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Theoretical study of the phonon spectra of hexagonal multiferroics RMnO₃

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Abstract

The phonon properties of hexagonal multiferroic RMnO₃ materials are studied using a Green's function technique. The calculations are performed on the basis of the Heisenberg and the transverse Ising model taking into account anharmonic spin–phonon and phonon–phonon interaction terms. The strong spin–phonon interaction leads to an anomaly in the phonon energy and the damping around the magnetic and ferroelectric phase transitions. The phonon spectrum is discussed for different exchange, magnetoelectric and spin–phonon interaction constants. It is shown that the phonon energy depends on the radius of the rare earth ion r_R . The influence of an applied magnetic field on the phonon spectrum is studied, too. The predictions are consistent with experimental results.

1. Introduction

Magnetoelectric multiferroics, materials which exhibit simultaneous magnetic and ferroelectric order, have attracted a lot of attention in recent years because of their potential for cross electric and magnetic functionality [1]. To obtain a fundamental understanding of multiferroics, the experimental observation and understanding of the coupling mechanism between the (anti)ferroelectric and (anti)ferromagnetic order are of great importance. However, very little is known about the behaviour of phonons in magnetoelectric multiferroics, even though investigations of phonons have in the past played a crucial role in the understanding of classic ferroelectrics. Phonons are also known to be influenced by spin correlation, thus offering a complementary tool [2, 3]. Recent investigations using Raman and infrared (IR) spectroscopy, by transmittance and reflectance measurements, have revealed the importance of phonon effects in multiferroics. There is experimental evidence for a strong spin–phonon coupling in these substances [4–13]. The experimental results reveal pronounced phonon anomalies around the magnetic phase transition temperature. These anomalies are attributed to the multiferroic character of the materials. Raman and infrared spectra of YMnO₃ were reported and discussed by Iliev *et al* [14] and Kim *et al* [15]. Martin-Carron *et al* studied the Raman phonons in RMnO₃ orthorhombic and hexagonal manganites as a function of the rare

earth ion and temperature [16]. The sign and magnitude of such anomalous phonon shifts appear to be correlated with the ionic radius R in the multiferroic system RMn_2O_5 [17], evolving from softening for $R = \text{Bi}$ to hardening for $R = \text{Dy}$ and showing an intermediate behaviour for $R = \text{Eu}$. Based on temperature dependence of the far-IR transmission spectra of multiferroic YMn_2O_5 and TbMn_2O_5 single crystals, Suchkov *et al* [18] reported observation of electromagnons in RMn_2O_5 compounds. The phonon energy and phonon damping are different for the different compounds. Different selection rules for electromagnons in RMn_2O_5 and RMnO_3 suggest different magnetoelastic coupling mechanisms in the two multiferroic systems. Cheong [19] has shown that acoustic phonons in hexagonal HoMnO_3 can be significantly influenced by an applied magnetic field H . The influence of a magnetic field on the frequency of the soft mode in incipient ferroelectric EuTiO_3 was studied theoretically by Jiang and Wu [20] using the soft-mode theory under a mean-field approximation.

The aim of the present paper is to study the phonon spectra in hexagonal multiferroic RMnO_3 substances using a Green's function technique beyond the random phase approximation.

2. The model

Following Wu *et al* [21] the Hamiltonian of a multiferroic system can be presented as:

$$H = H^e + H^m + H^{\text{me}}. \quad (1)$$

H^e denotes the Hamiltonian for the electrical subsystem which is dealt with within the framework of the transverse Ising model (TIM). Thus H^e in the presence of an electric field can be written as:

$$H^e = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - \mu E \sum_i S_i^z, \quad (2)$$

where S_i^x , S_i^z are the spin-1/2 operators of the pseudo-spins, E represents the external electric field, J_{ij} denotes the nearest-neighbour pseudo-spin interaction and Ω is the tunnelling frequency. In this system the mean electric polarization is proportional to the z component of the pseudo-spins introduced in the TIM. In the ordered phase we have the mean values $\langle S^x \rangle \neq 0$ and $\langle S^z \rangle \neq 0$, and it is appropriate to choose a new coordinate system rotating the original one used in (2) by an angle θ in the xy plane [2]. The rotation angle θ is determined by the requirement $\langle S^{x'} \rangle = 0$ in the new coordinate system.

H^m is the Hamiltonian for the magnetic subsystem, which is given by the Heisenberg Hamiltonian:

$$H^m = -\frac{1}{2} \sum_{\langle ij \rangle} A_1(i, j) \mathbf{B}_i \cdot \mathbf{B}_j - \frac{1}{2} \sum_{[ij]} A_2(i, j) \mathbf{B}_i \cdot \mathbf{B}_j - g\mu_B H \sum_i B_i^z, \quad (3)$$

where B_i is the Heisenberg spin at the site i , and the exchange integrals A_1 and A_2 represent the coupling between the nearest and next-nearest neighbours, respectively. H is the external magnetic field parallel to the z axis. $\langle ij \rangle$ and $[ij]$ denote a single summation over the nearest neighbours and the next nearest neighbours, respectively.

The most important term is H^{me} which describes the coupling between the magnetic and the electric subsystems in the ferroic compound:

$$H^{\text{me}} = -g \sum_{\langle ij \rangle} \sum_{kl} S_k^z S_l^z \mathbf{B}_i \cdot \mathbf{B}_j. \quad (4)$$

Here g is the coupling constant between the magnetic and the electric order parameters.

In order to investigate the phonon spectrum and the experimentally obtained strong spin–phonon coupling we have to include the following two terms in the Hamiltonian in equation (1):

$$H' = H_{\text{ph}} + H_{\text{sp-ph}}. \quad (5)$$

The first term H_{ph} contains the lattice vibrations including anharmonic phonon–phonon interactions:

$$H_{\text{ph}} = \frac{1}{2!} \sum_q (P_q P_{-q} + (\omega_q^0)^2 Q_q Q_{-q}) + \frac{1}{3!} \sum_{q, q_1} B(q, q_1) Q_q Q_{-q_1} Q_{q_1-q} \\ + \frac{1}{4!} \sum_{q, q_1, q_2} A(q, q_1, q_2) Q_{q_1} Q_{q_2} Q_{-q-q_2} Q_{-q_1+q}, \quad (6)$$

where Q_q , P_q and ω_q^0 are the normal coordinate, momentum and frequency, respectively, of the lattice mode with a wavevector \mathbf{q} . The vibrational normal coordinate Q_q and the momentum P_q can be expressed in terms of phonon creation and annihilation operators:

$$Q_q = (2\omega_q^0)^{-1/2} (a_q + a_{-q}^\dagger), \quad P_q = i(\omega_q^0/2)^{1/2} (a_q^\dagger - a_{-q}). \quad (7)$$

$H_{\text{sp-ph}}$ describes the interaction of the pseudo-spins of the ferroelectric subsystem and of the magnetic spins with the phonons. This is very important in order to explain the experimental data for Raman and IR spectroscopy lines in multiferroics.

$$H_{\text{sp-ph}} = - \sum_q \bar{F}_e(q) Q_q S_{-q}^z - \frac{1}{2} \sum_{q, p} \bar{R}_e(q, p) Q_q Q_{-p} S_{p-q}^z \\ - \sum_q \bar{F}_m(q) Q_q B_{-q}^z - \frac{1}{2} \sum_{q, p} \bar{R}_m(q, p) Q_q Q_{-p} B_{p-q}^z + \text{h.c.}, \quad (8)$$

where

$$\bar{F}_e(q) = \frac{1}{\sqrt{N}} \sum_h \frac{1}{|h|} (e_q h) J'(h) \exp(iqh), \quad (9)$$

$$\bar{R}_e(p, q) = \frac{1}{N} \sum_h \left(J''(h) - \frac{J'(h)}{|h|} \right) (e_{p-q} h) (\exp(ip.h) + \exp(iqh)). \quad (10)$$

The summation extend over the vectors $\mathbf{h} = \mathbf{r}_i - \mathbf{r}_j$ connecting all possible pairs of spin sites in the crystal and e_q is the polarization of the phonon with wavevector \mathbf{q} . $F_e(q) = \bar{F}_e(q)/(2\omega_q^0)^{1/2}$ and $R_e(q, p) = \bar{R}_e(q, p)/(2\omega_q^0)^{1/2}(2\omega_p^0)^{1/2}$ designate the amplitudes for coupling phonons to the pseudo-spin-wave excitations in first and second order, respectively. Analogous equations exist for the coupling constants between the phonons and the magnetic spins.

3. The phonon Green's function

The retarded phonon Green's function to be calculated is defined as

$$G(\mathbf{k}, \omega) = \langle\langle a_{\mathbf{k}}; a_{\mathbf{k}}^\dagger \rangle\rangle, \quad (11)$$

where $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^\dagger$ are the phonon annihilation and creation operators, respectively. For the approximate calculation of the Green's function we use a method proposed by Tserkovnikov [22], which is appropriate for spin problems. After a formal integration of the equation of motion for the Green's function (11), one obtains

$$G_{ij}(t) = -i\theta(t) \langle [a_i; a_j^\dagger] \rangle \exp(-i\omega_{ij}(t)t) \quad (12)$$

where

$$\omega_{ij}(t) = \omega_{ij} - \frac{i}{t} \int_0^t dt' t' \left(\frac{\langle [j_i(t); j_j^+(t')] \rangle}{\langle [a_i(t); a_j^+(t')] \rangle} - \frac{\langle [j_i(t); a_j^+(t')] \rangle \langle [a_i(t); j_j^+(t')] \rangle}{\langle [a_i(t); a_j^+(t')] \rangle^2} \right) \quad (13)$$

with the notation $j_i(t) = \langle [a_i, H_{int}] \rangle$. The time-independent term

$$\omega_{ij} = \frac{\langle [[a_i, H]; a_j^+] \rangle}{\langle [a_i; a_j^+] \rangle} \quad (14)$$

is the energy in the generalized Hartree–Fock approximation (GHFA). The time-dependent term in equation (13) includes damping effects.

We have calculated the phonon energy from equation (14) beyond the random phase approximation (RPA) taking into account the correlation functions. Below T_C $\omega_{\text{RPA}}(T) > \omega(T)$. The deviation between these curves increases when the temperature increases. In the RPA ω is a constant above T_C , which is obviously incorrect. This confirms the importance of the phonon correlation functions \bar{N}_q below and above T_C which we have taken into account. The following expression is obtained which contains the phonon energy ω_0 , two terms due to the anharmonic spin–phonon interactions R_e , R_m and two terms due to the anharmonic phonon–phonon interactions A , B :

$$\omega(\mathbf{k})^2 = \omega_0^2 - 2\omega_0 \left(0.5\sigma^2 \cos \theta R_e(\mathbf{k}) + M^2 R_m(\mathbf{k}) - \frac{1}{2N} \sum_q A_{kq} (2\bar{N}_q + 1) - B(\mathbf{k}) \langle Q(\mathbf{k}) \rangle \delta_{k0} \right), \quad (15)$$

with

$$\langle Q(\mathbf{k}) \rangle = \frac{\sigma^2 \cos \theta F_e(\mathbf{k}) - \frac{1}{N} \sum_q B_{kq} (2\bar{N}_q + 1) + M^2 F_m(\mathbf{k})}{\omega_0 - \sigma^2 \cos \theta R_e(\mathbf{k}) - M^2 R_m(\mathbf{k}) + \frac{1}{N} \sum_q A_{kq} (2\bar{N}_q + 1)}. \quad (16)$$

Above T_C the spin–phonon interactions do not contribute to the phonon energy (because σ and M vanish), and only the anharmonic phonon–phonon interactions remain. The phonon frequency ω is renormalized owing to the anharmonic phonon–phonon and spin–phonon interactions. If they are not taken into account, then ω is identical to the energy ω_0 of the uncoupled optical phonon. It will be independent of temperature. The calculations show that for $R = 0$, i.e. including only anharmonic phonon–phonon interaction, the phonon mode shows very weak temperature dependence. If we want to explain the experimental data for the nonlinear temperature dependence of the phonon modes in multiferroics we must include higher-order pseudo-spin–phonon interactions, which play an important role below T_C , i.e. we must not neglect the effects of spin ordering, and the Hamiltonian which describes the system must include terms taking into account not only the anharmonic phonon–phonon interaction but also the anharmonic spin–phonon interaction.

The phonon damping is calculated from equation (13) in second-order theory as

$$\gamma(\mathbf{k}) = \gamma_{\text{ph-ph}}(\mathbf{k}) + \gamma_{\text{sp-ph}}(\mathbf{k}). \quad (17)$$

For the damping due to the phonon–phonon interactions we have

$$\begin{aligned} \gamma_{\text{ph-ph}}(\mathbf{k}) = & \frac{3\pi}{N} \sum_q [B^2(\mathbf{q}, -\mathbf{k}, \mathbf{k} - \mathbf{q}) + B^2(\mathbf{q}, \mathbf{k} - \mathbf{q}, -\mathbf{q})] (\bar{N}_q - \bar{N}_{k-q}) \\ & \times [\delta(\omega_k - \omega_q - \omega_{k-q}) + \delta(\omega_k - \omega_q + \omega_{q-k})] \\ & + \frac{8\pi}{N^2} \sum_{q,p} [A^2(\mathbf{q}, -\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{q} - \mathbf{p}) + A^2(\mathbf{q}, \mathbf{p}, -\mathbf{k}, \mathbf{k} - \mathbf{q} - \mathbf{p})] \\ & \times [\bar{N}_p (1 + \bar{N}_q + \bar{N}_{p+k-q}) - \bar{N}_q \bar{N}_{p+k-q}] \delta(\omega_k - \omega_q + \omega_p - \omega_{k+p-q}). \quad (18) \end{aligned}$$

$\gamma_{\text{sp-ph}}$ is the damping due to the spin-phonon interactions:

$$\begin{aligned}
\gamma_{\text{sp-ph}}(\mathbf{k}) = & \frac{4\pi M^2}{N} \sum_q F_m^2(\mathbf{q}, \mathbf{q} - \mathbf{k})(\bar{m}_q - \bar{m}_{q-k})\delta(E_{m,q-k} - E_{m,q} - \omega_k) \\
& + \frac{4\pi M^2}{N^2} \sum_{q,p} (R_m^2(-\mathbf{k}, \mathbf{p}, \mathbf{q})(\bar{m}_q - \bar{m}_p)[(1 + \bar{N}_{k+p-q}) \\
& \times \delta(E_{m,p} - E_{m,q} - \omega_{k+p-q} + \omega_k) + \bar{N}_{q-k-p}\delta(E_{m,p} - E_{m,q} + \omega_{q-k-p} + \omega_k)] \\
& + [R_m^2(-\mathbf{k}, \mathbf{p}, \mathbf{q}) + R_m^2(\mathbf{k} - \mathbf{q} + \mathbf{p}, \mathbf{p}, \mathbf{q})]\bar{m}_q(1 + \bar{m}_p) \\
& \times [\delta(E_{m,p} - E_{m,q} - \omega_{k+p-q} + \omega_k) - \delta(E_{m,p} - E_{m,q} + \omega_{q-k-p} + \omega_k)]) \\
& + \frac{\pi}{N^2} \sum_{q,p} [R_m^2(-\mathbf{k}, \mathbf{p}, \mathbf{q}) + R_m^2(\mathbf{k} - \mathbf{q} + \mathbf{p}, \mathbf{p}, \mathbf{q})]\langle B_p^z B_{-p}^z \rangle \langle B_q^z B_{-q}^z \rangle \\
& \times [\delta(E_{m,p} - E_{m,q} - \omega_{k+p-q} + \omega_k) - \delta(E_{m,p} - E_{m,q} + \omega_{q-k-p} + \omega_k)] \\
& + \frac{\pi}{4} F_e^2(\mathbf{k})\delta(\omega_k - E_{e,k}) + \frac{\pi}{N} \sum_q F_e^2[(\bar{N}_q - \bar{n}_{k-q}) \\
& \times \delta(E_{e,k-q} - \omega_q - E_{e,k}) + (1 + \bar{N}_q + \bar{n}_{k-q})\delta(\omega_q + E_{e,k-q} - E_{e,k})] \\
& + \frac{\pi}{8N^2} \sum_q R_e^2(\mathbf{q}, \mathbf{k} + \mathbf{q})(\bar{N}_q - \bar{N}_{k+q})\delta(\omega_{k+q} - \omega_q - E_{e,k}) \\
& + \frac{\pi}{2N^2} \cos^2 \theta \sum_{q,p} R_e^2(\mathbf{k}, \mathbf{q}, \mathbf{p})[\bar{N}_p(1 + \bar{N}_q + \bar{n}_{k+q-p}) - \bar{N}_q \bar{n}_{k+p-q}] \\
& \times \delta(\omega_q - \omega_p + E_{e,k+p-q} - E_{e,k}), \tag{19}
\end{aligned}$$

where $\bar{N}_q = \langle a_q^\dagger a_q \rangle$, $\bar{m}_q = \langle B_q^- B_q^+ \rangle$ and $\bar{n}_q = \langle S_q^- S_q^+ \rangle$ are correlation functions which are calculated via the spectral theorem. For low temperatures the main contribution to the damping comes from the spin-phonon interaction, whereas in the vicinity of T_C and above, where the polarization and the magnetization vanish, only the anharmonic phonon-phonon interaction terms remain.

The quantity $\sigma(T)$ is the relative polarization in the direction of the mean field and is equal to $2\langle S^z \rangle$. $M(T) = \langle B^z \rangle$ is the relative magnetization. In order to obtain σ we must calculate the pseudo-spin wave energy E_e in the generalized Hartree-Fock approximation from the retarded Green's function for the ferroelectric subsystem: $G(\mathbf{k}, \omega) = \langle \langle S_{\mathbf{k}}^+; S_{\mathbf{k}}^- \rangle \rangle$

$$\begin{aligned}
E_e(\mathbf{k}) = & 2\Omega \sin \theta + \frac{1}{2}\sigma \cos^2 \theta J_{\text{eff}} - \frac{1}{4}\sigma \sin^2 \theta J_{\text{eff}}(\mathbf{k}) + \mu E \cos \theta \\
& - \frac{1}{N\sigma} \sum_q \left(\cos^2 \theta J_{\text{eff}}(\mathbf{k} - \mathbf{q}) - \frac{1}{2} \sin^2 \theta J_{\text{eff}}(\mathbf{q}) \right) \langle S_q^- S_q^+ \rangle. \tag{20}
\end{aligned}$$

It can be seen that the pseudo-spin exchange interaction constant J is renormalized due to the interaction constant between the electric and magnetic subsystems g and due to the spin-phonon coupling to J_{eff} :

$$J_{\text{eff}} = J_0 + 2g \langle B^z \rangle^2 + \frac{2(F_e^2 + F_m^2)}{\omega_0 - \sigma \cos \theta R_e + 0.5A - MR_m}. \tag{21}$$

For the rotation angle θ we have the following two solutions in the generalized Hartree-Fock approximation:

- (1) $\cos \theta = 0$, i.e. $\theta = \frac{\pi}{2}$, if $T \geq T_c$;
- (2) $\sin \theta = \frac{4\Omega}{\sigma J_{\text{eff}}} = \frac{\sigma_c}{\sigma}$, if $T \leq T_c$.

The relative polarization is given by

$$\sigma = \frac{1}{2} \tanh \frac{E_e(\mathbf{k})}{2k_B T}. \quad (22)$$

For the magnetic subsystem we obtain the spin-wave energy in the generalized Hartree–Fock approximation from the retarded Green’s function $g(\mathbf{k}, \omega) = \langle \langle B_{\mathbf{k}}^+; B_{\mathbf{k}}^- \rangle \rangle$:

$$E_m = g\mu_B H + \frac{1}{2\langle B^z \rangle} \frac{1}{N} \sum_q (A_1^{\text{eff}}(q) - A_1^{\text{eff}}(k-q)) (2\langle B_q^z B_{-q}^z \rangle - \langle B_{k-q}^z B_{k-q}^+ \rangle) \\ + \frac{1}{2\langle B^z \rangle} \frac{1}{N} \sum_q (A_2(q) - A_2(k-q)) (2\langle B_q^z B_{-q}^z \rangle - \langle B_{k-q}^z B_{k-q}^+ \rangle). \quad (23)$$

The spin exchange interaction constant between next-neighbours A_1 is renormalized, too, through the coupling between the electric and magnetic subsystems g and due to the spin-phonon coupling to A_1^{eff} :

$$A_1^{\text{eff}} = A_1 + 2g\sigma^2 \cos^2 \theta + \frac{2(F_e^2 + F_m^2)}{\omega_0 - \sigma \cos \theta R_e + 0.5A - MR_m}. \quad (24)$$

The relative magnetization M is given for arbitrary spin value S by

$$M = \frac{1}{N} \sum_k [(S + 0.5) \coth[(S + 0.5)\beta E_m(k)] - 0.5 \coth(0.5\beta E_m(k))]. \quad (25)$$

4. Numerical results and discussion

In this section we shall present the numerical calculations of our theoretical results taking the following model parameters which are appropriate for hexagonal YMnO₃ with $T_N = 80$ K and $T_C = 900$ K: $A_1 = 85$ K, $A_2 = -60$ K, $\Omega = 20$ K, $J = 3600$ K, $A = -1$ cm⁻¹, $B = 0.5$ cm⁻¹, $F_e = F_m = 10$ cm⁻¹, $\omega_0 = 680$ cm⁻¹, $g = 50$ K, $S = 2$ for the magnetic ions and $S = 0.5$ for the pseudo-spins. We have calculated the temperature dependence of the phonon energy in a hexagonal lattice for $\mathbf{k} = 0$ and different anharmonic spin-phonon interaction R_e and R_m constants which can be positive, $R > 0$, or negative, $R < 0$ [2, 3]. The frequency shift below T_N and T_C can be explained only if we assume a spin-dependent force constant given by the first and second derivatives of the exchange interaction $A_1(r_i - r_j)$ (or J_{ij}) between the i th and j th ions with respect to the phonon displacements u_i, u_j . This displacement is interpreted by taking the nearest-neighbour exchange integral $A_1(r_i - r_j)$ (or J_{ij}) and the next-nearest-neighbour exchange integral $A_2(r_i - r_j)$ (or K_{ij}). The squared derivatives of A_1 and A_2 (or J and K) with respect to the phonon displacement can have opposite signs. If we denote them by R_1 and R_2 accordingly, then the additional shift $\Delta\omega$ of the phonon frequency which is due to the spin-phonon interaction can be written as [23]

$$\Delta\omega = [-R_1 \langle S_1 S_2 \rangle + R_2 \langle S_1 S_3 \rangle] / \langle S_0^z \rangle^2. \quad (26)$$

$\langle S_1 S_2 \rangle$ and $\langle S_1 S_3 \rangle$ are the correlation functions between nearest-neighbour spins and next-nearest-neighbour spins, respectively. In our model the force constant R is equal to $-R_1 + R_2$. This can be connected with the interaction and competition for example between the zone-centre ferroelectric modes and the zone-corner antiferrodistorsive modes, or due to the complexity of the hybridized Mn d-states there are both ferromagnetic and antiferromagnetic contributions that differ for in-plane and out-of-plane neighbours. It is clear that $\langle S_1^z S_2^z \rangle / \langle S_0^z \rangle^2$ and $\langle S_1^z S_3^z \rangle / \langle S_0^z \rangle^2$ below T_C decrease when the temperature rises as $[\langle S_1^z S_2^z \rangle / \langle S_0^z \rangle^2] \geq [\langle S_1^z S_3^z \rangle / \langle S_0^z \rangle^2]$ because $K_0 < J_0$ (or $A_2 < A_1$). The correlation functions

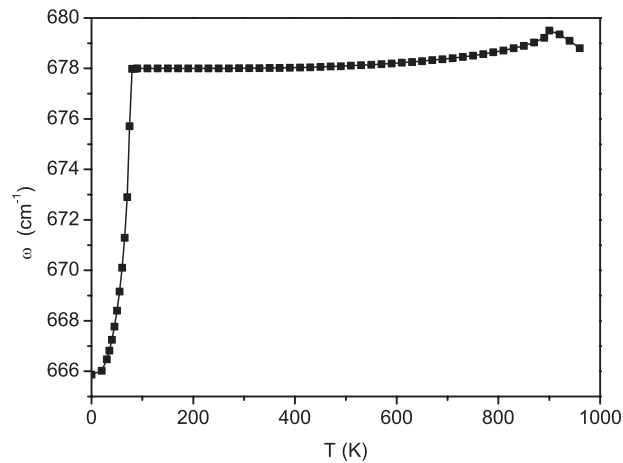


Figure 1. Temperature dependence of the phonon energy ω for the following spin-phonon interaction constants: $R_e = R_m = 6 \text{ cm}^{-1}$.

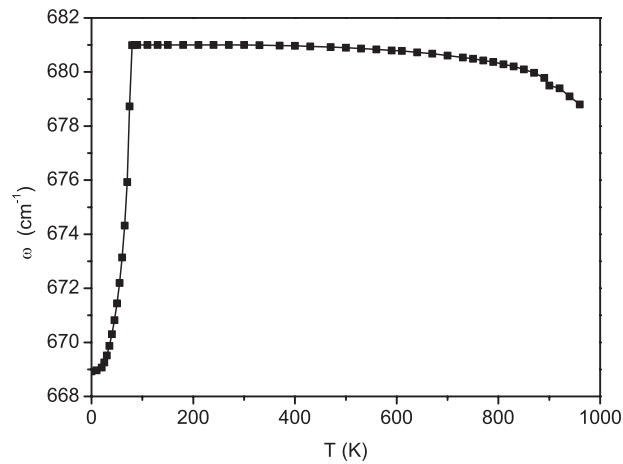


Figure 2. Temperature dependence of the phonon energy ω for the following spin-phonon interaction constants: $R_e = 6 \text{ cm}^{-1}$, $R_m = 6 \text{ cm}^{-1}$.

are equal at $T = 0 \text{ K}$ as the deviation between them increases when $T \rightarrow T_C$. From the above-mentioned qualitative conclusions it follows that if $R_2 > R_1$ then $d[\Delta\omega_j(T)]/dT < 0$, i.e. ω_j decreases with temperature. When $R_2 < R_1$ then $d[\Delta\omega_j(T)]/dT > 0$ and $\Delta\omega_j < 0$, i.e. ω_j grows with temperature. But the competition between the exchange interaction of nearest- and next-nearest-neighbours is only one of the possible explanations. In principle, the different sign of R can also be connected with different strains due to the influence of defects, mechanical strain, or with different ordering in the layers and between the layers in thin films etc.

The temperature dependence of the phonon energy for different R_e and R_m values is shown in figures 1–4. It can be seen that in all figures there is an anomaly, a kink around the magnetic phase transition temperature $T_N = 80 \text{ K}$ which arises from spin-phonon interactions. The phonons show a magnetic shift below T_N , where the rare earths moments in RMnO_3 start to order. The kink is due to the magnetoelectric effect, too. Above $T_C = 900 \text{ K}$ the phonon

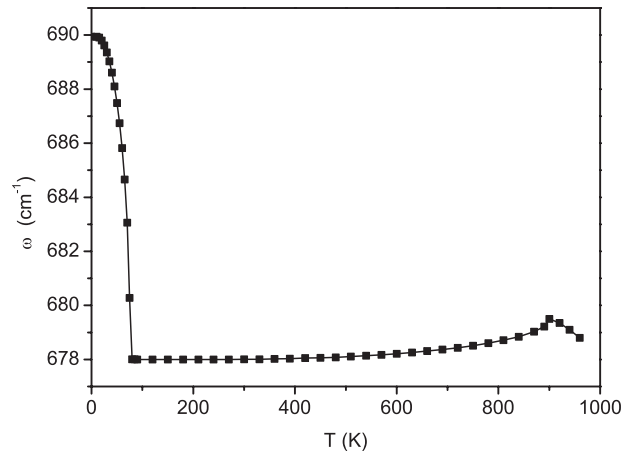


Figure 3. Temperature dependence of the phonon energy ω for the following spin-phonon interaction constants: $R_e = 6 \text{ cm}^{-1}$, $R_m = -6 \text{ cm}^{-1}$.

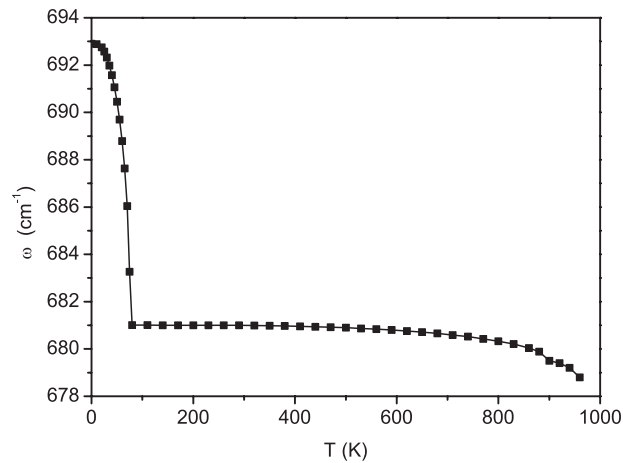


Figure 4. Temperature dependence of the phonon energy ω for the following spin-phonon interaction constants: $R_e = R_m = -6 \text{ cm}^{-1}$.

energy slightly decreases. It is plausible to expect these different behaviours of the phonon frequencies in figures 1–4, hardening or softening in dependence on the sign of R . The different multiferroic substances have different interactions between the two subsystems. In BiMnO_3 and YCrO_3 there is interaction between ferromagnetic and ferroelectric subsystems, in YMnO_3 and BiFeO_3 between antiferromagnetic and ferroelectric [1], and in BiCrO_3 films it was recently found that there is an interaction between antiferroelectricity and antiferromagnetism (or weak ferromagnetism) [24]. Modern studies of hexagonal YMnO_3 have revealed a coupling between the ferroelectric and magnetic ordering [25]. The obtained temperature behaviour in figure 4 was measured in the phonon spectra of BiFeO_3 by Haumont *et al* [8]. We will further discuss the influence of the parameters A_1 , R_m and g , because we will observe the anomalies around the magnetic phase transition. The pseudo-spin-phonon interaction R_e influences mainly the phonon energy between T_N and T_C .

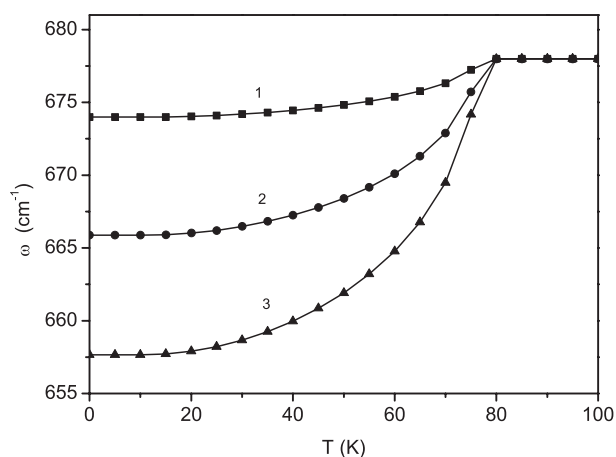


Figure 5. Temperature dependence of the phonon energy ω for $R_e = 6 \text{ cm}^{-1}$ and different magnetic spin-phonon interaction R_m : (1) $R_m = 2$, (2) 6, (3) 10 cm^{-1} .

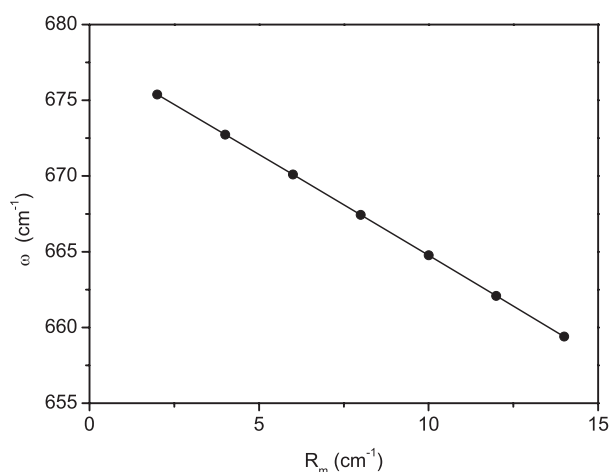


Figure 6. Temperature dependence of the phonon energy ω for $R_e = 6 \text{ cm}^{-1}$ and different magnetic spin-phonon interaction R_m : (1) $R_m = -2$, (2) -6 , (3) -10 cm^{-1} .

The shift of the phonon spectra is dependent not only on the sign of the spin-phonon interaction constant R_m but also on the magnitude of R_m which is indirectly connected with the radius of the rare earth ion. This is demonstrated in figures 5 and 6. With increasing magnetic spin-phonon coupling R_m the phonon frequency decreases linearly (figure 6). Our spin-phonon interaction constant R_m is connected through the first and second derivatives with the exchange interaction constant $A_1(r_i - r_j)$ which depends on the distance between the neighbouring spins. So it can be smaller when the distance is bigger, i.e. the radii of the ions are smaller, or greater for smaller distance, i.e. greater radius. So we have different R_m values in different multiferroic compounds. With decreasing R_m , i.e. with decreasing radius of the rare earth ion, the anomaly around T_N is smaller, for example for Y. The phonon energy shows a strong analogous dependence on the exchange interaction constant $A_1(r_i - r_j)$, which depends on the distance between the spins and indirectly on the radius of the ions. ω decreases with increasing A_1 . The magnetic phase transition temperature T_N increases with increasing A_1 .

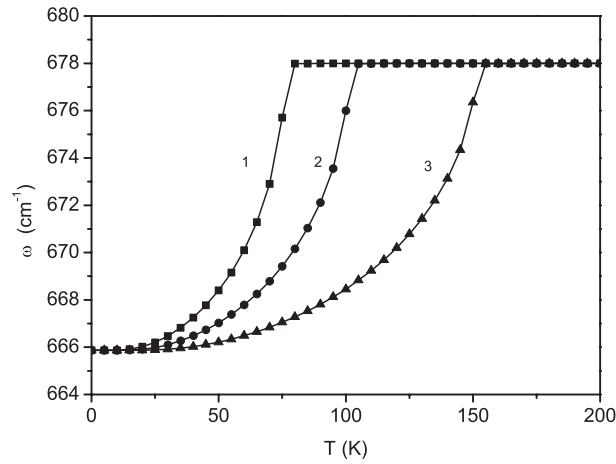


Figure 7. Temperature dependence of the phonon energy ω for $R_e = R_m = 6 \text{ cm}^{-1}$ and different g values: (1) $g = 50$, (2) 100 , (3) 200 cm^{-1} .

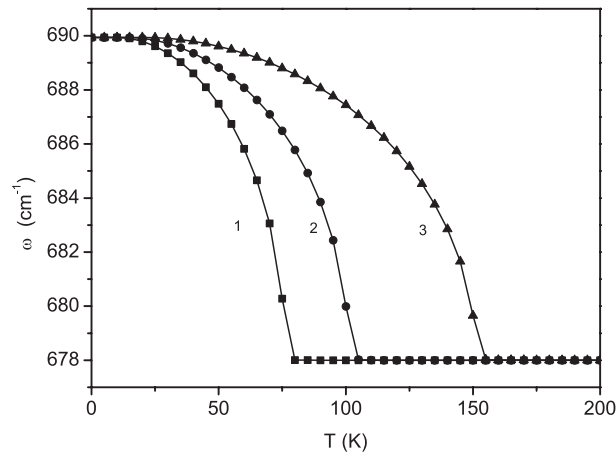


Figure 8. Temperature dependence of the phonon energy ω for $R_e = 6 \text{ cm}^{-1}$, $R_m = -6 \text{ cm}^{-1}$ and different g values: (1) $g = 50$, (2) 100 , (3) 200 cm^{-1} .

The effect of the coupling constant between the magnetic and electric subsystems g is shown in figures 7 and 8. It can be seen that the phonon energy depends strongly not only on g but also on the sign of the spin-phonon interaction R_m . With increasing g for $T = \text{const}$ the phonon energy is enhanced for $R_m < 0$ and reduced for $R_m > 0$. The magnetic phase transition T_N increases with increasing g and for $T_N = T_C = 900 \text{ K}$ the kink around T_N disappears. There is experimental evidence of different coupling strengths and different coupling mechanisms between the magnetic and ferroelectric systems in different multiferroics. The replacement of magnetic Ho by Y in YMnO_3 results in an even larger suppression of the thermal conductivity [5]. Sergienko *et al* [26] predicted that the polarization in HoMnO_3 would be enhanced by up to two orders of magnitude with respect to that in TbMnO_3 where the ME interaction term is linear in the electrical dipole moment.

We have calculated numerically the phonon damping in dependence on temperature and different interaction constants. The results are shown in figures 9 and 10. The damping γ

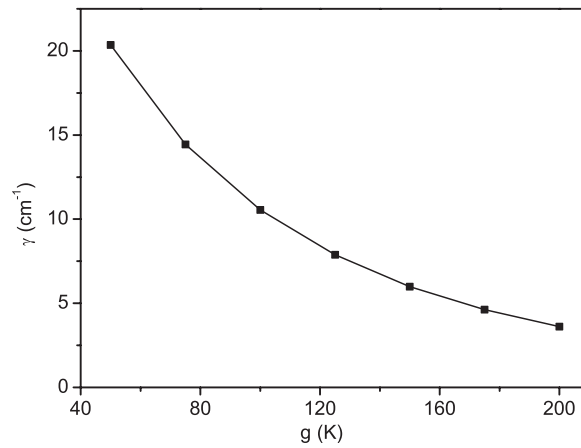


Figure 9. Dependence of the phonon damping γ on the magnetoelectric coupling g for $T = 60$ K and $R_e = R_m = 6$ cm⁻¹.

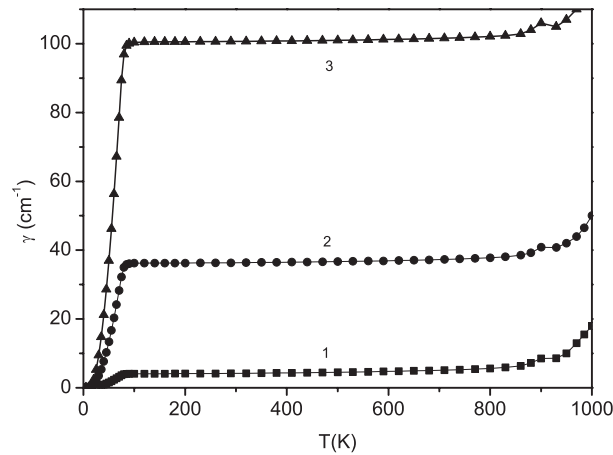


Figure 10. Temperature dependence of the phonon damping γ for $R_e = 6$ cm⁻¹, $g = 50$ cm⁻¹ and different values of the magnetic spin-phonon interaction constant R_m : (1) $R_m = 2$, (2) 6, (3) 10 cm⁻¹.

decreases with increasing magnetoelectric coupling constant g (figure 9). We obtain that γ increases with temperature and with increasing R_m (for the two cases $R_m > 0$ and $R_m < 0$, because the damping is proportional to R_m^2) (figure 10). It is clearly seen that around the phase transition temperatures T_N and T_C there are strong anomalies, in agreement with the experimental data of Haumont *et al* [8]. The damping increases with increase in the exchange interaction constants A_1 and J and with increase in the anharmonic pseudo-spin-phonon interaction constants R_m and R_e . The damping can be observed from the full width of the half maximum in Raman spectroscopic experiments. Sushkov *et al* [18] have obtained very different line widths in different multiferroic substances. The origin of the very different widths is not quite clear. We obtain that the damping of the phonon modes is strongly dependent on the magnetoelectric coupling g , on the exchange interaction constants A_1 , J and mostly on the spin-phonon interaction constants R_m and R_e . In figure 10 we have shown that the damping

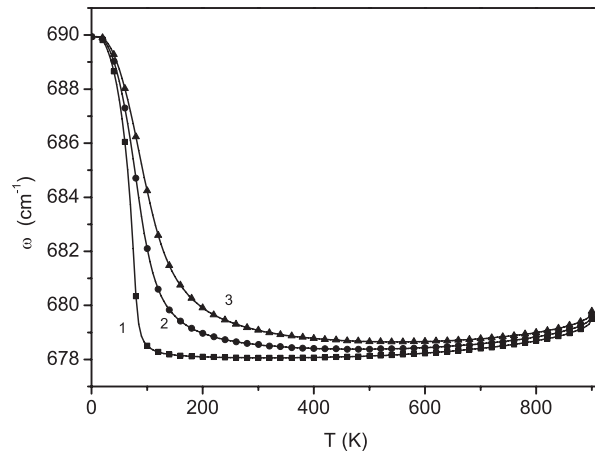


Figure 11. Temperature dependence of the phonon energy ω for $R_e = 6 \text{ cm}^{-1}$, $R_m = -6 \text{ cm}^{-1}$, $g = 50 \text{ cm}^{-1}$ and different H values: (1) $H = 0$, (2) 10, (3) 20 Oe.

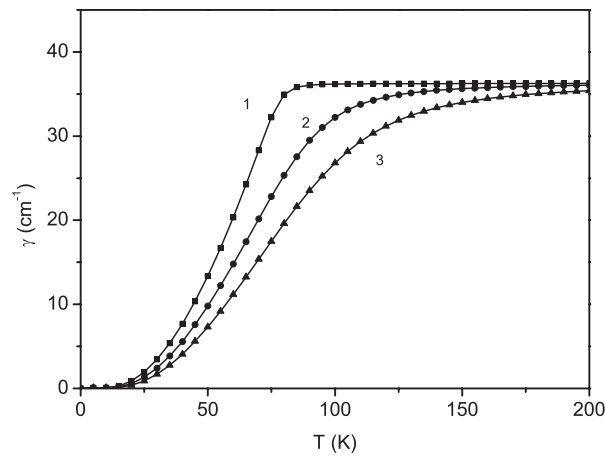


Figure 12. Temperature dependence of the phonon damping γ for $R_e = 6 \text{ cm}^{-1}$, $R_m = -6 \text{ cm}^{-1}$, $g = 50 \text{ cm}^{-1}$ and different H values: (1) $H = 0$, (2) 10, (3) 20 Oe.

decreases with decreasing R_m . R_m is indirectly connected with the radius of the rare earth ion, which is different in various multiferroics (see discussion after figures 5 and 6). So we have different R_m values in various multiferroic compounds which lead to different damping values, i.e. to different line widths in different multiferroic substances. The different anharmonic spin-phonon interactions are one of the possible explanations of the different line widths in different multiferroic substances.

The discussion above was given for $H = 0$. The influence of an applied magnetic field H on the phonon energy can be seen in figure 11. The phonon energy ω and the magnetic phase transition temperature T_N increase with increasing H and the kink around T_N disappears. This is in qualitative agreement with the experimental data of Cheong [19] and Barath *et al* [27]. The phonon damping decreases for larger values of the applied magnetic field H and the anomaly around T_N disappears, too (figure 12).

5. Conclusions

We have considered the coexistence and interplay of different properties—(anti)ferromagnetic, (anti)ferroelectric and phonon—in multiferroic materials based on the Heisenberg and transverse Ising models taking into account the anharmonic spin–phonon and phonon–phonon interaction terms. We have obtained for the first time the temperature dependence of the phonon spectrum including damping effects for different magnetoelectric couplings, exchange interactions and mostly for different spin–phonon interaction constants. The phonon energy and the phonon damping show strong anomalies around the two phase transition temperatures T_N and T_C which are due to the magnetoelectric and to the spin–phonon interaction. With decreasing magnetic spin–phonon coupling R_m , i.e. decreasing radius of the rare earth ion, the phonon frequency increases and the anomaly around T_N is smaller, for example for Y. We obtain that the phonon damping is strongly dependent on the magnetoelectric coupling g , on the exchange interaction constants A_1 and J and on the spin–phonon interaction constants R_m and R_e . The different anharmonic spin–phonon interaction constants (due for example to different rare earth ion radii or to different exchange interaction constants) are one of the possible explanations of the different line widths obtained in different multiferroic substances. The influence of an external magnetic field on the phonon spectrum is also calculated. We obtain that the phonon energy increases whereas the damping decreases with increasing H . The kink around T_N vanishes. The theoretical results are in qualitative agreement with the experimental data.

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