Resonant-radiation transfer and nonequilibrium phonons in ruby

I. B. Levinson

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

Submitted 16 January 1978


The usual Biberman-Holstein theory of resonant-radiation transfer is valid only when the reradiating center "forgets" after absorbing the radiation quantum, everything but the fact that it is excited. This is possible if the center interacts strongly with the "thermostat." In a number of cases, for example for resonant phonons in ruby, this is not the case. It is also possible to formulate an alternative transfer theory, and this theory is developed in this paper.

PACS numbers: 63.20.Dj, 71.36.+c

INTRODUCTION

An alternative to the known quantum theory of Biberman and Holstein\(^{1,2}\) is developed here for resonant-radiation transfer. The present work was stimulated by experiments on nonequilibrium phonons in ruby.\(^{3,4}\) We shall therefore deal henceforth with phonons and that arise in the experiment.

The Biberman-Holstein equation, the derivation of which will be analyzed in Sec. 1, presupposes that a strong interaction exists between the impurity centers and the "thermostat." This is precisely why it suffices, for a description of the nonequilibrium state of the system of centers, to know only the concentrations \(N_1\) and \(N_2\) of the centers at the lower level 1 and at the upper level 2; all other nonequilibrium parameters "are forgotten" in the course of interaction with the thermostat.

On the other hand if the system of centers interacts only with resonant radiation, then the description of its nonequilibrium state is much more complicated—the system "remembers" better the excitation conditions, and more parameters are needed for its description. Thus, for example, the excitation energy of the system of centers is described in the Biberman-Holstein equations in integral fashion—by the parameter \(N_p\). If, however, the system remembers the excitation conditions, then its description calls for knowledge of the spectral density \(F(w)\) of the center excitation energy \(w\) is the center excitation energy reckoned from the level \(E_i\). The total number, \(N_p\), of the excited centers, is obtained as an integral of \(F(w)\) with respect to the frequencies. Analogously, instead of the phonon distribution function the Biberman-Holstein equations in integral form.

The main premises on which the Biberman-Holstein equations are based are the following. For a complete description of the state of the system it suffices to know the phonon momentum distribution function \(\phi(w)\), the concentration \(N_1\) of the centers located at the lower level 1, and the concentration \(N_2\) of the centers on the upper level 2. All these quantities \((\omega, N_1, N_2)\) can depend on the position in space \(r\) and on the time \(t\).

The probability that a phonon with momentum \(q\) (and energy \(\omega\)) will be absorbed is assumed to be

\[ A^x \phi^x(\omega) \]

(1.1)

where \(A^x\) is a certain constant, and the function \(\phi^x(\omega)\) determines the absorption line shape, it is convenient to choose it such that \(\phi^x(\omega) = 1\) at the center of the absorption line, i.e., at \(\omega = \omega_0\).

The absorption line width is then

\[ b_\omega = \int \omega' \phi^x(\omega) \]

(1.2)

The phonon-production probability is assumed to be

\[ A^x \phi^x(\omega) \phi(\omega + \omega_0 + 1) \]

(1.3)
where $A^* \psi$ is a new constant, while the function $\psi^*(\omega)$, normalized in analogy with $\psi^*(\omega)$, describes the emission line shape.

Under these assumptions, the equation for the phonons takes the form

$$\frac{\partial}{\partial t} \psi + v_0 \frac{\partial}{\partial x} \psi = C_2(x, y, z) \frac{\partial^2}{\partial x^2} \psi,$$

where

$$C_2(x, y, z) = -\frac{f(x)}{\partial x} \psi(x, y, z) + \frac{\partial}{\partial x} \psi(x, y, z).$$

and the second term in the right-hand side of (1.6) is responsible for the phonon-phonon interactions.

Since each phonon absorption act is accompanied by a transition $1 \rightarrow 2$, and each emission act by a transition $2 \rightarrow 1$, we can easily write down the kinetic equations for $N_1$ and $N_2$:

$$\frac{\partial}{\partial x} \psi = \frac{\partial}{\partial x} \psi(x, y, z) = C_{12}(x, y, z) \frac{\partial^2}{\partial x^2} \psi,$$

and

$$\frac{\partial}{\partial x} \psi = \frac{\partial}{\partial x} \psi(x, y, z) = C_{21}(x, y, z) \frac{\partial^2}{\partial x^2} \psi.$$

Here $C_{12}$ and $C_{21}$ describe the pumping of the levels $E_1$ and $E_2$ by external sources, while $\tau_1$ and $\tau_2$ describe their deplation which is not connected with resonant phonons (for example in the $E_1 \rightarrow E_1$ and $E_2 \rightarrow E_2$ transitions to the lower level $E_2$).

Let us discuss the premises on which the foregoing equations are based. The most serious is the assumption (1.3) concerning the distribution of the phonons emitted by the excited centers. It means that the spectrum of the phonons radiated by the system of centers depends neither on the system state nor on its prior history, while the total number of emitted phonons depends on a single parameter $N_1$.

We emphasize first of all that in the Biberman-Holstein theory the width $\omega_0$ cannot be due to the natural width $\gamma_0$, since an isolated center, as is known from the theory of resonant fluorescence, forgets the prior history only in the case of broadband excitation. The width $\omega_0$ can be due to the scatter of the energies of the $E_1 \rightarrow E_2$ transition for different centers (inhomogeneous broadening) or to splitting of the transition $E_2 \rightarrow E_1$ at one center (vibrational structure). In either case the assumption (1.3) means that the relative probabilities of filling different states of the "level" $2$ are fixed, although the absolute ones are arbitrary and are determined by the parameter $N_1$. This is possible only if the system of centers exchange intensively energies of the order $\omega_0$ with the thermostat, and the distribution over the states of the level $2$ is determined by the thermostat. The arbitrariness of $N_1$ means that exchange of high energies is difficult, therefore the interaction with the thermostat does not change the total number of excited centers.

One might think that the role of the interaction with the thermostat can be played also by an interaction $V$ between centers, which satisfies the condition $\omega_0 \ll V \ll \omega_0 E_2 - E_1$. This interaction does indeed conserve the number of excited centers and establishes some equilibrium between them. This interaction, however, conserves not only the number of the excited centers but also their energy. Therefore even the relative occupation numbers of the states of the level $2$ should remember the excitation conditions.

The situation is the same with the assumption (1.1).

If we assume that Eqs. (1.4), (1.6), and (1.7) are valid also for the described states which are closed to thermodynamic equilibrium, then the parameters of the emission and absorption lines should coincide:

$$A = \frac{A^*}{\omega_0}, \quad \psi^*(\omega) = \psi_0(\omega), \quad \omega_0 \psi_0 = \omega_0 \psi_0 = \omega_0.$$

In fact, under thermodynamic equilibrium we have $A_0 = 0$. It is easy to verify that this identity is satisfied at temperatures $T > 2kT$ only if (18) holds.

The constant $A^*$ can be expressed in terms of the probability $\gamma^{-1}$ of the spontaneous emission of the phonon. The number of phonons produced in $1 \text{ cm}^2$ per second in spontaneous emission is

$$\int_{\omega_0}^{\omega_0} \gamma(\omega) \frac{\partial^2}{\partial \omega} \psi(\omega) d\omega = \gamma \omega_0 \psi_0.$$

It is clear from (1.9) that

$$\gamma^{-1} = \omega_0 \psi_0.$$

The gist of the last remark, which pertains to the region of applicability of the system (1.4), (1.6), and (1.7), is the following. Since this system makes use of the phonon distribution function $\psi_0$, this means that the width of the phonon distribution should exceed the reciprocal absorption time, i.e.,

$$\omega_0 > \frac{1}{\gamma}.$$

In many cases the depletion of the lower level is negligible, i.e., $N_1 \ll N_2$. Then, adding (1.6) and (1.7), we have

$$\frac{\partial}{\partial t} N_2 = \frac{1}{\gamma} N_2 \beta G_2 + G_2.$$

This equation yields $N_2 = N_2^0 \exp(\beta \gamma)$ and we are left with two equations for $N_1$ and $N_2$. If furthermore $\beta \gamma = 1$, then these equations can be written in the form

$$(\frac{\partial}{\partial t} + v_0 \frac{\partial}{\partial x}) \psi_{1,2} = -\frac{\partial}{\partial x} \psi_{1,2} = \frac{\partial}{\partial x} \psi_{1,2},$$

and

$$\frac{\partial}{\partial t} N_2 = \frac{1}{\gamma} N_2 \beta G_2 + \frac{1}{\gamma} N_2 G_2.$$

If we neglect the phonon-phonon interactions (this can always be done for photons), then we use (1.14) to express $N_2$ in terms of $N_1$. Substituting this in (1.15), we obtain an equation for $N_2$ if we neglect retardation in this equation, i.e., the time of ballistic flight of the photon through the active volume (this can always be done for photons), we obtain the well-known Biberman-Holstein equation.

2. GENERAL EQUATIONS

In this section we derive the equations for the propagation of excitation in a system of randomly disposed..
two-level centers that interact with the phonon field. The reason why the system is not at equilibrium is that the centers are optically pumped also under the influence of the phonon momentum injected on the crystal boundary.

The nonstationarity and spatial inhomogeneity of the system are determined by the excitation conditions, i.e., by the geometric dimensions of the excited regions and by the duration of the excitation (or by the duration of the relaxation of the consequences of this excitation).

Owing to the microinhomogeneity of the crystal, the centers located at one macroscopic point \( \mathbf{x} \) can have several different energies of the \( E_i - E_j \) transition. Writing this in the form \( E_i - E_j = \omega_i + \gamma \), where \( \omega_i \) is the average transition energy, we obtain the parameter \( \gamma \) that characterizes the center. The distribution of the centers in \( \gamma \) is given by the function \( \phi(\gamma) \), normalized by the condition

\[
\int_0^\infty \phi(\gamma) d\gamma = 1. \tag{2.1}
\]

The quantity \( \Delta \omega \) can be called the inhomogeneous broadening.

Bearing applications to ruby in mind, it must be recognized that the levels \( E_i \) and \( E_j \) are in fact Kramers doublets (see Figs. 1 and 2). The degeneracy of these levels can be lifted by an external magnetic field or by the random magnetic fields of neighboring centers. Therefore the magnetic field \( H \) at the location of the center serves, in addition to \( \gamma \), as a parameter that characterizes the center. The components of each doublet will be marked by an additional index \( a \) (spin orientation), and their splittings will be designated \( \Delta H \). Thus the functions \( G(R; t, \gamma, H) \) are functions of the generalized occupation numbers, widths, and shifts depend on \( r \) and \( t \).

The state of the system of centers is described by Green's functions of the following type:

\[
G_c(R; \gamma, H; t, \tau) = \int dR' (\Delta H)^n(\mathbf{R}) \phi(\gamma, H) G_c(R; \gamma, H; t') G_c(R'; \gamma, H; \tau),
\]

where \( (\Delta H)^n(\mathbf{R}) \) is the operator of electron production on a center located at the point \( \mathbf{R} \) in a state \( s = 1 \) or 2 and with corresponding spin orientation. We shall assume that the states of the different centers are not correlated, i.e., \( G = 0 \) if \( R \neq R' \), and that the centers are excited "incoherently," i.e., only the "diagonal" functions \( G_{11} = G_{11}^* \) and \( G_{22} = G_{22}^* \) differ from zero. We assume next that the inhomogeneity and the nonstationarity of the system are weak. Therefore the dependence on the discrete \( R \) in the Green's function \( G(R; \gamma, H, t) \) is transformed into a dependence on the macroscopic coordinate \( x \). The macroscopic time will be \( t = \frac{1}{4} (T_i + T_f) \), and it is natural to take the Fourier transform with respect to the difference \( t_i - t_f \) and change over to the variable \( \xi \). Thus the functions \( G_c(R; \gamma, H, t) \) figure in the theory. In view of the foregoing, these functions depend also on the parameters \( \gamma \) and \( H \) that characterize the "type" of the center.

The equations for these functions are derived with the aid of the Keldysh diagram technique[114]; it is convenient to transform these equations into generalized kinetic equations[115]. The generalized kinetic equations are functions of the generalized occupation numbers \( \eta(\gamma, H, t) \), the level widths \( y(z, H, t) \), and the level shifts \( \Delta(z, H, t) \). The Green's functions are replaced by the generalized occupation numbers \( \eta(\omega, q) \), by the widths \( y(z, q) \), and by the shifts \( \Delta(z, q) \). All the occupation numbers, widths, and shifts depend on \( \gamma \) and \( H \).

The broadenings and the shifts of the levels lead to the appearance of broadened and shifted delta functions; for examples, for photons we get in place of \( \delta(\omega - \omega') \)

\[
\Delta(\omega, q) = \frac{1}{2\pi} \left\{ \int \left[ \frac{1}{2\pi} \delta(\omega - \omega') \right] \right\}, \tag{2.2}
\]

The functions \( \Delta_c(\omega) \) for the centers are determined in similar fashion.

Having made these remarks, we can write down the generalized kinetic equations on the basis of their formal analogy with the ordinary kinetic equations[116, 117].

The balance equations for the centers is

\[
\Delta^*_{c}(\omega) - \frac{\partial}{\partial t} \Delta_{c}(\omega) = a_{1} + a_{2} \delta(z) (\eta_{c}(\omega) - \Delta_{c}(\omega)) \quad \text{and} \quad \eta_{c}(\omega), \tag{2.3}
\]

These include the broadenings of the levels of the centers.
\begin{align}
\Gamma^*(q) &= \frac{1}{\pi} \int \frac{d\omega}{\frac{d\omega}{d\omega}} \int d\Delta \langle \omega(q) | \Delta \rangle (\omega(q) + 1) \\
&\times \left( 4 \Delta^*(\omega(q)) \left( \frac{d\omega}{d\omega} \right) + \frac{1}{\Delta^*(\omega(q))} \right), \\
(2.4) \\
\Gamma^*(q) &= \frac{1}{\pi} \int \frac{d\omega}{\frac{d\omega}{d\omega}} \int d\Delta \langle \omega(q) | \Delta \rangle (\omega(q) + 1) \\
&\times \left( 4 \Delta^*(\omega(q)) \left( \frac{d\omega}{d\omega} \right) + \frac{1}{\Delta^*(\omega(q))} \right), \\
(2.5) \\
\end{align}

Here \( \tau^2 \) is the lifetime of level 2 relative to the transition to level 1 in spontaneous emission of a phonon without spin flip. \( \tau^2 \), the time of the transitions \( 2^{-1} \), analogously, \( \tau^2 \) is the time of the \( 2^{-1} \) transitions with spin flip (see Fig. 1). The total lifetime \( \tau \) of the level 2 relative to spontaneous emission of the phonon is determined by the relation \( \tau^2 = \tau^1 + \tau^2 \). The times \( \tau_1 \) and \( \tau_2 \) have the same meaning as \( \tau \).

Next, the arrival terms in (2.3) are given by

\begin{align}
B^*(q) &= \frac{1}{\pi} \int \frac{d\omega}{\frac{d\omega}{d\omega}} \int d\Delta \langle \omega(q) | \Delta \rangle (\omega(q) + 1) \\
&\times \left( \frac{1}{4} \Delta^*(\omega(q)) \left( \frac{d\omega}{d\omega} \right) + \frac{1}{\Delta^*(\omega(q))} \right), \\
(2.6) \\
B^*(q) &= \frac{1}{\pi} \int \frac{d\omega}{\frac{d\omega}{d\omega}} \int d\Delta \langle \omega(q) | \Delta \rangle (\omega(q) + 1) \\
&\times \left( \frac{1}{4} \Delta^*(\omega(q)) \left( \frac{d\omega}{d\omega} \right) + \frac{1}{\Delta^*(\omega(q))} \right), \\
(2.7) \\
\end{align}

The terms \( g \) in (2.3) describe the level population due to the optical pumping. The equations for the centers do not indicate explicitly the parametric variables \( n_1, n_2, \) and \( \tau_1, \tau_2 \) that are contained in them and on which \( \gamma^* \) and \( \gamma^* \) depend. The variables \( s \) and \( E \) parametrize as parameters because the phonon-mediated transitions take place within one center. The pumps \( g \) are assumed to be the same for all types of centers and for both components of the doublet. The variables \( \tau \) and \( \tau \) enter in the right-hand side as parameters for another reason: assuming the inhomogeneity and the nonstationarity to be small, we calculated the interaction of the centers with the phonons in the same manner as in a homogeneous and stationary system.

The phonon balance equation is

\begin{equation}
\Delta \langle \omega(q) | \Delta \rangle = \gamma^*(q) - \gamma^*(q) + 2 \delta(q, q), \\
(2.8) \\
\end{equation}

It includes the phonon width due to the interaction with the centers:

\begin{align}
\gamma^*(q) &= \frac{N}{\tilde{E} \tau^2} \int d\Delta \Delta^*(\omega(q)) \left( \omega(q) + 1 \right) \\
&\times \left( 4 \Delta^*(\omega(q)) \left( \frac{d\omega}{d\omega} \right) + \frac{1}{\Delta^*(\omega(q))} \right), \\
(2.9) \\
\end{align}

The data in the last formula stand for terms obtained from those written out by replacing \( + \) by \( - \) and vice versa. The symbols "\( \Delta \)" denotes averaging over the centers of all types, i.e., over \( \nu \) and \( E \); the total concentration of the centers is \( N \). The arrival term due to the interaction of the phonons with the centers is of the form

\begin{align}
B(q) &= \frac{N}{\tilde{E} \tau^2} \int d\Delta \Delta^*(\omega(q)) \left( \omega(q) + 1 \right) \\
&\times \left( 4 \Delta^*(\omega(q)) \left( \frac{d\omega}{d\omega} \right) + \frac{1}{\Delta^*(\omega(q))} \right), \\
(2.10) \\
\end{align}

It is seen from the last two formulas that \( \gamma^* \) and \( B \) are in fact independent of \( q \). The physical reason for this is the random disposition of the centers. The term \( \Delta \omega(q) \) is responsible for the phonon-phonon interactions.

We have written out above only the broadenings \( \gamma^* \) and \( \gamma^* \), the corresponding level shifts \( \Delta \omega \) and \( \Delta \omega \) can be easily obtained from (2.4), (2.5), and (2.9) with the aid of the dispersion relations.

We discuss now the assumptions made in the derivation of the equations for the centers and the phonons. The assumption that the excitations of various centers are not correlated and that the excitation of each center is not coherent can be justified, of course, only for a definite form of optical pumping. Optical pumping in ruby is realized in nonradiative transitions to the levels 1 and 2 from the broad absorption band which does introduce some degree of coherence into the system, this coherence is lost in the case of a multiphonon nonradiative transition. (The energy of the \( (F_2, S) \) transition in ruby is 3500 cm\(^{-1}\).)

The same circumstance justifies the assumption that \( g \) is the same for both components of the doublet.

The correlations that are established in the system independently of the degree of correlation of the excitation are determined by the "width of the band of occupied states," i.e., in our case by the total width \( \Delta \omega \) of the \( 2^{-1} \) transition, which consists of the inhomogeneous with \( \Delta \omega \), and the "homogeneous broadening" \( \tau^2 \).

The assumption that the excitations of various centers are not correlated and that the excitation of each center is not coherent can be justified, of course, only for a definite form of optical pumping. Optical pumping in ruby is realized in nonradiative transitions to the levels 1 and 2 from the broad absorption band which does introduce some degree of coherence into the system, this coherence is lost in the case of a multiphonon nonradiative transition. (The energy of the \( (F_2, S) \) transition in ruby is 3500 cm\(^{-1}\).)

The same circumstance justifies the assumption that \( g \) is the same for both components of the doublet.

The correlations that are established in the system independently of the degree of correlation of the excitation are determined by the "width of the band of occupied states," i.e., in our case by the total width \( \Delta \omega \) of the \( 2^{-1} \) transition, which consists of the inhomogeneous with \( \Delta \omega \), and the "homogeneous broadening" \( \tau^2 \).

The assumption that the excitations of various centers are not correlated and that the excitation of each center is not coherent can be justified, of course, only for a definite form of optical pumping. Optical pumping in ruby is realized in nonradiative transitions to the levels 1 and 2 from the broad absorption band which does introduce some degree of coherence into the system, this coherence is lost in the case of a multiphonon nonradiative transition. (The energy of the \( (F_2, S) \) transition in ruby is 3500 cm\(^{-1}\).)

The same circumstance justifies the assumption that \( g \) is the same for both components of the doublet.

The correlations that are established in the system independently of the degree of correlation of the excitation are determined by the "width of the band of occupied states," i.e., in our case by the total width \( \Delta \omega \) of the \( 2^{-1} \) transition, which consists of the inhomogeneous with \( \Delta \omega \), and the "homogeneous broadening" \( \tau^2 \).

The assumption that the excitations of various centers are not correlated and that the excitation of each center is not coherent can be justified, of course, only for a definite form of optical pumping. Optical pumping in ruby is realized in nonradiative transitions to the levels 1 and 2 from the broad absorption band which does introduce some degree of coherence into the system, this coherence is lost in the case of a multiphonon nonradiative transition. (The energy of the \( (F_2, S) \) transition in ruby is 3500 cm\(^{-1}\).)
simpler.

At \( n = 1 \) it follows directly from (2.5) that \( \Gamma_2 = \Gamma_2^\prime + \Gamma_2^\prime \) and \( \Delta \varepsilon = 0 \). The radiative broadening of \( \Gamma_2^\prime \) can be neglected, since \( \tau_s \approx \tau_s = 4 \times 10^{-8} \) sec. Therefore, reckoning the energy from \( E_s = 0 \), we have

\[
\Delta \varepsilon^\prime (v, H, E) = (\frac{1}{A} - \frac{1}{A}) = A^\prime \nu^\prime \Delta \varepsilon^\prime (v, H, E).
\]

(3.1)

where

\[
\Delta \varepsilon^\prime (v, H, E) = \Delta \varepsilon^\prime (v, H, E) = \Delta \varepsilon^\prime (v, H, E).
\]

(3.2)

It is seen from (2.4) that \( \Gamma_1 \) consists of two small terms: one \( \Gamma_1^\prime \) and the other proportional to \( \nu \). We can therefore attempt to seek a solution in which \( \Gamma_1^\prime = 0 \) and \( \Delta \varepsilon = 0 \), i.e.,

\[
\Delta \varepsilon^\prime (v, H, E) = \Delta \varepsilon^\prime (v, H, E).
\]

(3.3)

In addition, we shall assume that \( \eta^\prime = \eta \).

Substituting (3.3) in (2.7) and (3.9) we get from (2.3), the equation

\[
\frac{\partial \Delta \varepsilon^\prime (v, H, E)}{\partial t} = \frac{\Delta \varepsilon^\prime (v, H, E)}{\tau_{\varepsilon}}.
\]

(3.4)

which, of course, follows under the assumptions made also from the equations.

We simplify first the expression for \( v^\prime (w) \). We introduce for this purpose the form factor of the transition between unsplit doublets

\[
v^\prime (w) = \alpha \Phi (v) \theta (v) (v^\prime - \omega^\prime - \omega),
\]

(3.5)

where \( \omega \) is defined by the condition \( \omega (w) = 1 \). Then the \( H \)-dependent form factors of the transitions between individual components of the split doublets are

\[
v^\prime (w) = \omega (w) \Phi (v) \theta (v).
\]

(3.6)

Substituting (3.1) and (3.3) in (2.9) we get

\[
\tau_{\varepsilon} = \frac{1}{\tau_{\varepsilon}^\prime} \Phi (v) \theta (v),
\]

(3.7)

where

\[
\frac{1}{\tau_{\varepsilon}^\prime} = \frac{1}{\tau_{\varepsilon}} - \frac{1}{\tau_{\varepsilon}^\prime}, \quad \tau_{\varepsilon} = 2 \hbar \hbar.
\]

(3.8)

and

\[
\Phi (v) = \frac{1}{2} \left[ (\nu^\prime - \nu^\prime - \nu^\prime) + (\nu^\prime - \nu^\prime + \nu^\prime) \right] + \left[ (\nu^\prime - \nu^\prime - \nu^\prime) + (\nu^\prime - \nu^\prime - \nu^\prime) \right].
\]

(3.9)

The meaning of the time \( \tau_{\varepsilon}^\prime \) is clearest at \( H = 0 \), when

\[
\Phi (v) = \Phi (v).
\]

(3.10)

where \( \lambda_s \) is the wavelength of the resonant phonon. It suffices now to note that \( \lambda_s \) is the concentration of the metastable centers, the parentheses contain the fraction of the centers that are resonant for the given phonon.
for $s(w, q)$, namely

$$\left( \frac{d^2}{dr^2} + 2 \frac{d}{dr} \right) \varphi(r) - \Lambda \varphi(r) \gamma^* \varphi(r)$$

$$+ \beta^2 \varphi(r) + \frac{\gamma^*}{\beta^2} \Lambda \varphi(r) \varphi(r).$$

(3.20)

The term responsible for the phonon anharmonicity is

$$F(w, q) = \varphi(r) \gamma^* \varphi(r).$$

(3.21)

The terms responsible for the radiation of the phonons are $\gamma^* s$ and $s^2$, where the corresponding arrival term is

$$F(w, q) \varphi(r) \gamma^* \varphi(r) + \varphi(r) \gamma^* \varphi(r) \varphi(r).$$

(3.22)

The integral kernel in this equation is expressed in the form of a mean value over the magnetic fields:

$$R(w, q) = R(w, q) = \frac{1}{2} \left( \frac{1}{2} + \frac{1}{2} \varphi(r) \gamma^* \varphi(r) + \varphi(r) \gamma^* \varphi(r) \varphi(r) \right).$$

(3.23)

Using (3.16) to express $F(w)$ and substituting in (3.22), we obtain ultimately

$$F(w, q) \varphi(r) \gamma^* \varphi(r) + \varphi(r) \gamma^* \varphi(r) \varphi(r).$$

(3.24)

The non-integral in the frequencies in (3.24) describes radiation processes that do not alter the spin state of the metastable center on the level 1 (radiation without spin flip, see Fig. 2), and the integral term stands for processes in which the spin state of the center on the level 1 changes after the radiation (radiation with spin flip). In the first process are coupled only the components of the spectral density $s(w, q)$ with a single frequency $\omega$, while in the second are coupled components with frequencies that differ by the splitting of the lower level $\Delta \omega$. It is obvious that the splitting of the upper level does not lead to such an effect. An indication that the frequency is changed by radiation with spin flip is contained in Ref. 6.

Equation (3.4) can be rewritten in the form

$$\int \frac{d^2 \omega}{d \omega^2} \varphi(r, t) = 0.$$  

(3.25)

It's solution yields the distribution of the concentration of the metastable atoms $N^*(r, t)$. The width $\gamma^*(w)$ then becomes, according to (3.8), a known function of $r, t$, and $\omega$; from the dispersion relations we can reconstruct $\Delta \omega(r, t)$ and obtain $\Delta \omega(r, q, t)$ from (2.2). It remains now to solve Eq. (3.20) for the function $s(w, q, r, t)$ with an arrival term in the form (3.24). Calculating next $s(w)$, we can find from (3.16) the function $F(w, q, t)$. Knowledge of $F$ makes it possible to calculate from (3.19) the spatial distribution and the time dependence of the $R_t$-luminescence, which is proportional to $N^*(r, t)$.

It is necessary to add to (3.20) the conditions imposed on $s(w, q)$ on the crystal boundary; these conditions are determined by the character of the phonon reflection from the helium-crystal interface. The excitation of the system by the thermal momentum also enters via the boundary conditions: besides the reflection conditions, an additional flux $S_P(w, q)$ is specified on the crystal--emitter boundary for $\gamma^*$ directed in the interior of the crystal.

In conclusion, we discuss the criterion for the validity of the approximations used to simplify the equations. The widths of all the functions in terms of $w$ and $\omega$ are determined by the quantities $\gamma^*$ and $\beta^2$. Therefore the approximation $\Gamma_t \propto w_0$ means in fact that $\Gamma_t \propto \omega_0^2$. On the other hand it is seen from (2.4) that $\Gamma_t \propto \omega_0^2 + \omega$. Since $\omega_0 \gg \omega$, the condition on $\Gamma_t$ reduces at $n \ll 1$ to the inequality $\gamma^* \ll \omega^2$, or, equivalently, $n \ll \alpha$, where $\alpha = \pi^2/\gamma^* \omega_0$. This parameter has a simple meaning: it is the ratio of the number of electronic degrees of freedom to the number of phonon degrees of freedom in the band $\omega_0$; in the theory of spin-lattice relaxation it is sometimes called the narrowness factor of the phonon bottleneck. Thus, the condition for the applicability of the equations of the present section is

$$n < 1, \quad \alpha < \gamma^* \omega_0.$$  

(4.1)

By way of example, we mention that in ruby $p_0 = 1.3 \times 10^5$ sec-cm$^{-1}$ (for the three phonon branches), so that a typical value is $p_0 \omega_0 = 10^{12}$ cm$^{-1}$. Typical values of $N_0$ range from $10^4$ to $10^5$ cm$^{-2}$.

4. SPECTRAL DIFFUSION

If there is no external magnetic field, then the splitting $2\Delta \omega$ is connected only with local magnetic fields. The splitting can be estimated in this case from the width of the EPR line on the metastable level 1. In ruby at $N = 2 \times 10^4$ cm$^{-3}$ (0.05% of spin$^2$ by weight) we have $2\Delta \omega = 2 \times 10^4$ cm$^{-1}$ according to Ref. 26. Since $2\Delta \omega \ll \Delta \omega$, the change of the frequency in reradiation with spin flip can be visualized as spectral diffusion. Expanding, as usual, in terms of $\delta_0$ and $\delta_1$, we can easily transform the integral term of (3.24) into a differential term:

$$\frac{1}{\gamma^*} \varphi(r, t) = \frac{g_0}{\gamma^*} \varphi(r, t).$$

(4.1)

We have introduced here the spectral-diffusion coefficient

$$D_0(\omega) = \frac{g_0}{\gamma^*} \varphi(r, t).$$

(4.2)

where

$$\varphi(r, t) = \frac{1}{\gamma^*} \varphi(r, t).$$

(4.3)

The spectral diffusion is significant at times $t$ such that

$$\int \varphi(r, t) = \frac{1}{\gamma^*} \varphi(r, t).$$

(4.4)

The value of $\chi$ in ruby, as seen from the data at the end of Sec. 2, lies in the interval from 0.1 to 1. A typical time of the long-range $R_t$-luminescence decay, observed in the experiment, is $\tau_{R_t} = 1$ msec. Therefore the spectral diffusion is significant at $N_0 \geq 10^{12}$ cm$^{-2}$. Experiments on the initial decay of $R_t$ luminescence yielded $\tau_{R_t} = 10$ msec; in this case the spectral diffusion is apparently insignificant.

Spectral diffusion should be distinguished from redistribution over the frequencies in the Holstein-Biberman equations, although qualitatively it can sometimes
lead to analogous effects. First, spectral diffusion calls for splitting of the lower level; second, it is characterized by a definite rate and is not instantaneous as in the Holstein-Biberman equations.

Turning on an external magnetic field $H_0$ enhances the spectral diffusion. If the field $H_0$ is weak, so that the $q$-level is adiabatic, then this field may be taken into account by changing $\delta^2$ in the diffusion coefficient. On the other hand if the field is strong, so $\delta^2(q,t)$ is small compared with $\delta_0$, then the field may be neglected, the diffusion coefficient remaining constant.

The essential difference between our equations and the Holstein-Biberman equations is the presence of a resonant component of the spectral density, $s(w)$, even for $w$ close to $\omega_0$. For this purpose it is necessary to be able to make the replacement $s(w,q) \rightarrow F(w)$. This procedure is obviously possible only when the density at a given $q$ is distributed over $q$ in accord with $\delta^2(q,t)$, i.e., the probability of the reradiation depends not on $q$ but on $\omega$, therefore after the reradiation this probability does not change.

It is instructive also to understand when Eq. (5.1) reduces to the ordinary kinetic equation for $\rho_\omega$ in other words, when we can confine ourselves to consideration of $s(w,q)$ on the mass shell $\omega = \omega_0$. It is seen from (5.1) that for this purpose it is necessary to be able to make the replacement $s(w,q) \rightarrow \delta^2(w-q)$. Only then can we seek a solution in the form $s(w,q) = \delta^2(w-q)$ and, cancelling out $\delta^2(w-q)$, we obtain an equation for $\rho_\omega$.

This procedure is obviously possible only when the width of the function of $\delta^2(w,q)$ in terms of $w$ is less than the width of the function $F(w)$, i.e., when $\tau^* \ll \delta_0$.

6. SPATIAL DIFFUSION

It is known that the Biberman-Holstein equations do not go over into the diffusion equation for the total phonon concentration $\rho_\omega$, $\phi$ is the reason that the reradiation process increases the number of phonons with larger $w$ as free paths relative to resonant absorption. In our Eq. (5.1), as already indicated, the mean free path relative to absorption by the centers is not charged in the course of reradiation of the spectral density. Therefore in the case when the nonstationarity and spatial inhomogeneity are small not only compared with $\delta_0$ but also compared with $\tau^* \ll \delta_0$, $\phi$ is a relaxation time for the local magnetic field into account by changing $\delta^2$ in the diffusion coefficient. It is seen from (3.4) that the role of the magnetic field does not reduce in this case to a "dragging under" the phonon packets, as is sometimes tacitly assumed—the redistribution among them must also be taken into account.

5. COMPARISON WITH THE BIBERMAN-HOLSTEIN EQUATIONS

If there is no external magnetic field, and the local fields can be neglected, then the equation for $s(w,q)$ takes the following form:

$$\frac{d}{dt} s(w,q) = -\gamma(w)s(w,q) + \frac{\delta^2}{\rho_\omega} F(w) + \frac{\delta^2}{\rho_\omega} \delta^2(w,q) s(w,q).$$

(5.1)

Let us compare this equation with (1.14) and Eq. (3.16) for $F(w)$ with (1.15). It can be stated that the crossing terms of the system (3.16), (5.1) describe reradiation of spectral density $s(w,q)$ with conservation of $w$ and with variation of $q$ (as should be the case with scattering by an immobile center); after the reradiation, the spectral density at a given $w$ is distributed over $q$ in accord with $\delta^2(q,t)$.

It is important, however, that the probability of the reradiation depends not on $q$ but on $\omega$, therefore after the reradiation this probability does not change. We integrate (5.1) with respect to $q$ and add to Eq. (3.16) multiplied by $\varphi(w)$. We then obtain the law of conservation of the spectral density in the phonons + centers system:

$$\frac{d}{dt} s(w) = -\gamma(w)s(w) + \frac{\delta^2}{\rho_\omega} \frac{\delta^2(w,q)}{\delta^2(w-q)} s(w) - \frac{\delta^2}{\rho_\omega} \frac{\delta^2(w,q)}{\delta^2(w-q)} \gamma(w)s(w).$$

(5.2)

We substitute here in place of $F(w)$ its expression in terms of $s(w)$. It is possible to replace $s$ under the integral sign, and express $s$ in terms of $s$ with $s^* \sim n_2$. Then we obtain the diffusion equation of interest to us:

$$\frac{d}{dt} s(w) = \frac{\delta^2}{\rho_\omega} \frac{\delta^2(w,q)}{\delta^2(w-q)} - \frac{\delta^2}{\rho_\omega} \frac{\delta^2(w,q)}{\delta^2(w-q)} \gamma(w) n_2,$$

(5.3)

where we have introduced the coefficient of spatial diffusion of the spectral density $D_\omega = \frac{\delta^2}{\rho_\omega} \frac{\delta^2(w,q)}{\delta^2(w-q)}$. The presence of an additional term proportional to $\varphi(w)$ under the sign of the time derivative is connected with the fact that part of the energy in the system has been accumulated in the form of excitation of the centers. This part, however, does not contribute to the energy transfer; there is therefore no such term in the flux.

The author is grateful to R. Katilyus, V. Perel', and G. Pikus for a discussion of individual aspects of this paper.
Screening of charges and Friedel oscillations of the electron density in metals having differently shaped Fermi surfaces

A. M. Gabovich, L. G. Il'chenko, E. A. Pashitskii, and Yu. A. Romanov

Physics Institute, Ukrainian Academy of Sciences

15 March 1976

Zh. Eksp. Teor. Fiz. 73, 249–264 (July 1978)

Analytic and numerical integration methods are used to obtain the spatial distribution of the screened Coulomb potential of point charges in the interior and on the surface of metals having different Fermi-surface shapes. It is shown that in isotropic metals with quasi-two-dimensional or quasi-one-dimensional conduction electron distribution the electron density decreases along normals to a cylindrical or plane Fermi surface, like $r^{-2n}$, and along the surface of an isotropic metal with a spherical Fermi surface, the decrease is power-law like $r^{-k_{F}}$. In the Thomas-Fermi approximation, the screened charge potential in a homogeneous metal takes the form $r^{-1/3}$ regardless of the shape of the Fermi surface, and along the surface of a semi-infinite metal it decreases in power-law fashion like $r^{2k_{F}}$. An expression is obtained for the potential energy of the charges near the surface of a metal. This expression, together with the image forces, describes the Friedel oscillations and the dipole-dipole interactions. The results explain, in particular, the experimental data on the ordering of adsorbed Sr and La films on the (112) face of W and Mo single crystals.

PACS numbers: 74.45.Jp, 71.25.–3, 71.90.+q

1. INTRODUCTION

It is known that the steplike character of the Fermi distribution of the conduction electrons in metals leads to the appearance of so-called Friedel oscillations of the screened Coulomb potential, which by virtue of the spherical Fermi surface over large distances from the charge, $r^{-1/3}$ ($k_{F}$ is the Fermi momentum, $r=1$) decrease like $r^{-1/3}$ ($k_{F}$ is the Fermi momentum, $r=1$) decrease like $r^{-1/3}$. For the same reason, the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction between the magnetic moments of nuclei or paramagnetic impurities in an isotropic metal behaves asymptotically like $r^{-1/3}$.

The law governing the decrease of the Friedel oscillations depends, however, on the "dimensionality of the metal" $d$, i.e., on whether we are dealing with a bulky metal, with a film, or with a thin film. Therefore even in the case of a three-dimensional isotropic electron spectrum, as shown by Adamov, the perturbation $\delta$ of the electron density decreases like $r^{-1/3}\cos 2k_{F}r$ at $d=2$ and like $r^{-1/3}\sin 2k_{F}r$ at $d=1$. If at the same time the electron spectrum is two-dimensional at $d=3$ and one-dimensional at $d=1$, then the screened Coulomb potential decreases respectively like $r^{-1/3}\sin 2k_{F}r$ (Ref. 5) and $r^{-1/3}\cos 2k_{F}r$.  

Translated by J. G. Adamsko