QUADRUPOLE SELECTION RULE IN IRON GROUP SPIN-PHONON INTERACTIONS*

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(Received July 29, 1959)

It is the purpose of this note to point out a fact which has not been explicitly stated in the literature and which has important experimental implications, namely, that spin-phonon transitions in non S-state iron-group paramagnets obey quadrupole selection rules. This means that for odd half-integer spin systems of $S > \frac{1}{2}$, the direct spin-phonon transition is approximately forbidden between any pair of spin states, $|1\rangle$, $|2\rangle$, of the form

$$|1\rangle = a|m_s\rangle + b|-m_s\rangle,$$
$$|2\rangle = c|m_s\rangle + d|-m_s\rangle,$$
$$\langle 1|2\rangle = 0. \tag{1}$$

Consider Cr^{+++} ($S = \frac{3}{2}$) in ruby as an example. The rule implies that in small magnetic fields, the spin-phonon interaction within either pair of Kramers doublets is very feeble. In larger fields (10^3 - 10^4 gauss) with $\vec{H}$ parallel to the ruby optic axis, the interaction is weak between the $|+\frac{1}{2}\rangle$, $|-\frac{1}{2}\rangle$ pair of levels and between the $|+\frac{3}{2}\rangle$, $|-\frac{3}{2}\rangle$ pair, both of which satisfy (1).

The rule stems from the fact that the dominant term in the spin-phonon interaction is the quadrupolar spin operator, $S_iS_j + S_jS_i$, and, as is well known, this vanishes between states of the form (1). To prove these statements, we write the Hamiltonian for a single spin in the crystal as

$$H = H_{\text{spin}} + H_{\text{lattice}} + H_{\text{int}}, \tag{2}$$

where

$$H_{\text{spin}} = H_0 + 2\beta\vec{S}\cdot\vec{H} + \lambda\vec{L}\cdot\vec{S} + \beta\vec{L}\cdot\vec{H}; \tag{3}$$

$$H_{\text{lattice}} = \sum_k \hbar\omega_k [a_k{}^\dagger a_k + \tfrac{1}{2}]; \tag{4}$$

$$H_{\text{int}} = \sum_{f,k} V_f A_{fk}(a_k{}^\dagger + a_k). \tag{5}$$

Here, H_0 is the energy of the ion in the crystal electric field, $a_k{}^\dagger$ and a_k are the phonon creation and annihilation operators for the kth normal lattice mode, $A_{fk}(a_k{}^\dagger + a_k)$ is the contribution of the kth lattice mode to the fth normal mode (Q_f) of the spin nearest neighbors, and V_f is the coefficient of the linear terms in the expansion of the crystal field in terms of the Q_f's.[1] We now obtain an equivalent Hamiltonian for H_{int}, which is good to second order in spin operators and displays the spin dependence explicitly. We diagonalize H_{spin} by the method of Löwdin,[2] taking $H^0 = H_0 + 2\beta\vec{S}\cdot\vec{H}$ as the unperturbed part (with ground eigenstates, ϕ_a, and excited eigenstates, ϕ_α), and $P = \lambda\vec{L}\cdot\vec{S} + \beta\vec{L}\cdot\vec{H}$ as the perturbation. This yields the spin-Hamiltonian equation,

$$\sum_a C_{sa}\, H_{ba}{}^0 + P_{ba} + \sum_\alpha \frac{P_{b\alpha}P_{\alpha a}}{E_s - E_\alpha} = 0, \tag{6}$$

for the second-order ground energy levels, E_s, and

$$\psi_s = \sum_a C_{sa}\left\{\phi_a + \sum_\alpha \frac{P_{\alpha a}}{E_s - E_\alpha}\phi_\alpha + \sum_{\alpha,\beta}\frac{P_{\alpha\beta}P_{\beta a}\phi_\alpha}{(E_s - E_\alpha)(E_s - E_\beta)} - \tfrac{1}{2}\sum_{\alpha,b,b'} C_{sb}{}^* C_{sb'}\frac{P_{b\alpha}P_{\alpha b'}}{(E_s - E_\alpha)^2}\phi_a\right\} \tag{7}$$

for the corresponding normalized second-order spin eigenstates. If we designate the lattice states γ_l, then the simultaneous eigenstates of $H_{\text{spin}} + H_{\text{lattice}}$ can be written $|ls\rangle = \gamma_l\psi_s$. We can now compute the direct spin-phonon interaction by forming the matrix element $\langle ls|H_{\text{int}}|l's'\rangle$. When this is done, we find that the result can be stated in the form of the equivalent Hamiltonian,

$$H_{(\text{spin-phonon})} = \sum_{k,f,i>j} A_{fk}(a_k{}^\dagger + a_k)\left\{2\beta\lambda H(g_{ss'} + \Delta_{aa'})\mathcal{L}_i{}^f S_i + 2\beta\lambda\mathcal{L}_{ij}{}^f(S_iH_j + H_iS_j) + \lambda^2\mathcal{L}_{ij}{}^f(S_iS_j + S_jS_i)\right\}, \tag{8}$$

where

$$\mathcal{L}_i^f = \sum_n \frac{\langle 0|L_i|n\rangle\langle n|V_f|0\rangle}{(E_n - E_0)^2}, \tag{9}$$

$$\mathcal{L}_{ij}^f = \sum_{n,n'} \frac{[\langle 0|L_i|n\rangle\langle n|L_j|n'\rangle\langle n'|V_f|0\rangle + \langle L_i V_f L_j\rangle + \langle V_f L_i L_j\rangle]}{(E_n - E_0)(E_{n'} - E_0)}. \tag{10}$$

In Eq. (8), $g_{ss'}$ represents the spectroscopic splitting factor for the spin levels s, s', and

$$\Delta_{aa'} = 1 \text{ with } E_a > E_{a'}$$
$$= 0 \text{ with } E_a = E_{a'}$$
$$= -1 \text{ with } E_a < E_{a'}.$$

The spin anticommutator arises from the symmetry of L_{ij}, which results from the relation $\langle n|L_i|n'\rangle = -\langle n'|L_i|n\rangle$.[3]

Now, since $L_i^f \sim L_{ij}^f$, the ratio of the quadrupolar term to the dipolar term is $\sim\lambda^2/4\beta\lambda H$. If we take as a typical case $H = 10^4$ gauss and $\lambda = 100\ \text{cm}^{-1} = 2\times10^{-14}$ erg, we find that the quadratic term dominates by a factor of 50, when the spin anticommutator is of order unity. On the other hand, it is easily shown by using the properties of the S_+, S_-, S_z operators that $S_iS_j + S_jS_i = 0$ between states of form (1). In this case, the spin-phonon interaction proceeds through the linear terms in (8), and is correspondingly smaller. Thus the quadrupole selection rule is proved.

This rule has implications for proposed acoustic experiments.[4,5] According to the rule, for example, it should be impossible to observe acoustic saturation of low-frequency ($\sim 10^7$ cps) paramagnetic-resonance signals within Kramers doublets in a spin-$\frac{3}{2}$ system. It also predicts that, in a microwave acoustic experiment, it should be possible to see a radical decrease in phonon attenuation when $\vec{H}$ becomes parallel to the crystal optic axis.

We note also that it would be desirable to examine the existing data on gain-bandwidth product in ruby masers that amplify between nearly pure, and more strongly mixed, $\pm\frac{1}{2}$ levels, to see if these data are compatible with our selection rule.

*This work was supported in part by the U.S. Army (Signal Corps), the U. S. Air Force (Office of Scientific Research, Air Research and Development Command), and the U. S. Navy (Office of Naval Research).

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EDGE AND IMPURITY EMISSION IN CADMIUM SULFIDE

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(Received July 13, 1959; revised manuscript received September 21, 1959)

A model[1,2] has recently been proposed for the band structure of cadmium sulfide which purports to explain much of the observed optical phenomena in terms of conduction and valence band extrema centered about $k = 0$. Although this model does fit the observed dichroism, polarization of edge emission, and the like, several pieces of data can be cited which cannot be explained in terms of this simple structure. One set of observations will be described here; another set, on edge emission, will be published shortly.

Figure 1 shows two curves of intensity of emission versus angle of polarization. The curve having its peak in a direction perpendicular to the c axis of the crystal is that of edge emission taken at liquid nitrogen temperature. The curve having its peak parallel to the c axis of the sample is that of the emission at 6380 A due to copper,