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Magnetic Field Effects in Crystal Field Excitations and Sound Velocity in Paramagnetic Insulators[1]

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Structural phase transitions from tetragonal to monoclinic crystal symmetry induced by an external magnetic field are studied on the basis of a simple three-level model. It is argued that the model is capable of describing the phenomena in f-electrons rare earth insulators and solid oxygen. The applied theoretical method is the equation of motion for the spin and phonon Green functions. The width of the crystal-field excitation line and the soft-mode phonon velocity are numerically studied and presented in diagrams.

KEY WORDS: crystal field excitations; phase transitions; rare-earth paramagnet; sound velocities.

1. INTRODUCTION

The studies of structural phase transitions induced by an external magnetic field is a vast domain of physical investigations in solids. For instance, it includes the examining of the phase transitions in the perovskites [1, 2], in insulating rare-earth orthophosphates and orthovanadates with the zircon structure. The latter compounds are archetypes of the cooperative Jahn–Teller effect [3–6]. This effect is one of the very few microscopic mechanisms of structural phase transitions which occur in solids [7]. The 4f-electronic states in the mentioned materials are split by the crystalline electric field, and the external magnetic field further reconstructs 4f-energy level schemes. The driving force of these structural transitions is the electron-phonon interaction, which manifests itself as an interaction of the

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total 4f-shell with phonons and can be represented, in general, as a phonon-mediated quadrupole-quadrupole interaction.

The above phenomena are usually described by appropriate spin or pseudospin Hamiltonians. In most of the papers these Hamiltonians are treated by the simplest and most crude method—the molecular field approximation. In the present paper a more sophisticated and powerful method is applied to a three-level model of the crystal field, which, e.g., can describe the phenomena in $TmAsO_4$. It is worth adding that while applying the simple three-level spin Hamiltonian and acoustic phonons, one neglects the rotational deformations [8]. This model can be, however, also applied to the description of the solid oxygen in which the three-states system (singlet-doublet) is of other physical origin [9].

2. MODEL, METHOD, AND CONCLUSIONS

Consider the Hamiltonian,

$$\mathscr{H} = \mathscr{H}_{\text{ph}} + \mathscr{H}_{\text{ion}} + \mathscr{H}_{\text{int}} \tag{1}$$

in which the first term stands for mutually noninteracting phonons,

$$\mathscr{H}_{\text{ph}} = \sum_{\mathbf{k}} \omega_{\mathbf{k}}^{\text{o}} (\alpha_{\mathbf{k}}^{+} \alpha_{\mathbf{k}} + \tfrac{1}{2}), \qquad \omega_{\mathbf{k}}^{\text{o}} = v_0 \, |\mathbf{k}| \tag{2}$$

and assume that the phonon operators $\alpha_{\mathbf{k}}^{+}$ create an acoustic transversal wave of the wave vector $\mathbf{k} = (k, 0, 0)$ and the polarization $\mathbf{e} = (0, 0, 1)$ which is connected with the elastic constant c_{44} of a tetragonal crystal. The second term in Eq. (1) describes the crystal field energy,

$$\mathscr{H}_{\text{ion}} = \sum_{m=1}^{N} \{D[2(J_z^m)^2 - (J_x^m)^2 - (J_y^m)^2] - hJ_z^m\},$$
$$D, h \geqslant 0, \quad J = 1 \tag{3}$$

in which D is the the crystal field splitting constant and h is the strength of the external magnetic field. The interaction of these two systems is described by the last term in Eq. (1), which is as follows:

$$\mathscr{H}_{\text{int}} = -\frac{\text{i}}{4} \frac{g}{\sqrt{2M}} \frac{1}{\sqrt{N}} \sum_{m=1}^{N} \sum_{\mathbf{k}} \frac{k}{\sqrt{\omega_{\mathbf{k}}^{\text{o}}}} (\alpha_{\mathbf{k}} e^{\text{i}\mathbf{k}\mathbf{R}_m} - \alpha_{\mathbf{k}}^{+} e^{-\text{i}\mathbf{k}\mathbf{R}_m})$$
$$\cdot (J_+^m J_z^m + J_z^m J_+^m + J_-^m J_z^m + J_z^m J_-^m), \tag{4}$$

where g is the magnetoelastic constant and $\mathbf{R}_m$ denotes the ion site. The total system consists of N ions of mass M and of angular momentum of f-shell $\mathbf{J}$ ($J_\pm = J_x \pm \mathrm{i}J_y$). For the assumed positive value of D, the ground state of each ion is singlet ($|J_z = 0\rangle$) and, for $h = 0$, the excited state is the doublet.

It is convenient to introduce the operators a^+ and b^+ which have the effect of transforming the ground state into the two upper states: $|0\rangle \to |+1\rangle$ and $|0\rangle \to |-1\rangle$, respectively,

$$a^+ = \frac{1}{2\sqrt{2}}(J_+J_z + J_zJ_+ + J_+), \qquad J_z = a^+a - b^+b, \tag{5}$$

$$b^+ = \frac{1}{2\sqrt{2}}(J_- - J_-J_z - J_zJ_-), \qquad J_z^2 = a^+a + b^+b. \tag{6}$$

The commutation relations of these raising and lowering operators a, b are

$$[a^+, a] = \mathscr{P}_1 \equiv \tfrac{1}{2}J_z + \tfrac{1}{2}(3J_z^2 - 2), \tag{7}$$

$$[b, b^+] = \mathscr{P}_2 \equiv \tfrac{1}{2}J_z - \tfrac{1}{2}(3J_z^2 - 2). \tag{8}$$

We shall express the dynamical properties of our system in terms of the frequency (ω)-dependent Fourier transforms of the retarded commutator Green functions: $\langle\langle a; a^+\rangle\rangle_\omega$ and $\langle\langle b; b^+\rangle\rangle_\omega$. To present appropriate equations, we introduce

$$O_1^\pm = a \pm a^+, \qquad O_2^\pm = b \pm b^+. \tag{9}$$

For the Hamiltonian under consideration, the following linear relations can be be shown to be valid:

$$\begin{aligned}\langle\langle a; a^+\rangle\rangle_\omega = \tfrac{1}{4}[&\langle\langle O_1^+; O_1^+\rangle\rangle_\omega - \langle\langle O_1^-; O_1^-\rangle\rangle_\omega \\ &+ \langle\langle O_1^-; O_1^+\rangle\rangle_\omega - \langle\langle O_1^+; O_1^-\rangle\rangle_\omega],\end{aligned} \tag{10}$$

$$\begin{aligned}\langle\langle b; b^+\rangle\rangle_\omega = \tfrac{1}{4}[&\langle\langle O_2^+; O_2^+\rangle\rangle_\omega - \langle\langle O_2^-; O_2^-\rangle\rangle_\omega \\ &+ \langle\langle O_2^-; O_2^+\rangle\rangle_\omega - \langle\langle O_2^+; O_2^-\rangle\rangle_\omega],\end{aligned} \tag{11}$$

from which follows the self-energy,

$$\mathfrak{M}_s(\omega, h) = \left(\frac{g}{4\sqrt{2M}}\right)^2 \frac{1}{N}\sum_k \frac{k^2}{\omega_k^{\circ}}[\langle\mathscr{P}_1\rangle_\circ\, f_1(k, \omega, h) + \langle\mathscr{P}_2\rangle_\circ\, f_2(k, \omega, h)], \tag{12}$$

related to the the energy level $D-h_z$ and $\mathfrak{M}_s(\omega, -h)$ to the level $D+h_z$. The quantities in the above equation are defined below:

$$\begin{aligned} f_1(k,\omega,h) = {} & 2\coth\frac{D-h}{2T}\left[-\frac{2\omega_k^{\mathrm{o}}}{(\omega_k^{\mathrm{o}})^2-(D-h)^2}+\frac{1}{\omega_k^{\mathrm{o}}-\omega}\frac{\omega_k^{\mathrm{o}}-(D-h)}{\omega_k^{\mathrm{o}}+(D-h)}\right. \\ & \left.+\frac{1}{\omega_k^{\mathrm{o}}+\omega}\frac{\omega_k^{\mathrm{o}}+(D-h)}{\omega_k^{\mathrm{o}}-(D-h)}\right] \\ & +2\coth\frac{\omega_k^{\mathrm{o}}}{2T}\left[\frac{2(D-h)}{(\omega_k^{\mathrm{o}})^2-(D-h)^2}+\frac{1}{\omega_k^{\mathrm{o}}-\omega}\frac{2\omega_k^{\mathrm{o}}}{\omega_k^{\mathrm{o}}+(D-h)}\right. \\ & \left.-\frac{1}{\omega_k^{\mathrm{o}}+\omega}\frac{2\omega_k^{\mathrm{o}}}{\omega_k^{\mathrm{o}}-(D-h)}\right] \\ & -\frac{1+\coth(\omega_k^{\mathrm{o}}/2T)}{\omega_k^{\mathrm{o}}+2h+\omega}-\frac{1-\coth(\omega_k^{\mathrm{o}}/2T)}{\omega_k^{\mathrm{o}}-2h-\omega}, \end{aligned} \tag{13}$$

$$\begin{aligned} f_2(k,\omega,h) = {} & \coth\frac{D+h}{2T}\left[\frac{2\omega_k^{\mathrm{o}}}{(\omega_k^{\mathrm{o}})^2-(D+h)^2}-\frac{1}{\omega_k^{\mathrm{o}}-2h-\omega}\frac{\omega_k^{\mathrm{o}}-(D+h)}{\omega_k^{\mathrm{o}}+(D+h)}\right. \\ & \left.+\frac{1}{\omega_k^{\mathrm{o}}+2h+\omega}\frac{\omega_k^{\mathrm{o}}+(D+h)}{\omega_k^{\mathrm{o}}-(D+h)}\right] \\ & +\coth\frac{\omega_k^{\mathrm{o}}}{2T}\left[-\frac{2(D+h)}{(\omega_k^{\mathrm{o}})^2-(D+h)^2}-\frac{1}{\omega_k^{\mathrm{o}}-2h-\omega}\frac{2\omega_k^{\mathrm{o}}-(D+h)}{\omega_k^{\mathrm{o}}+(D+h)}\right. \\ & \left.+\frac{1}{\omega_k^{\mathrm{o}}+2h+\omega}\frac{2\omega_k^{\mathrm{o}}+(D+h)}{\omega_k^{\mathrm{o}}-(D+h)}\right], \end{aligned} \tag{14}$$

$$\langle\mathscr{P}_1\rangle_0 = \frac{e^{h/T}-e^{D/T}}{e^{D/T}+2\cosh(h/T)} \tag{15}$$

$$\langle\mathscr{P}_2\rangle_0 = \frac{e^{D/T}-e^{-h/T}}{e^{D/T}+2\cosh(h/T)}. \tag{16}$$

The self-energy [Eq. (12)] is of physical interest since it includes information on the broadening of the crystal field excitations caused by the spin-phonon interaction [Eq. (4)], i.e., their damping. This is, of course, also related to the shape of the crystal field excitation line. The damping manifests itself mathematically if the theory is applied up to the second order in the interaction strength g as in the present paper. In order to present the final numerical results, we have to perform the summation over the wavevector $\mathbf{k}$ in Eq. (12). For this purpose we assume the Debye model and analyze the behavior of quantities which are directly or indirectly measured experimentally.

The numerical analysis of the self-energy [Eq. (12)] allows us to find the temperature dependence of the crystal field linewidth, Γ, for given values of the external magnetic field strength. The behavior of Γ in the vicinity of the structural phase transition is interesting for experimentalists since this quantity is a measure of the phenomenon known as the critical slowing down (narrowing of the line), which is usually observed in the phenomena of the neutron scattering when the system approaches a continuous phase transition.

In Fig. 1 we present the dependence of the reduced (dimensionless) Γ as a function of the temperature at temperatures rather high in comparison to the transition temperatures. The field strength is, however, of the order at which the transition occurs. Note that the system is in the tetragonal phase and it is driven to the monoclinic one by the magnetic field (field-induced Jahn–Teller effect), the strength of which is presented in the figure in the units of D ($x = h/D$). The most interesting finding of these numerical studies is the fact that the narrowing of the linewidth occurs below a certain temperature for a given field strength, what manifests itself as a maximum of our dependences.

As concerns the phonon system the phonon damping manifests itself within the above perturbation scheme as an effect of the fourth order. Even for the simple three-level system, which we apply here, consideration of the shape of the phonon lines is a complicated mathematical problem which demands a separate paper. Thus, our present paper will be only devoted to sound propagation problems, which follow from our model within the second-order perturbation scheme. In order to find the renormalized sound

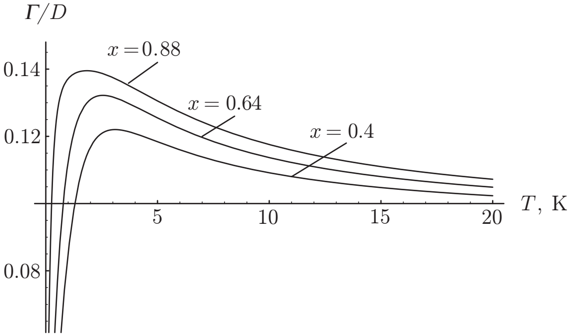

Fig. 1. Temperature dependence of the linewidth at the field strength approaching the crossover of the crystal field energy levels. The transition temperature is 23.7 mK. Assumed values of the parameters are: $\omega = 10$ MHz, $D = 5$ K, the Debye temperature is assumed to be 180 K and $G^2 = 0.1$ K, and $x = h/D$.

velocity (being proportional to the square root of the relevant elastic constant c_{44}), we have to calculate the retarded commutator Green function,

$$\langle\langle \phi_{\mathbf{k}}(t); \phi_{\mathbf{k}}^{+}(t) \rangle\rangle = -\mathrm{i}\theta(t)\langle [\phi_{\mathbf{k}}(t); \phi_{\mathbf{k}}^{+}(t)] \rangle, \tag{17}$$

where

$$\phi_{\mathbf{k}} = \alpha_{\mathbf{k}} + \alpha_{-\mathbf{k}}^{+}. \tag{18}$$

and $\theta(t)$ is the step function. The final form of the phonon Green function is

$$\langle\langle \phi_k; \phi_k^{+} \rangle\rangle_{\omega} = \frac{2v_{\mathrm{o}}k}{\omega^2 - k^2 v^2(\omega)}, \tag{19}$$

where the sound velocity v as a function of the frequency ω is [10]

$$\left[\frac{v(\omega)}{v_0}\right]^2 = 1 - \frac{G^2}{2D}\left[\langle \mathscr{P}_2 \rangle_0 \frac{1+x}{(1+x)^2 - (\omega/D)^2} - \langle \mathscr{P}_1 \rangle_0 \frac{1-x}{(1-x)^2 - (\omega/D)^2}\right] \tag{20}$$

with $G^2 = g^2/(2Mv_0{}^2)$.

In Fig. 2 we present the reduced square of the sound velocity as a function of the temperature. Note that it corresponds to the elastic constant c_{44} for the tetragonal phase and that the assumed magnitude of the frequencies ω of the order of MHz and GHz is applied by experimentalists

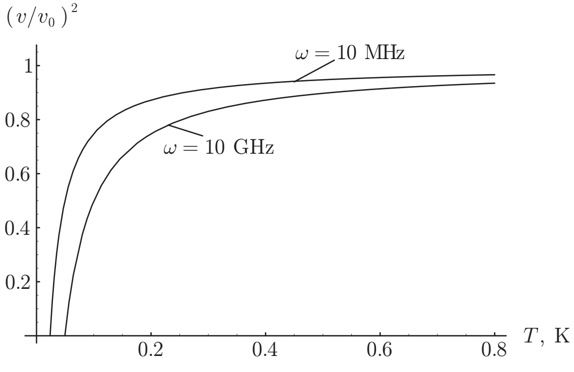

Fig. 2. Sound velocity *vs* temperature in the megahertz and gigahertz frequency region. Assumed values of the parameters are: $D = 5$ K, $G^2 = 0.1$ K, and $x = 0.996$.

[11, 12]. It should be stressed that this figure shows that at least for the assumed values of the parameters the mode softens at $T_c = 23.7\,\text{mK}$ for the frequency $\omega = 10$ MHz and for the frequency $\omega = 10$ GHz it softens at the higher temperature $T_c = 49.5\,\text{mK}$. The present figure shows that the soft elastic constant c_{44} is strongly frequency dependent.

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