dividual particles. As expected, no echo can be detected for a very small number of particles. In the continuum limit the echo shape given by Eq. (3) is the same as the analogous spin echo.

The model outlined here to explain the long T_1's is based entirely on the physical rotation of the individual particles as a consequence of the torque exerted on an oscillating dipole by an applied rf field. It is important to note that the sample polarization which gives rise to the echo is the total pattern of individual particle rotations. The pattern can be probed many times to create an echo, as long as the field of the probing pulse does not exceed the fields used to create the pattern. In conclusion we remark that the only particle-particle interactions which have been included in the model are those giving rise to the angular damping constant Γ of Eq. (2). Interparticle coupling may be important in determining T_2[7] and T_1.

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Phonon-Assisted Energy Transport in Inhomogeneously Broadened Systems*

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Recent experiments have demonstrated Anderson localization in inhomogeneously broadened paramagnetic spin systems. We examine two-phonon processes which can frequency shift the individual spin packets, and thereby allow energy transfer to take place. We make specific application to ruby, and show that the dominant phonon-induced energy-transfer rate is directly proportional to the (spin-nonflip) $\overline{E} \rightarrow 2\overline{A}$ rate [varying as $\exp(-42/T)$], and inversely proportional to the square of the energy mismatch of the participating spin packets.

Recently, Hsu and Powell[1] and, independently, Koo, Walker, and Geschwind[2] have reported evidence of Anderson localization[3] in inhomogeneously broadened optical transitions in paramagnetic crystals (the former in $CaWO_4$:Sm; the latter in Al_2O_3:Cr, ruby). Also, Flach et al.[4] have reported evidence of phonon-assisted energy transfer within an inhomogeneously broadened optical line.

The purpose of this Letter is to calculate the two-phonon-assisted contribution to energy transfer in inhomogeneously broadened spin systems. Because of the wealth of information available for ruby, we shall make direct application of our results to that system, though our approach is considerably more general. Our findings are that, for the case of ruby, (1) there is no significant

one-phonon-assisted energy transfer; (2) the two-phonon-assisted resonance process involving the $\bar{E}$ and the $2\bar{A}$ levels [proportional to $\exp(-42/T)$] dominates over the two-phonon-assisted nonresonance process involving the same levels (proportional to T^7) and the two-phonon-assisted process within the $\bar{E}$ level (proportional to T^3). In other materials, the situation may be reversed, depending on the relevant phonon matrix elements and the positions of the excited energy levels.

These processes will always allow for energy transfer. Their rates may be so small, however, that Anderson localization will be observed. Our purpose in calculating them, apart from their intrinsic interest, is to determine the contribution of phonon-assisted energy transfer to the breakdown of Anderson localization, and to establish the temperature above which this breakdown should occur.

Energy transfer in ruby is thought to occur via the exchange interaction between Cr ions,[5] and is pictured in Fig. 1(a). The short-range character of the exchange integral allows for Anderson localization, and an explicit calculation of the critical concentration for energy transport was performed by Lyo.[6] Koo, Walker, and Geschwind[2] observed "mobility edges" at 1.6 K at concentrations in rough agreement with Lyo's prediction. The magnitude of the inhomogeneous broadening for ruby is of the order of 1 cm^{-1} at the concentrations utilized in Ref. 2.

The question of the effect of phonon-spin interactions on the transport properties of paramagnetic systems can be formulated either in terms of a phenomenological linewidth approach, or by a direct calculation of energy transfer, treating the phonons on an equal footing with the exchange coupling. We choose the latter.

For inhomogeneous lines as narrow as that of ruby, one-phonon-assisted energy-transfer processes are negligible. The energy mismatch of 1 cm^{-1} must be equal to the phonon energy,[7] and phase space and coupling considerations combine to make the transfer rate unimportant. (This may not be the case for, say, rare-earth impurities in glasses where the inhomogeneous widths may be of the order of 100 cm^{-1}.[8]) It is then necessary to examine higher-order phonon processes. It turns out that the two-phonon-assisted transfer process dominates. For the case of ruby, where the $2\bar{A}$ lies within 42 K of the $\bar{E}$,
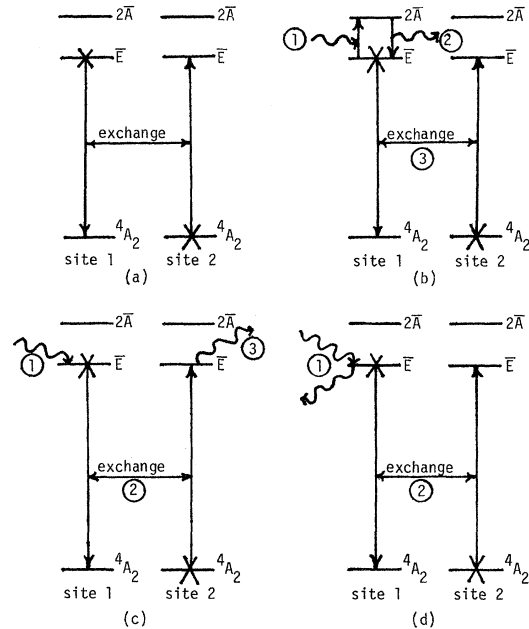

FIG. 1. (a) Bare exchange-induced energy transfer in ruby, leading to Anderson localization for sufficiently dilute Cr concentrations. The crosses denote initial occupancies, the arrows the sense of transition. (b) Two-phonon-assisted resonant and nonresonant energy transfer. The circled numbers indicate the order of transitions. (1) and (2) are phonon transitions, (3) is exchange. There are two other processes of the same type (different order of the phonon and exchange transitions), and three more corresponding to inversion of the phonon lines. (c) Two-phonon nonresonant energy transfer, diagonal in the electron coordinates. The one-phonon-spin Hamiltonian is taken twice, and the circled numbers indicate the order of transitions. There are a total of sixteen processes of this kind. (d) Two-phonon nonresonant energy transfer, diagonal in the electron coordinates. The two-phonon-spin Hamiltonian is taken once, and the numbers indicate the order of transitions. There are a total of four processes of this kind.

three types of processes need to be considered. These are pictured in Figs. 1(b), 1(c), and 1(d). We consider each in turn.

Resonance-phonon-assisted energy transfer.—We denote the exchange couplings which transfer excitations from one spin site in the R_1 or R_2 state to another spin site by J_1 or J_2, respectively. The energy mismatch of the spin packets is denoted by ΔE_{12}, and the phonon-lifetime-induced width of the $2\bar{A}$ levels by $\Gamma(2\bar{A})$. We find a transfer rate for the resonance-phonon-assisted transfer pictured in Fig. 1(b) of magnitude

$$W_{\mathrm{res}} = \left[J_1{}^2 + \frac{(\Delta E_{12})^2 J_2{}^2}{(\Delta E_{12})^2 + \Gamma(2\bar{A})^2}\right] \frac{[1 + \exp(-\Delta E_{12}/k_B T)]}{(\Delta E_{12})^2} W_{\bar{E} \to 2\bar{A}}, \tag{1}$$

where $W_{\overline{E} \to 2\overline{A}}$ is the phonon-induced transition rate (without spin flip) from the $\overline{E}$ to the $2\overline{A}$. According to Blume et al.[9] this rate equals $3 \times 10^9 \exp(-42/T) \sec^{-1}$. The criterion for Anderson localization is that $J_1 < |\Delta E_{12}|$, so that the energy-transfer rate induced by the resonant-two-phonon process will be less than $W_{\overline{E} \to 2\overline{A}}$.

We should remark that, in using (1), we have taken ΔE_{12} equal to an energy disorder parameter, $\langle \Delta E_{12}^2 \rangle^{1/2} \approx 1 \text{ cm}^{-1}$. This implies the assumption that the occurrence of unusually small ΔE_{12} ($|\Delta E_{12}| \lesssim J_1$) for particular pairs will not play an important role in the overall energy transfer. A definitive justification of this assumption requires a percolation treatment, which we reserve for a future paper.

Nonresonant-phonon-assisted energy transfer involving the $2\overline{A}$ level.—The activation character of W_{res} precludes the observation of this process at low temperatures. We therefore investigate the nonresonant part of the two-phonon-assisted energy-transfer process involving the intermediary of the $2\overline{A}$ level [pictured in Fig. 1(b)]. Making the usual phonon averages over polarizations and propagation directions, we find

$$W_{\text{nonres}}^{\text{I}} = [(2/\pi\hbar)(2J_1)^2/(\Delta E_{12})^2][(k_B T)^7 6 ! \Gamma^2(2\overline{A})/\delta^8]\langle h_{\text{I}} \rangle, \tag{2}$$

where δ is the $\overline{E}$ to $2\overline{A}$ energy separation of 42 K, and $\langle h_{\text{I}} \rangle$ is an angular average over thermal phonons of an interference factor

$$h_{\text{I}}(\vec{q},\vec{q}') = |\exp[i(\vec{q} - \vec{q}') \cdot \vec{r}_0] - 1|^2.$$

Here, $\vec{r}_0$ is the position vector connecting the two participating spin sites, and $\vec{q}$, $\vec{q}'$ are the wave vectors of the incoming and outgoing phonons, respectively. In the subsequent evaluations of the rate (2), we shall take $\langle h_{\text{I}} \rangle \simeq 1$.

A comparison of (1) and (2) leads to

$$W_{\text{nonres}}^{\text{I}}/W_{\text{res}} = 5.6 \times 10^{-1} e^x x^{-7} \tag{3}$$

where $x = \delta/k_B T$. The ratio (3) has its minimum value for $x = 7$, but is still of order 10^{-3} at 4.2 K. Hence, W_{res} would appear to be the more important process, at least for ruby.

Finally, two other types of two-phonon processes, pictured in Figs. 1(c) and 1(d), must be considered. One involves the one-phonon Hamiltonian taken to second order [Fig. 1(c)], the other the two-phonon Hamiltonian taken to first order [Fig. 1(d)]. Both act diagonally in the spin coordinates.

Nonresonant-phonon-assisted energy transfer within the $\overline{E}$ level: One phonon.—Denoting the one-phonon–spin Hamiltonian matrix elements by

$$\langle 2\overline{A}, n_{\vec{q}'} + 1 | H | 2\overline{A}, n_{\vec{q}'} \rangle = f_0 \langle n_{\vec{q}'} + 1 | \epsilon | n_{\vec{q}'} \rangle,$$
$$\langle \overline{E}, n_{\vec{q}} - 1 | H | \overline{E}, n_{\vec{q}} \rangle = f_1 \langle n_{\vec{q}} - 1 | \epsilon | n_{\vec{q}} \rangle, \tag{4}$$

where ϵ is the strain operator, the one-phonon second-order nonresonant phonon-assisted transfer rate [Fig. 1(c)] equals

$$W_{\text{nonres}}^{\text{II}} = (2\pi/\hbar) \sum_{\vec{q}, \vec{q}'} [J_1^2 (f_1 - f_0)^4/\hbar^2(\omega_{\vec{q}}\omega_{\vec{q}'})^2] |\langle n_{\vec{q}'} + 1 | \epsilon | n_{\vec{q}'} \rangle \langle n_{\vec{q}} - 1 | \epsilon | n_{\vec{q}} \rangle|^2 h_{\text{II}} \delta(\hbar\omega_{\vec{q}'} - \hbar\omega_{\vec{q}} - \Delta E_{12}), \tag{5}$$

where

$$h_{\text{II}} = |\exp(i\vec{q} \cdot \vec{r}_0) + \exp(-i\vec{q}' \cdot \vec{r}_0) - 1 - \exp[i(\vec{q} - \vec{q}') \cdot \vec{r}_0]|^2.$$

In (4), $\omega_{\vec{q}}$ is the phonon frequency associated with phonon wave vector $\vec{q}$, and h_{II} is an interference factor. It should be noted that $W_{\text{nonres}}^{\text{II}}$ is essentially independent of the energy mismatch, ΔE_{12}, whereas all the other transfer rates [e.g., (1)] evaluated in this Letter are inversely proportional to $(\Delta E_{12})^2$.

Nonresonant-phonon-assisted energy transfer within the $\overline{E}$ level: Two phonons.—In an obvious notation (g represents the strength of the two-phonon–spin coupling constant), the two-phonon first-order nonresonant-phonon-assisted transfer rate [Fig. 1(d)] equals

$$W_{\text{nonres}}^{\text{III}} = (2\pi/\hbar) \sum_{\vec{q}, \vec{q}'} (J_1/\Delta E_{12})^2 (g_1 - g_0)^2 |\langle n_{\vec{q}'} + 1, n_{\vec{q}} - 1 | \epsilon^2 | n_{\vec{q}'}, n_{\vec{q}} \rangle|^2 h_{\text{I}} \delta(\hbar\omega_{\vec{q}'} - \hbar\omega_{\vec{q}} - \Delta E_{12}). \tag{6}$$

Evaluation of (5) leads to a T^3 temperature dependence, while (6) yields a T^7 temperature dependence. Their ratio is

$$\frac{W_{nonres}{}^{II}}{W_{nonres}{}^{III}} = \frac{(f_1 - f_0)^4 (\Delta E_{12})^2}{(g_1 - g_0)^2 (k_B T)^4}. \tag{7}$$

If one makes the usual assumption[7] that $f \approx g$, ignores the cancellations in (5) and (6), and takes the values $f \simeq 10^3$ cm^{-1} and $\Delta E_{12} \simeq 1$ cm^{-1}, the ratio (7) equals $10^6/T^4$. This value is large for temperatures in the liquid-helium range. The two-phonon one-step process, $W_{nonres}{}^{III}$, is therefore inconsequential compared to the one-phonon, two-step process, $W_{nonres}{}^{II}$, for ruby in this temperature range.

Finally, evaluating (5) in the long-wavelength limit allows for a comparison of $W_{nonres}{}^{II}$ with $W_{nonres}{}^{I}$ given by (2). Defining the spin-phonon matrix element between the $\overline{E}$ and $2\overline{A}$ levels by $\langle 2\overline{A} | H | \overline{E} \rangle = A\epsilon$, where ϵ is the strain operator, one finds the ratio

$$\frac{W_{nonres}{}^{I}}{W_{nonres}{}^{II}} = \frac{|A|^4 (k_B T)^4}{(\delta \Delta E_{12})^2 (f_1 - f_0)^2}. \tag{8}$$

If one takes $A \simeq 10^3$ cm^{-1} (as in Ref. 9), and uses the above representative values for the other parameters in (8), the ratio $W_{nonres}{}^{I}/W_{nonres}{}^{II} = 10^{-3} T^4$. This shows the two processes are comparable at the upper end of the liquid-helium range. However, using (3), both are small compared to the resonant-phonon-assisted energy-transfer rate in ruby. The situation may be reversed in other materials, especially if no close-lying excited state is available through which either of the two processes W_{res} or $W_{nonres}{}^{I}$ can act.

It would be interesting to see if these ideas are confirmed by experiment. The experiments of Koo, Walker, and Geschwind[2] were performed at a single temperature (1.6 K) so that all of the rates we have considered would have been unobservable. Higher temperatures should exhibit

the behavior displayed in (2) for the single-ion–single-ion energy-transfer rate.

In summation, we have addressed ourselves to the question of how phonon activation can break down Anderson localization. We have calculated all of the two-phonon-assisted energy-transfer rates, and shown that the resonant process dominates energy transfer for ruby. The activation character of the temperature dependence insures that this process will be negligible at very low temperatures, but it could contribute sufficiently to be observable at the upper end of the liquid-helium range. In other materials, the lack of a close-lying excited level may make the resonant-phonon-assisted transfer rate of no consequence. In such cases $W_{nonres}{}^{II}$ will dominate, leading to a T^3 temperature dependence for energy transfer. Now that Anderson localization has been reported, it would be of great interest to see if the result of increasing the temperature results in energy transfer by virtue of the processes considered in this Letter.

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