrational frequencies. An understanding of the breadth of narrow lines requires a somewhat different point of view and is the subject of this discussion.

The thermal broadening in both instances may be considered as resulting from transfer of energy to the lattice vibrations, or phonon field, simultaneous with the electron transition (or nuclear transition in the case of the Mössbauer line), and the fact that there is an uncertainty in the amount of this energy transfer. The qualitative difference is that in the case of broad lines the transfer typically involves the excitation of several or many phonons while in the narrow-line problem the total number of phonons remains unchanged.

The discussion will be in terms of a greatly oversimplified model of an electron with two allowed energy states. In the ground state the energy of the electron is assumed independent of phonon coordinates and in the excited states the energy varies as the square of the local strain. The theory and arguments of Van Vleck,[2] familiar in the discussion of linewidths in magnetic resonance, predict many of the features, including the linewidth, of the absorption line associated with this simple model. The phonon field is treated in the Einstein, the Debye, and an optical branch model with the surprising result that the predictions concerning the linewidth, even in the high-temperature limit, are qualitatively different for the Einstein and the other two models. Finally the narrow red lines of the ruby spectrum and the Mössbauer effect are discussed in terms of this model.

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[1] J. J. Markham, Revs. Modern Phys. **31**, 956 (1959).
[2] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

MODEL

The formal discussion in the following sections will be in terms of a simple system which will illustrate the important features of the broadening mechanism to be described. No serious attempt will be made to justify the applicability of the model to real systems though the arguments which lead to its construction are essentially those of the Born-Oppenheimer approximation.[1]

In that approximation one treats the combined electronic-nuclear problem in two steps. The first is to solve the electron problem for fixed nuclear coordinates. The second is to use the electronic energy eigenvalue, which depends on the assumed nuclear coordinates, as a potential for the nuclear problem. The problem of concern here is a system with two allowed electronic energies and the calculation of the line shape of the transition between these two levels. The Born-Oppenheimer procedure must now be used to describe both the ground and excited states.

Throughout the paper, in most of the numbered equations, all energies will be expressed in units of angular frequency (equivalent to setting $\hbar=1$) and both ω and ν will be used to denote angular frequency. ω_D will denote either the Einstein frequency or the Debye frequency according to the model in use. Temperatures will be expressed in units of the characteristic temperature, $\hbar\omega_D/k$, for the model in question.

The simplest model which shows the qualitative features suggested by the Born-Oppenheimer approach is described by the Hamiltonian

$$H=H_e+H_p+H_c\delta(e,1). \tag{1}$$

H_e describes the energy of the electron for the equilibrium positions of the nuclei which are assumed to be the same in the ground and excited electronic states. (E_1-E_0) will denote the difference in energy of the excited $(e=1)$ and ground $(e=0)$ electronic states for these nuclear positions.

The phonon Hamiltonian and its dependence on the electronic eigenstate are expressed by the remaining

two terms. In the ground electronic state ($e=0$) the phonon Hamiltonian is simply

$$H_p=\sum_i \omega_i(a_i a_i^\dagger+\tfrac{1}{2}), \tag{2}$$

where the $a_i^\dagger$ and a_i are the creation and annihilation operators for the ith normal mode of the system. In the excited electronic state ($e=1$), the phonon Hamiltonian contains the additional term, H_c.

A simple assumption for H_c, with the condition that the equilibrium nuclear positions are the same for both electronic states, is the quadratic form

$$H_c=(1/N)(\sum_i \alpha_i\xi_i)^2. \tag{3}$$

N is the number of normal modes contributing to the broadening, ξ_i the coordinate of the ith mode, and α_i a measure of the coupling of the ith mode to the electron.

Markham,[1] and references quoted there, discuss the various degrees of sophistication with which the Born-Oppenheimer approach may be applied. The present example is the simplest and may result in the neglect of important contributions to the linewidth. The object of this paper is to understand one mechanism in detail, not to establish that this mechanism dominates. The many approximations implied by Eq. (1) will not be discussed, except for one assumption.

The apparently most severe assumption in Eq. (3) is the neglect of linear terms in the ξ_i, or the assumption of zero nuclear displacement upon excitation of the electron. In first-order perturbation such terms do not give a lifetime breadth since in typical problems the electronic energy (E_1-E_0) is greater than any of the phonon energies. In higher order they can contribute to radiationless decay of the excited state and hence to lifetime broadening. This case can be easily identified experimentally if fluorescence measurements can determine the excited state liftime. Finally such linear terms can contribute in various orders to a continuous background similar to the $\Delta n=2$ transitions discussed later in this this paper. Although the existence of these terms may influence the intensity of the observed narrow lines, they do not contribute to the observable breadth. Hence, the linear coupling terms in H_c are neglected not because they may be shown to be small, but because they are of no interest for the present problem.

In the electron problem the term H_c arises because of the dependence of the force constants of the normal modes on the electronic state or, alternatively, H_c represents the dependence of the electronic energy on the normal coordinate amplitudes, presumably through the local strain at the electron associated with the mode excitations. For the ith mode, the associated strain is proportional to the gradient of the displacement field or to the wave vector of the ith mode. In the Debye approximation, since the wave vector of a mode is proportional to the frequency of the mode, the coefficients, α_i, will be proportional to the mode frequencies, ω_i.

In the Mössbauer problem Josephson[3] has shown that the second-order Doppler shift can be treated by using for H_c the difference in kinetic energies of the ground and excited nuclear states which results from the excess mass, $\delta M=(E_\gamma/c^2)$, of the excited nucleus. The term, $\alpha_i\xi_i$, in H_c is, therefore, proportional to $(\delta M)^{1/2}\omega_i\xi_i$ and again α_i is proportional to ω_i.

Noting that for either problem α_i is proportional to ω_i, and using the transformation to the second quantization representation,

$$\xi_i=(\hbar/2m\omega_i)^{1/2}(a_i+a_i^\dagger), \tag{4}$$

one has

$$H_c=(\alpha/N)[\sum_i \omega_i^{1/2}(a_i+a_i^\dagger)]^2, \tag{5}$$

where

$$\alpha=(\alpha_i^2/\omega_i^2)(\hbar/2m). \tag{6}$$

The magnitude of the coupling coefficient, α, is conveniently expressed as the ratio of the zero-point shift of the line [see Eq. (15a) below] to the characteristic frequency of the phonon spectrum. For the case of ruby, Kiel[4] calculates an α of about 0.5, and for the Fe^{57} Mössbauer line a typical $\alpha=\frac{3}{4}E_\gamma/Mc^2$ is 2×10^{-7}. The following calculations are based on the small value of the parameter α since it is the inequality $\alpha\ll1$ which characterizes the qualitatively different behavior of the narrow- and broad-line spectra.

METHOD OF MOMENTS

The problem now is to calculate the line shape associated with the transition between the ground and excited electronic states of the system described by the Hamiltonian (1). In the absence of the interaction term, H_c, the line would not be broadened since (a) the energy of the excited electron would not depend on the phonon occupation number and (b) the selection rule $\Delta n_i=0$ for each mode would assure that no energy could be transferred to the lattice vibrations by phonon excitations. If the interaction term, H_c, is included, however, neither of the above conditions is satisfied. (a) Because of the dependence of the excited state energy on the normal coordinate, there will be a temperature-dependent energy shift which is proportional to the mean square excitation of the various modes and a line breadth resulting from the statistical fluctuations of the excitation of these modes. (b) The term H_c implies that the set of coordinates, ξ_i, which diagonalize the lattice Hamiltonian in the ground electronic state, do not form a set of normal coordinates when the electron is excited. If the labels, i, for the ground-state normal modes are used also for the normal modes of the excited states, then one may say that H_c relaxes the selection rule $\Delta n_i=0$ and the consequent excitation or de-excitation of the normal modes gives an additional contribution to the line breadth.

[3] B. D. Josephson, Phys. Rev. Letters 4, 341 (1960).
[4] A. Kiel, Phys. Rev. 126, 1292 (1962).

Although it may be very difficult to calculate the detailed shape of the absorption implied by this model, the calculation of the first few moments may be carried through by standard techniques,[2,5] and a knowledge of these moments *may* give some meaningful indications concerning the observed line broadening. The eigenstates of the system will be indexed by an electronic quantum number $e=0$ or 1 and by a set of N phonon occupation number, n_i, which will be indicated schematically by a simple index l for the ground electronic state and l' for the excited electronic state. Remember that because of the term H_c the sets of phonon occupation numbers, l', refer to different normal modes than the sets l. The phonon states l' are eigenstates of H_p+H_c while the states l are eigenstates of H_p alone. The normalized nth moment of the line may be written as

$$\langle\nu^n\rangle=A\sum_l \exp(-E_l/kT)\sum_{l'}|(0l|P|1l')|^2 \times(E_1+E_{l'}-E_0-E_l)^n, \quad (7)$$

$$(1/A)=\sum_l \exp(-E_l/kT)\sum_{l'}|(0l|P|1l')|^2. \quad (8)$$

P is the operator coupling the electron or nucleus to the electromagnetic field which gives rise to the observed optical or γ-ray transition.

In the Condon approximation[1] (already implied by the form of the Hamiltonian) the matrix element $(0l|P|1l')$ may be written as the product of an electronic or nuclear matrix element, $(0|P|1)$, with the projection, $(l|l')$, of the initial phonon state upon the final one. It is convenient to suppress the electronic contribution to the energy, (E_1-E_0), by computing the moments of the lines with respect to (E_1-E_0) as origin, and in all subsequent relations the origin of frequency is taken as (E_1-E_0). Factoring the matrix element $(0|P|1)$, and noting that in Eq. (8) $\sum_{l'}|(l|l')|^2=1$, Eq. (7) becomes

$$\langle\nu^n\rangle=\langle\textstyle\sum_{l'}|(l|l')|^2(E_l-E_{l'})^n\rangle_T, \quad (9)$$

where

$$\langle f(l)\rangle_T=[\textstyle\sum_l f(l)\exp(-E_l/kT)]/\sum_l \times\exp(-E_l/kT). \quad (10)$$

The great difficulty in predicting the line shape is the complexity of finding the eigenstates of the Hamiltonian

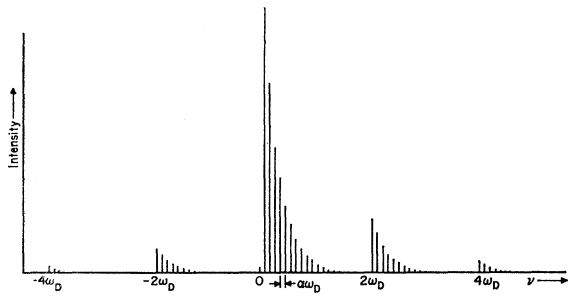

FIG. 1. The spectrum at moderate temperatures for the Einstein phonon dispersion.

[5] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

H_p+H_c and their projections, $(l|l')$, onto the unperturbed phonon states. The power of the method of moments is that this step is not necessary. Note that expressions such as $(l|l')(E_{l'}-E_l)^n$ may equally well be written as $(l|(E_{l'}-E_l)^n|l')$. If $(E_{l'}-E_l)^n$ is expanded with terms in $E_{l'}$ on the right and terms in E_l on the left, then E_l may be replaced by H_p and $E_{l'}$ by H_p+H_c since

$$(l|\,H_p=(l|\,E_l, \quad (11a)$$

and

$$(H_p+H_c)\,|l')=E_{l'}\,|l'). \quad (11b)$$

Note that one can *not* simply replace $(E_{l'}-E_l)$ by H_c. When $(E_{l'}-E_l)$ has been replaced by an operator equivalent, the sum over l' simply represents a matrix product and the first four moments simplify[6] to

$$\langle\nu\rangle=\langle(l|H_c|l)\rangle_T, \quad (12a)$$

$$\langle\nu^2\rangle=\langle(l|H_c^2|l)\rangle_T, \quad (12b)$$

$$\langle\nu^3\rangle=\langle(l|H_c^3+1/2[[H_c,H_p],H_c]|l)\rangle_T, \quad (12c)$$

$$\langle\nu^4\rangle=\langle(l|H_c^4+[H_c^2,[H_c,H_p]]-[H_c,H_p]^2|l)\rangle_T. \quad (12d)$$

The moments (12) will not give useful predictions concerning the shape of the *observed* spectral line. Consider a typical term in the Hamiltonian, H_c, which will be of the form $(a_i^\dagger a_j^\dagger+a_ia_j+a_ia_j^\dagger+a_i^\dagger a_j)$ and assume for the moment that all of the normal modes have a single frequency, ω_D. It is easy to show by perturbation arguments that the spectrum will be as shown in Fig. 1. The term $(a_i^\dagger a_j^\dagger+a_ia_j)$ relaxes the selection rules to allow the creation or annihilation of phonon pairs (or quartets in higher order) simultaneous with the electron transition. These transitions appear as the lines near $\nu=\pm2\omega_D$, $\pm4\omega_D$, $\cdots$ in Fig. 1 and correspond classically to frequency modulation of the electronic transition by the lattice vibrations. The term $(a_ia_j^\dagger+a_i^\dagger a_j)$ gives the dependence of the excited state energy on the total number of phonons, $\sum n_i$, and produces the fine-scale asymmetric broadening of each of the components.

In calculating the moments (12) the satellite lines contribute significantly to the second moment and completely dominate the higher moments. Since only the central component is seen experimentally, these moments give no useful information about the observed line. This same problem of domination of the higher moments by satellite lines is encountered in magnetic resonance problems[2] and may be eliminated by suitable truncation of the Hamiltonian. If the offensive terms, $(a_i^\dagger a_j^\dagger+a_ia_j)$, are simply omitted and the moments (12) calculated using

$$H'=(\alpha/N)\textstyle\sum_{ij}\omega_i^{1/2}\omega_j^{1/2}(a_ia_j^\dagger+a_i^\dagger a_j) \quad (13)$$

in place of H_c, these moments will correspond to the de-

[6] These results are obtained most easily by putting $n/2$ powers of $(E_{l'}-E_l)$ into the element $(l|l')$ and the remainder into the element $(l'|l)$.

sired experimental line shape. (In the Einstein model the truncation removes some intensity, of order α^4, from the central component, which is unimportant for small α. For the other phonon models, used later, the corresponding terms in α^4 give no contribution to the narrow line. Hence, for most cases of interest, this error introduced by truncation is negligible.) In the following sections the moments of the line will be calculated for several phonon models using (12) with H_c replaced by H'. This truncation procedure may be contrasted with the problem of broad-line spectra where the vibrational sidebands are not resolvable. Here, the full Hamiltonian would be used to calculate the moments.

EINSTEIN MODEL

The simplest model for the lattice vibration spectrum of a solid is the Einstein model in which the normal mode frequencies are degenerate. The normal mode coordinates in this model are typically chosen to correspond to independent oscillations of individual atoms. On the basis of this choice, Snyder and Wick[7] predict a line shift and linewidth for the Mössbauer line which is essentially the same as that given by Eqs. (15a) and (15b) below.

One is led to an apparent contradiction, however, in using another of the conclusions of Snyder and Wick, namely, that if N nonlocalized modes are important in describing the motion of the nucleus, then the width is of order $(1/N)^{1/2}$ smaller than that given by the single-mode model. The contradiction arises because in the Einstein model the assumed degeneracy of the normal frequencies implies that any orthonormal set of linear combinations of atom displacements can serve as a set of normal coordinates. Hence, one should obtain physically equivalent results starting either from localized modes or extended modes, yet apparently the two approaches give different conclusions.

The moment calculation of Snyder and Wick assumes the selection rule, $\Delta n_i=0$, that none of the oscillators should change its occupation number. This corresponds, in the present formalism, to a further truncation of H_c, namely to

$$H''=(\alpha/N)\sum_i \omega_i(a_i a_i^\dagger+a_i^\dagger a_i). \tag{14}$$

If one includes only the less restrictive selection rule, $\sum_i \Delta n_i=0$, that the total number of phonons be conserved, and computes the moments from (12) using Eq. (13) for H', then the results are entirely equivalent to the single-mode calculation of Snyder and Wick and give

$$\langle\nu\rangle=\alpha\omega_D(2\bar{n}+1), \tag{15a}$$

$$\langle\nu^2\rangle=\alpha^2\omega_D^2(8\bar{n}^2+8\bar{n}+1), \tag{15b}$$

$$\langle\nu^3\rangle=\alpha^3\omega_D^3(48\bar{n}^3+72\bar{n}^2+26\bar{n}+1), \tag{15c}$$

$$\langle\nu^4\rangle=\alpha^4\omega_D^4(384\bar{n}^4+768\bar{n}^3+464\bar{n}^2+80\bar{n}+1), \tag{15d}$$

[7] H. S. Snyder and G. C. Wick, Phys. Rev. **120**, 128 (1960).

with

$$\bar{n}=\langle n\rangle_T=[\exp(\hbar\omega/kT)-1]^{-1}. \tag{16}$$

Thus, there is no contradiction when the extended-mode model is correctly treated, the important point being the necessity of including the interference terms between different modes. These terms, included in H', Eq. (13), but not in H'', Eq. (14), give rise to "Raman transitions" in which some modes gain energy, while other modes lose energy during the electronic transition. This description is somewhat awkward in the case of the Einstein model, where the localized mode picture is much simpler, but is necessary in understanding the behavior of real crystals where the dispersion of the phonon spectrum cannot be neglected.

The results of this section, atlhough useful in introducing the method of calculation, are applicable to real systems only in the case of broadening by very narrow phonon bands or by localized modes. The first case will be considered in more detail in a later section. For the second, it is straightforward to calculate exactly the spectrum, which will have resolved components of spacing $\alpha\omega_D$ (similar to Fig. 1), and it is pointless to use the present methods.

One comment of interest is that in the limit of zero temperature all of the moments about the mean, $\langle\nu\rangle=\alpha\omega_D$, become zero, showing that there is no zero-point breadth to the line, in contrast with broad-line spectra. The reason, of course, is that the zero-point breadth of the broad lines arises from the same terms which give the satellite lines in this calculation. These satellites remain at absolute zero but do not contribute to the width of the central component.

MOMENTS IN THE DEBYE MODEL

Unfortunately, the Einstein model does not give even an approximately realistic picture of the broadening by the lattice vibrations, even in the high-temperature limit where the Debye and Einstein models typically give similar predictions. This is because of the strong qualitative dependence of the commutator $[H',H_p]$ on the nature of the phonon dispersion. Evaluation of the commutator gives

$$\begin{aligned}[H',H_p]&=(\alpha/N)\sum_{ijk}\omega_i^{1/2}\omega_j^{1/2}\omega_k \\ &\quad\times[(a_i a_j^\dagger-a_i^\dagger a_j),\, a_k a_k^\dagger] \\ &=(2\alpha/N)\sum_{ij}\omega_i^{1/2}\omega_j^{1/2}(\omega_i-\omega_j)a_i a_j^\dagger,\end{aligned} \tag{17}$$

which is zero if all of the ω_i's are the same.

For any model with appreciable phonon dispersion, and in the limit of small α, the terms containing $[H',H_p]$ in the third and fourth moments completely dominate these moments. Hence, the effect of the phonon dispersion is to increase the third and fourth moments of the line without altering significantly the first and second moments. This is reminiscent of the effect of exchange or motional contributions to the Hamiltonian in magnetic

resonance problems[2,8] which likewise contribute to higher moments but not the second. As in the magnetic resonance problem, the increase in fourth moment without alteration of the second moment may be achieved by extending the wings of the line and narrowing the center of the line. The extension of the wings of the line is easy to see physically. It was shown in the previous section that transitions described by $\Delta n_i=+1$ and $\Delta n_j=-1$ must be included to get physically reasonable results. With phonon dispersion, such transitions will involve an energy transfer $(\omega_i-\omega_j)$ to the phonon field and one expects contributions to the line from the wings as far out as ω_D, which is much greater than the root second moment of the line if α is small.

Thinking classically, one may interpret these transitions as the result of frequency modulation of the electron transition by the combined action of modes i and j, giving sidebands at $|\omega_i-\omega_j|$ from the central line. If the modulation index, or ratio of frequency deviation to modulation frequency, is large or of the order of one the sideband will be strong, but if the modulation index is small the line will be very weak. The problem is to find, in a system of many modes, for what range of frequency differences, $|\omega_i-\omega_j|$, the modulation index is large, since this range will roughly be the linewidth.

The program is to calculate the moments of the line and then to fit these moments to a plausible line shape which will be called the "model line." The width of the model line should correspond to the spectral width observed experimentally. The weak point of the argument is, of course, the choice of the "plausible line shape." In the analogous magnetic resonance problem the choice of a Lorentzian line shape with a cutoff in the extreme wings has received theoretical justification.[8] The same model line will be used here, though without justification beyond its consistency with the computed moments.

The calculation of the moments is straightforward and gives, neglecting terms of order $1/N$,

$$\langle\nu\rangle=(\alpha/N)\sum_i\omega_i(2\bar{n}_i+1), \tag{18a}$$

$$\langle\nu^2\rangle=(\alpha/N)^2\sum_{ij}\omega_i\omega_j[8\bar{n}_i\bar{n}_j+8\bar{n}_i+1], \tag{18b}$$

$$\langle\nu^3\rangle=(\alpha/N)^3\sum_{ijk}\omega_i\omega_j\omega_k \times[48\bar{n}_i\bar{n}_j\bar{n}_k+72\bar{n}_i\bar{n}_j+26\bar{n}_i+1] +4(\alpha/N)^2\sum_{ij}\omega_i\omega_j(\omega_i-\omega_j)\bar{n}_j, \tag{18c}$$

$$\langle\nu^4\rangle=(\alpha/N)^4\sum_{ijkl}\omega_i\omega_j\omega_k\omega_l[384\bar{n}_i\bar{n}_j\bar{n}_k\bar{n}_l +768\bar{n}_i\bar{n}_j\bar{n}_k+464\bar{n}_i\bar{n}_j+80\bar{n}_i+1] +8(\alpha/N)^3\sum_{ijk}\omega_i\omega_j\omega_k \times(\omega_i-\omega_k)(\bar{n}_k-\bar{n}_i)(2\bar{n}_j+1) +4(\alpha/N)^2\sum_{ij}\omega_i\omega_j(\omega_i-\omega_j)^2(\bar{n}_i+1)\bar{n}_j. \tag{18d}$$

Note that the first and second moments and the leading terms in the third and fourth moments are simply generalizations of the moments obtained in the Einstein model. The largest terms in the third and fourth moments are those of order α^2 which arise because of the commutator $[H',H_p]$ in Eqs. (12). In the remaining arguments α will be assumed small and only the terms of order α^2 in the third and fourth moments will be retained.

These moments may be rewritten by replacing the sum over normal modes by an integration over a Debye spectrum. Making the replacement

$$(1/N)\sum_i f(\omega_i)\rightarrow\int_0^{\omega_D}3(\omega^2/\omega_D{}^3)d\omega, \tag{19}$$

and defining

$$A_n=\omega_D{}^n\int_0^{\omega_D}3(\omega^{2+n}/\omega_D{}^{3+n})d\omega=3\omega_D{}^n/(n+3), \tag{20}$$

and

$$B_n=\omega_D{}^n\int_0^{\omega_D}\frac{3\omega^{2+n}d\omega}{\omega_D{}^{3+n}[\exp(\hbar\omega/kT)-1]}, \tag{21}$$

the moments become

$$\langle\nu\rangle=\alpha(2B_1+A_1), \tag{22a}$$

$$\langle\nu^2\rangle=\alpha^2(8B_1{}^2+8B_1A_1+A_1{}^2), \tag{22b}$$

$$\langle\nu^3\rangle\approx4\alpha^2(A_2B_1-B_2A_1) \tag{22c}$$

$$\langle\nu^4\rangle\approx4\alpha^2[2(B_3B_1-B_2{}^2)+A_3B_1-2A_2B_2+A_1B_3]. \tag{22d}$$

It is important for later arguments to note that in the expressions for the second through fourth moments the terms of the form AB involve interference between the zero-point motion of one mode and the thermally excited motion of another mode while the terms of the form B^2 give the contribution to the moments from interference between thermal motion of two modes. Similarly the terms involving only A give pure zero-point effects. There is a zero-point shift, but again no zero-point width since the dispersion is zero at absolute zero.

LINE SHAPES IN THE DEBYE MODEL

The moments (22) give the formal conclusions of the Debye theory in the approximation $\alpha\ll1$. It remains to interpret these moments in terms of actual line shapes. Because of the complexity of the expressions for the moments this will be attempted only for the limits of high and low temperature.

The low-temperature case is the more difficult and will be considered first. In this limit the integrals B_n are given by

$$B_n=\omega_D{}^nT^{3+n}3(n+2)!\zeta(n+3), \tag{23}$$

where T is the temperature in units of the Debye temperature and ζ is the Riemann zeta function. Converting the moments (22) to moments about the mean, the terms of lowest order in T are

$$\langle(\nu-\langle\nu\rangle)^2\rangle\approx\alpha^2\omega_D{}^2[54\zeta(4)T^4+O(T^5)+\cdots], \tag{24a}$$

[8] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

$$\langle(\nu-\langle\nu\rangle)^3\rangle\approx\alpha^2\omega_D{}^3[(216/5)\zeta(4)T^4+O(T^5)+\cdots], \quad (24b)$$

$$\langle(\nu-\langle\nu\rangle)^4\rangle\approx\alpha^2\omega_D{}^4[36\zeta(4)T^4+O(T^5)+\cdots]. \quad (24c)$$

These expressions derive from terms in the moments of the form AB which correspond to the following process: Simultaneously with the electron transition, a thermally excited phonon is destroyed and a second mode is excited from its zero-point level to a one phonon state. Since only low-frequency modes will be thermally excited, the phonon which is destroyed will be of low frequency while the one excited may be of any frequency. Hence, these terms give a broad spectrum, see Fig. 2, which extends from within kT of $\nu=0$ to the Debye frequency. These terms do not contribute to any peaking near $\nu=0$ and should not be included when determining the shape of the central peak. This will be true of all of the terms of the form AB and can be verified even more directly for the case where only the leading term ($\propto T^4$) contributes to each moment. Perturbation theory arguments, appropriate for discussing the wings of the line but not the center, indicate that the intensity contributed by the AB terms will be

$$I_{AB}(\nu)=K\nu, \quad (25)$$

for $\nu>\omega_D T$. The contribution of this part of the line to the moments will be

$$\langle(\nu-\langle\nu\rangle)^2\rangle_{AB}=K\omega_D{}^4/4, \quad (26a)$$

$$\langle(\nu-\langle\nu\rangle)^3\rangle_{AB}=K\omega_D{}^5/5, \quad (26b)$$

$$\langle(\nu-\langle\nu\rangle)^4\rangle_{AB}=K\omega_D{}^6/6. \quad (26c)$$

Note that if K is chosen to be

$$K=216(\alpha^2/\omega_D{}^2)\zeta(4)T^4, \quad (27)$$

the perturbation theory line shape (25) predicts correctly the moments (24). Hence it is concluded that the AB terms contribute only to the broad background, not experimentally observable, and that the breadth of the central spike is associated with the B^2 type terms.

The shape of the central line is described by the terms in (22) of the form B^2 which result from Raman processes in which both of the modes are thermally excited. Since only modes with frequency up to several kT are appreciably excited the tail of the line associated with the B^2 terms can only extend several kT from $\nu=0$. A Lorentzian model line will be used with half-width Δ and a cutoff in the wings at δ. The argument above suggests that δ should be several times kT, or, in the appropriate units, several times $\omega_D T$. The dispersion and fourth moments of the model line, in the limit $\Delta\ll\delta$, are[9]

$$\langle(\nu-\langle\nu\rangle)^2\rangle=2\Delta\delta/\pi, \quad (28a)$$

$$\langle(\nu-\langle\nu\rangle)^4\rangle=2\Delta\delta^3/3\pi. \quad (28b)$$

These are to be compared with the contributions of the B^2 terms to the moments which are, in lowest order in T,

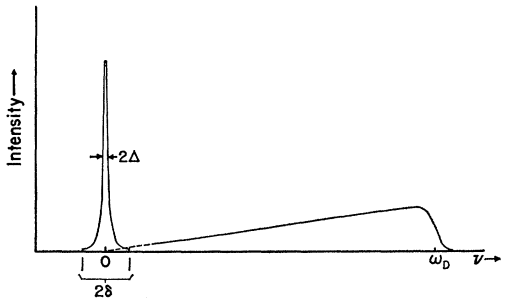

FIG. 2. The spectrum at very low temperature for the Debye phonon dispersion.

$$\langle(\nu-\langle\nu\rangle)^2\rangle_{BB}\approx 1.5\times 10^3\alpha^2\omega_D{}^2T^8, \quad (29a)$$

$$\langle(\nu-\langle\nu\rangle)^4\rangle_{BB}\approx 1.3\times 10^4\alpha^2\omega_D{}^4T^{10}. \quad (29b)$$

Equating the actual moments to the model line moments gives for the model line half-width,

$$\Delta=480(\alpha\omega_D T^4)^2/\omega_D T, \quad (30)$$

and for the cutoff,

$$\delta=5\omega_D T. \quad (31)$$

This cutoff is in gratifying agreement with that estimated on physical grounds and gives confidence in the consistency of the model line shape.

The result for the linewidth, Eq. (30), has been expressed in a form similar to that encountered in magnetic resonance problems.[2,8,10] $\alpha\omega_D T^4$ is the linewidth that one would expect from the B^2 terms of Eq. (22) if all of the contributing normal mode frequencies were the same. The actual linewidth is reduced by the ratio of that width to the "motional frequency" which in this case is the dispersion in frequency of the contributing modes, $\omega_D T$, or (kT/h) in conventional units.

Note that the temperature dependence of the linewidth is much greater than that of the line shift (which varies as T^4), and also that the predicted width is much less than the shift, by roughly the ratio of the shift to kT.

The same procedure is followed in the high-temperature limit where the coefficients B_n are,

$$B_n=\omega_D{}^n[3/(n+2)]T+O(T^0). \quad (32)$$

Keeping only terms of highest order in T, the moments are

$$\langle\nu\rangle\approx\alpha\omega_D 2T, \quad (33a)$$

$$\langle(\nu-\langle\nu\rangle)^2\rangle\approx\alpha^2\omega_D{}^2 4T^2, \quad (33b)$$

$$\langle(\nu-\langle\nu\rangle)^3\rangle\approx\alpha^2\omega_D{}^3(3/20)T, \quad (33c)$$

$$\langle(\nu-\langle\nu\rangle)^4\rangle\approx\alpha^2\omega_D{}^4(3/10)T^2. \quad (33d)$$

The asymmetry of the line, indicated by $\langle(\nu-\langle\nu\rangle)^3\rangle$, results from the same type of transitions which gave the

[9] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

[10] D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

background ($I_{AB}=K\nu$) in the low-temperature limit and represents interference terms between the thermal and zero-point motion. This third moment is only linear in T and in the high-temperature region the line becomes symmetric.

Assuming the same model line, the cutoff is expected to be the order of the Debye frequency since that is the maximum energy transfer possible in a process $\Delta n_i=+1$, $\Delta n_j=-1$. Comparison of Eqs. (28) with Eqs. (33) gives a cutoff

$$\delta=0.48\omega_D, \tag{34}$$

and a half-width of the model line

$$\Delta=13(\alpha\omega_D T)^2/\omega_D. \tag{35}$$

Again the cutoff is consistent with physical arguments about the line shape. The linewidth again shows motional narrowing—it is the width that would be calculated on the Einstein model but reduced by the ratio of that width to the Debye frequency.

LINE SHAPES FOR AN OPTICAL PHONON BAND

The expressions (18) for the moments of the line are appropriate for any choice of the phonon dispersion. A particularly simple choice, and one which is useful in estimating the contribution of optical phonon branches to the linewidth, is a model with a constant density of modes in a bandwidth W about a mean frequency ω_D The sums of Eqs. (18) are replaced by integrals:

$$(1/N)\sum_i f(i)\rightarrow(1/W)\int_{\omega_D-W/2}^{\omega_D+W/2} f(\omega_i)d\omega_i, \tag{36}$$

which are easily evaluated in the limit $W\ll\omega_D$ and $W^2\ll\omega_D{}^2T$. [If the inequalities are both satisfied then all terms of the integrals may be considered constant except the differences, $(\omega_i-\omega_j)$.] To lowest order in this approximation the moments become

$$\langle\nu\rangle\approx\alpha\omega_D(2\bar{n}+1), \tag{37a}$$

$$\langle(\nu-\langle\nu\rangle)^2\rangle\approx4\alpha^2\omega_D{}^2(\bar{n}^2+\bar{n}), \tag{37b}$$

$$\langle(\nu-\langle\nu\rangle)^3\rangle\approx0, \tag{37c}$$

$$\langle(\nu-\langle\nu\rangle)^4\rangle\approx(2/3)\alpha^2\omega_D{}^2W^2(\bar{n}^2+\bar{n}). \tag{37d}$$

In this example the cutoff of the model line is expected to be about W, and comparison of (28) with (37) gives

$$\delta=(1/\sqrt{2})W, \tag{38}$$

which is consistent with the prediction. The half-width of the model line becomes, for any temperature,

$$\Delta=2\sqrt{2}\pi[\alpha^2\omega_D{}^2(\bar{n}^2+\bar{n})/W], \tag{39}$$

again showing the characteristic form of a motionally narrowed line.

An interesting feature of most of the linewidth results is that the temperature variation of the linewidth is roughly as the square of that of the line shift. This relation is obeyed at high temperature for both Debye and optical branch models and in the Debye model at low temperature. The exception is the optical branch model at low temperature, $\bar{n}^2\ll\bar{n}$, where the linewidth is proportional to the shift, but reduced by the narrowing ratio, $(\alpha\omega_D/W)$.

The other important feature is that the effectiveness of an optical branch in broadening such a spectral line is inversely proportional to the width of the branch. Of course, if the width W of the phonon band is small enough to be comparable with the square root of the second moment, Eq. (37b), then the narrowing does not occur and the results reduce essentially to those of the Einstein model.

APPLICATIONS

The calculations above show the existence of a thermal broadening of the Mössbauer line via the second-order Doppler shift even when a large number of modes contribute to the shift. It is convenient to express the width for the Debye model at high temperature, Eq. (35), in terms of the second-order shift, (33a), as

$$2\Delta=6.5\langle\nu\rangle^2/\omega_D.$$

Because of the "motional narrowing," the width is smaller than the shift by the ratio of the shift to the Debye frequency or about 10^{-7} for Fe^{57}, corresponding to a width of only about 10^{-6} of the lifetime broadening. Hence, though the width implied by the value of the second moment would be comparable with the shift, the narrowed width is far less than one would expect to observe.

If there is significant interaction with an extremely narrow optical branch of the lattice vibration spectrum this width will be enhanced but probably not enough to be observable. If, however, localized modes exist at the nucleus then the arguments of Snyder and Wick are applicable and the broadening may be appreciable. Note that if the broadening is associated with a single localized mode it should appear in the form of structure as indicated in Fig. 1, not as a simple smearing of the line. This assumes, of course, that other sources of broadening allow resolution of the structure.

Schawlow's experimental results, Fig. 2 of reference 4, on the thermal broadening of the R lines of ruby stimulated the development of the results given above. Although the ideas developed in this analysis may be pertinent to a qualitative understanding of Schawlow's results, a detailed picture must undoubtedly be quite complex. This results from two observations. First, α may *not* be assumed small since the coupling estimated by Kiel corresponds to an α of one half. As noted below, this may not be a serious problem for low temperatures. Second, the very complex phonon spectrum of Al_2O_3 precludes the use of a simple Debye model. The results

of Raman spectroscopy[11] and the presence of vibrational sidebands in the ruby infrared spectrum show the presence of optical modes in the frequency range 140 cm^{-1} to 900 cm^{-1}. For the experimental range of temperatures, these modes should certainly contribute to the linewidth comparably with the acoustic modes with a Debye temperature, based on calculations from the elastic constants, of 600°K. Despite this complexity, a few remarks may be useful.

It seems unlikely that the width is due to acoustic modes alone. The fact that the observed width is much less than kT over the whole range of interest, or that $\Delta \ll \delta$, allows the use of Eqs. (29, 30) even though $\alpha \sim 1$. But these equations imply a T^7 dependence of Δ which is in marked disagreement with experiment.

It is proposed that the breadth is, in fact, dominated by optical rather than acoustical modes, since there appear to be modes available which would achieve appreciable thermal excitation at these temperatures. By a suitable choice of the coupling to the various modes and of the breadth of the branches it should be possible to fit almost any experimental curve. Hence attempts to fit the experimental curve in detail seem rather pointless. It would certainly be fruitful to study the width of narrow line electronic spectra in hosts with a simple phonon spectrum.

[11] R. S. Krishnan, Proc. Indian Acad. Sci. **26**, 450 (1947).

CONCLUSIONS

A greatly simplified Hamiltonian is proposed and studied in an attempt to understand the linewidth of certain narrow optical and γ-ray transitions in solids. The analysis illustrates how to obtain meaningful results for the observable linewidths in terms of the calculable moments of the line. Several models for the phonon spectrum are treated and shown to have markedly different qualitative behavior as regards their influence on the observed line width. The study shows that in principle the Mössbauer line has a finite breadth as a result of the coupling to the phonon field via the second-order Doppler shift, though, except in the case of localized modes, the breadth is probably not observable. In the case of the ruby narrow line spectrum, though the mechanism of line broadening proposed by Kiel[4] is probably qualitatively correct, the complexity of the phonon spectrum for Al_2O_3 prevents detailed comparison of theory with experiment.

ACKNOWLEDGMENTS

This analysis resulted from an attempt to clarify the broadening mechanism suggested by Dr. A. Kiel and I am indebted to him for the preprint of reference 4 which is the starting point for this paper. Dr. G. Chester has contributed greatly in discussion and criticism of the manuscript.

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Anomalous Quadrupole Coupling in Europium Ethylsulfate*

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Hyperfine structure, apparently of pure quadrupolar form, has been observed in the Eu^{3+} ion in a neodymium ethylsulfate lattice. It has twice the predicted magnitude and opposite sign to that calculated on the basis of a pure ground electronic configuration of the type $4f^n$. Arguments are presented for ascribing the anomaly to the admixing, through the crystal-field potential, of the state $5p^5 6p\ ^1D_2$ into the closed-shell state $5p^6\ ^1S_0$. For Eu^{152}, we find $P_{152} = -(6.7 \pm 0.5) \times 10^{-4}$ cm^{-1} and for Eu^{154}, $P_{154} = -(8.3 \pm 0.7) \times 10^{-4}$ cm^{-1}. The spin and parity assignments of 2− for the 1531-keV state in Sm^{152} and the 1400- and 1723-keV states in Gd^{154}, as well as the electric-dipole multipolarities of the radiations depopulating these states, are confirmed. The quadrupole moment of Eu^{154} is found to be 3.29 ± 0.37 b.

I. INTRODUCTION

ONE of the significant trends in chemical and atomic physics in the past few years has been the increasing awareness, both experimental and theoretical, of small hyperfine structure effects which cannot be explained by the very simplest models, involving only valence electrons in pure, noninteracting hydrogen-like orbitals. These effects are observed, for example, in some internal magnetic fields, in antishielding, and in the influence on hyperfine structure of higher-order crystal-field interactions and deviations from Russell-Saunders coupling.

We report herein a case in which such subtle effects are clearly present, namely, the existence of hyperfine structure in the ground state of Eu^{3+}. This ion has (in the usual approximation) the electronic configura-

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