SOVIET PHYSICS JETP VOLUME 15, NUMBER 3 SEPTEMBER, 1962

ON THE THEORY OF SPIN-LATTICE RELAXATION IN PARAMAGNETIC IONIC CRYSTALS

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Submitted to JETP editor July 6, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) 42, 783-786 (March, 1962)

It is shown that for the case when the limiting phonon energy is greater than the Stark splitting of the levels of the paramagnetic ion, the probability of two-phonon transitions (with one phonon emitted and the other absorbed) can be expressed in second-order perturbation theory in terms of the probability of single-phonon transitions to an intermediate level. The temperature dependence of the transition probabilities due to different relaxation processes is considered.

THE usual methods for studying relaxation phenomena in some salts of the iron group of elements, successfully applied by Van Vleck,[1] do not work in a number of cases. For example, a divergent integral is obtained when the probability of two-phonon transitions in crystals containing rare-earth ions is calculated by these methods.[2] The reason for this is the neglect of the finite width of the energy levels of the ion. It is therefore interesting to consider the relaxation processes from the point of view of the general theory of quantum transitions, including damping effects. According to this theory, the probability of a transition in unit time from the state O to the state n is given by the expression[3]

$$w_{nO} = \frac{2\pi}{\hbar} |U_{nO}(E_n)|^2 \delta(E_n - E_O). \tag{1}$$

The term $U_{nO}(E)$ fully determines the time behavior of the quantum system and obeys the equation

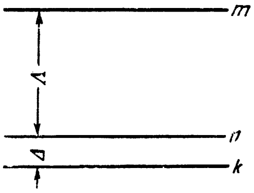
$$U_{nO}(E) = H_{nO} + \sum_{m\neq 0} H_{nm}\zeta(E - E_m)U_{mO}(E),$$
$$n \neq 0, \qquad U_{OO} = 0, \tag{2}$$

which is, in fact, the form of the time-dependent Schrödinger equation in E-space. Here H is the perturbing Hamiltonian producing the transition and the value of $\zeta(x)$ is determined by the relation

$$\zeta(x) = \mathrm{P}\frac{1}{x} - i\pi\delta(x), \tag{3}$$

where P is the symbol for the principal part.

Let us consider the following problem, often encountered in studying relaxation phenomena in solid paramagnets. Paramagnetic resonance can be observed between levels n and k (see the figure) of the ion. Level m participates as an intermediary in the transition processes n → k, with



$\Lambda = E_m - E_n$ much greater than $\Delta = E_n - E_k$. It is necessary to calculate the probability of a transition of the ion in unit time from level n to level k under the influence of spin-phonon interaction. We shall consider separately the different processes which lead to the transition n → k. Such a treatment is valid since one of the mechanisms for the transition usually predominates. We shall use indices λ and σ, indicating both the frequency and polarization of phonons to label states differing from the initial in the number of phonons.

If we now limit ourselves to considering states differing by one phonon from the initial, then the system (2) and Eq. (1) lead to the usual expression for the total probability of a one-phonon transition:

$$w_{kn}^{(1)} = \frac{2\pi}{\hbar}\langle |H_{k\Delta,n}|^2 \rho_\Delta\rangle. \tag{4}$$

The index Δ corresponds to phonons with energy Δ and the bracket indicates averaging over all such phonons.

Both the part H of the perturbing Hamiltonian, linear in the lattice vibrations, and the part H′, quadratic in these vibrations, can lead to transitions n → k, accompanied by two phonons. The following expression is obtained for the transition probability due to H′

$$w_{kn}^{(3)} = \frac{2\pi}{\hbar}\sum\left\langle\int |H_{k\lambda\sigma,n}|^2 \rho_\lambda\rho_\sigma d\lambda\right\rangle, \tag{5}$$

which consists of two parts, for the first the sum of the energies of the phonons λ and σ is equal to

Δ, and for the second their difference equals Δ.

Let us now consider the two-phonon transition $n \rightarrow k$ under the action of H in second-order perturbation theory. In the intermediate state the ion is then in the level m and the phonon λ is absorbed (or phonon σ is emitted). In this case the system of equations (2) is written in the form

$$U_{m\lambda,\,n} = H_{m\lambda,\,n} + \sum_{\sigma} H_{m\lambda,\,k\lambda\sigma} U_{k\lambda\sigma,\,n} \zeta(E - E_{k\lambda\sigma}), \qquad \text{(6a)}$$

$$U_{m\sigma,\,n} = H_{m\sigma,\,n} + \sum_{\lambda} H_{m\sigma,\,k\lambda\sigma} U_{k\lambda\sigma,\,n} \zeta(E - E_{k\lambda\sigma}), \qquad \text{(6b)}$$

$$U_{k\lambda\sigma,\,n} = H_{k\lambda\sigma,\,m\lambda} U_{m\lambda,\,n} \zeta(E - E_{m\lambda}) + H_{k\lambda\sigma,\,m\sigma} U_{m\sigma,\,n} \zeta(E - E_{m\sigma}). \qquad \text{(6c)}$$

In order to find the probability required, according to (1) one must know $U_{k\lambda\sigma,n}$ for $E = E_{k\lambda\sigma}$. If $\Lambda > k\Theta_D$, where Θ_D is the Debye temperature, then the system (6) and Eq. (1) lead to the usual expression for the transition probability via an intermediate state.

If, however, $\Lambda < k\Theta_D$, $E_{k\lambda\sigma} - E_{m\lambda} = E_k - E_m + \hbar\omega_\sigma$ can become zero for certain ω_σ, while the difference $E_{k\lambda\sigma} - E_{m\sigma}$ is negative for all λ, σ. The second term in (6c) can therefore be neglected and the simultaneous solution of (6a) and (6c) gives

$$U_{k\lambda\sigma,\,n} = H_{k\lambda\sigma,\,m\lambda} H_{m\lambda,\,n} / [E - E_{m\lambda} + \tfrac{1}{2} i\hbar\gamma(E)], \qquad \text{(7)}$$

where

$$\frac{\hbar}{2}\gamma(E) = i \sum_{\sigma} |H_{k\lambda\sigma,\,m\lambda}|^2 \zeta(E - E_{k\lambda\sigma}).$$

The real part of γ gives the total probability per unit time of a transition of the ion from level m to level k, while the imaginary part gives the shift in level m under the influence of this transition.[3] If we take into account that the ion can return to the initial level as a result of a two-phonon process, $\mathrm{Re}\,\gamma$ in (7) must be replaced by $\mathrm{Re}\,\gamma'$ — the total probability of a transition from level m to levels n and k. We will not take the shifts of levels into account, so that

$$\gamma(E) = \frac{2\pi}{\hbar} \sum_{\sigma} |H_{k\lambda\sigma,\,m\lambda}|^2 \delta(E - E_{k\lambda\sigma}). \qquad \text{(8)}$$

γ practically does not depend on E, so that γ can be considered a constant. Substituting (7) into (1), we obtain

$$w_{k\lambda\sigma,\,n} = \frac{2\pi}{\hbar} \frac{|H_{k\lambda\sigma,\,m\lambda}|^2 |H_{m\lambda,\,n}|^2}{(E_{k\lambda\sigma} - E_{m\lambda})^2 + \hbar^2\gamma'^2/4} \delta(E_{k\lambda\sigma} - E_n). \qquad \text{(9)}$$

For sufficiently small width of level m, i.e., if the value of γ is small, we can write the following approximate equality:

$$[(E_{k\lambda\sigma} - E_{m\lambda})^2 + \tfrac{1}{4}\hbar^2\gamma'^2]^{-1} \approx \frac{2\pi}{\hbar\gamma'} \delta(E_{k\lambda\sigma} - E_{m\lambda}). \qquad \text{(10)}$$

Equation (9) then takes the form

$$w_{k\lambda\sigma,\,n} = (4\pi^2/\hbar^2\gamma') |H_{k\lambda\sigma,\,m\lambda}|^2 |H_{m\lambda,\,n}|^2 \times \delta(E_{k\lambda\sigma} - E_n)\, \delta(E_{m\lambda} - E_n).$$

This expression must be summed over all λ, σ to obtain the total probability of a two-phonon transition. Taking (8) into account, we obtain the following interesting result:

$$w_{kn}^{(2)} = \frac{2\pi}{\hbar} \frac{\gamma}{\gamma'} \langle |H_{m\Lambda,\,n}|^2 \rho_\Lambda \rangle, \qquad \text{(11)}$$

where γ/γ' represents the ratio of the probability of the transition $m \rightarrow k$ to the total probability of transitions from the level m to the levels n, k. For the case $\Lambda < k\Theta_D$ the probability of the two-phonon transition $n \rightarrow k$ with the intermediate level m taking part is determined by the probability of single phonon transitions $n \rightarrow m$, $m \rightarrow k$. Finn, Orbach and Wolf[4] proposed that this sequence of single-phonon transitions should be considered as a new relaxation process. If the maximum of the δ-function (10) is considerably different from the maximum of the expression $|H_{k\lambda\sigma,\,m\lambda}|^2 \, |H_{m\lambda,\,n}|^2$, then the usual probability of two-phonon transitions is added to (11), with the integration over the phonon frequencies not including the neighbourhood of $\Lambda/\hbar$.

An analogous consideration of the transition $n \rightarrow k$ under the action of H with the emission of two phonons leads to the following expression for the probability of such a process:

$$w_{kn}^{(4)} = \frac{8\pi}{\hbar} \left\langle \int \left| \frac{H_{k\sigma,\,n} H_{m\lambda,\,n}}{\Lambda} \right|^2 \rho_\sigma \rho_\lambda \, d\lambda \right\rangle, \qquad \text{(12)}$$

with the sum of the energies of phonons λ and σ equal to Δ.

We shall consider briefly the temperature dependence of the probabilities of transitions for $\Lambda < k\Theta_D$, which is characteristic for many compounds of the rare earth elements. The temperature enters expressions (4), (5), (11), and (12) through the mean quantum number of the phonons:

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

The quantities Δ and Λ enter into these equations because of the density of the final states and the dependence of the matrix elements of the perturbation energy on the phonon frequency. Expressing the dependence on T and Δ in (4), we have

$$w_{kn}^{(1)} = A_{kn}\Delta^3 \exp(\Delta/kT)/[\exp(\Delta/kT) - 1]. \qquad \text{(13)}$$

For $\Delta \ll kT$ this leads to a linear dependence on temperature, while it ceases to depend on temperature for $\Delta \gg kT$, going over to the probability of the spontaneous emission of a single phonon of frequency $\Delta/\hbar$. If the lower doublet is a Kramers doublet, then Δ enters in (13) to the fifth power.

If we assume $\Lambda \gg kT$ and neglect the magnitude of Δ compared with Λ, we can express (11) in the form

$$w_{kn}^{(2)} = B_{kn}\Lambda^3 \exp(-\Lambda/kT). \qquad (14)$$

The functions A_{kn} and B_{kn} depend uniquely on the density of the substance and the velocity of sound in it. In spite of the rapid decrease in the value of $w_{kn}^{(2)}$ with temperature, the presence of the factor Λ^3 in (14), which is large compared with Δ^3 (or large compared with Δ^5/Λ^2 in the case of a Kramers doublet), can make $w^{(2)} > w^{(1)}$ down to temperatures around 2°K, as occurs in cerium magnesium nitrate ($\Lambda = 34°$ K, $\Delta = 0.2°$K).[4]

The probability (5) has two parts — the probability of emission of two phonons, the sum of whose energies equals Δ, and the probability of emission of one phonon and absorption of the other with energy less than the energy of the emitted phonon by Δ. The first part can be written in the form

$$w_{1kn}^{(3)} = C_{1kn}\int_0^{\Delta} \frac{\omega^3(\Delta-\omega)^3 \exp(\Delta/kT)}{[\exp(\omega/kT)-1]\,[\exp((\Delta-\omega)/kT)-1]}\, d\omega.$$

For $\Delta \ll kT$ this leads to a quadratic temperature dependence, and for $\Delta \gg kT$ this expression practically ceases to depend on temperature, going over to the probability of the spontaneous emission of two phonons, the sum of whose energies is Δ. The law of the temperature change of the probability (12) is the same.

The second part of (5) is of the form

$$w_{2kn}^{(3)} = C_{2kn}\int_0^{k\Theta_D} \frac{\omega^3(\omega+\Delta)^3 \exp((\omega+\Delta)/kT)}{[\exp(\omega/kT)-1]\,[\exp((\omega+\Delta)/kT)-1]}\, d\omega.$$

This part varies with temperature as T^7 for not very high temperatures ($T \ll \Theta_D$).

We thus see that the relative importance of different relaxation processes varies with the temperature. Since the coefficients in the expressions for the transition probabilities will be different for different substances (mainly because of the difference in the matrix elements in these coefficients), the law governing the increase in relaxation time with decreasing temperature can be completely different for them within the same temperature interval.

Having obtained this law from experiment, it is possible to judge the character of the relaxation process for a substance in a given temperature region.

In conclusion, I express my thanks to S. A. Al'tshuler for his valuable suggestions in the carrying out of this work.

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Translated by R. Berman
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