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Influence of Magnetic Order in Insulators on the Optical Phonon Frequency

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Summary. The frequency shift of long wavelength optical phonons in ferromagnetic insulators due to magnetic order is calculated. The relative frequency change is expected to be of order 10^{-3} to 10^{-2}.

Introduction

The theory of the superexchange interaction responsible for the order in magnetic insulators, does not yet allow a prediction of the superexchange coupling constants with resonable accuracy. The rough estimates which can be made are based on oversimplified models [1]. In these circumstances it is helpful to realize that the theory should furnish not only one constant, but a set of related parameters which are accessible to measurement.

Measurements of the magnetization under pressure or of the expansion coefficient determine the dependence of the superexchange interaction on the lattice constant [2, 3]. We show here that the effect of the magnetic order on the long wavelength optical phonon frequency can provide further information about the superexchange interaction. This is due to the fact that optical phonons involve the *relative* displacement of a non-magnetic lattice, which transmits the interaction, with respect to the magnetic lattice. This displacement is large enough so that second derivatives of the spin energy become important.

The Model

The Hamiltonian $H = H^l + H^m$ contains the 'pure lattice' energy H^l including anharmonic terms, and the spin energy

$$H^m = \sum_{i<j} I_{ij}\, \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{1}$$

where I_{ij} is the superexchange coupling constant between magnetic ions i, j and $\boldsymbol{S}$ the ion spin operator. Single ion spin dependent terms [4] will be neglected.

Specifically we treat compounds with Europium Oxide structure, and we suppose that the Curie temperature T_C is much smaller than the Debye temperature T_D. We confine ourselves to the nearest neighbour (n.n.) spin interaction. We consider an arbitrary magnetic ion with index o, and denote by the index n the n.n. spins ($n = 1, \ldots, 12$ for EuO structure).

The n.n. superexchange coupling constant I_{on} we suppose to be of the form

$$I_{on} = \sum_r J(d_1^{nr}, d_2^{nr}, x^{nr}) \tag{2}$$

where d_1^{nr} and d_2^{nr} are the distances between the n.n. magnetic ions o, n and the adjacent non-magnetic ions r ($r = 1, 2$ for EuO structure), and $x^{nr} = \cos\alpha^{nr}$, with α^{nr} the angles between these links (Fig. 1). J is a symmetric function of d_1 and d_2.

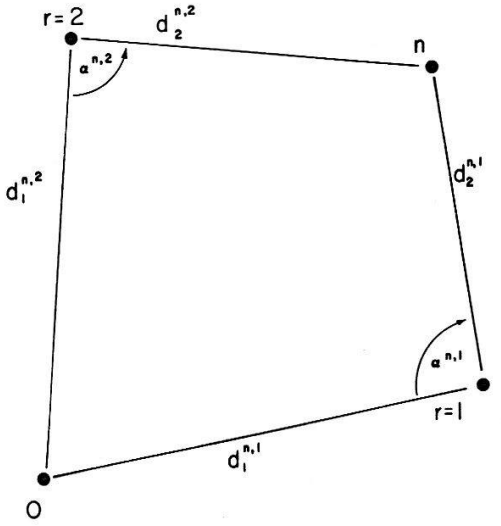

Figure 1

Symbols used in the description of the n.n. superexchange coupling constant I_{on}.

The Frequency Shift

In crystals with two atoms per unit cell optical phonons in the limit of infinite wavelength are described by the relative displacement $\boldsymbol{y}$ of the two sublattices [5]. The 'pure lattice' Hamiltonian therefore becomes for each mode a linear oscillator with the inter-sublattice potential V^l and the reduced mass μ of the sublattices.

$$V^l = \frac{1}{2} V_2^l y^2 + \text{anharmonic terms} \tag{3}$$

where V_2^l is related to the optical phonon frequency ω_0 (longitudinal or transverse) by $V_2^l = \mu \omega_0^2$ within the harmonic approximation ($T \ll T_D$). The displacement $\boldsymbol{y}$ is counted from the equilibrium position determined by the 'pure lattice' lattice constant a_0. Experimentally a_0 is obtained by extrapolating $a(T)$ for $T \gg T_C$, where no magnetic contribution occurs, to $T = 0$.

In magnetic crystals the lattice potential is perturbed by the order dependent spin energy. Its development in terms of displacements around a_0 contains a linear term, so that the lattice constant changes to a new equilibrium value $a_0 + \Delta a = a$. The harmonic term of the development of the spin energy in the displacement $\boldsymbol{u}$ around this equilibrium position reads

$$\frac{1}{2} V_2^m u^2 . \tag{4}$$

The volume change $\Delta\Omega$ produces a frequency shift through the anharmonic terms of the lattice potential, which is given by [6]

$$\frac{\Delta_1\omega}{\omega_0} = -\gamma_l \frac{\Delta\Omega}{\Omega} = -3\gamma_l \frac{\Delta a}{a_0} \tag{5}$$

within the usual approximation of considering a unique lattice Grüneisen constant γ_l.

The total potential then becomes

$$V = \frac{1}{2}\mu\left[(\omega_0 + \Delta_1\omega)^2 + \frac{1}{\mu} V_2^m\right] u^2 + \text{anharmonic terms}. \tag{6}$$

Since we are interested in the temperature range $0 < T \sim T_C \ll T_D$ the anharmonic terms of (6) can be neglected, and the total relative frequency shift becomes

$$\frac{\Delta\omega}{\omega_0} = \frac{\Delta_1\omega}{\omega_0} + \frac{V_2^m}{2\mu\omega_0^2} \tag{7}$$

disregarding terms of order $(\Delta_1\omega/\omega_0)^2$.

Our next task is to relate the quantities $\Delta_1\omega$ and V_2^m with the Hamiltonian H^m given by (1) and (2). Since all n.n. magnetic ion pairs are equivalent and the final result must include a thermodynamic average $\langle\ldots\rangle$ over the spin system, we can work from the beginning with the average spin energy

$$U^m = \frac{N}{2}\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1\rangle \sum_{n,r} J(d_1^{nr}, d_2^{nr}, x^{nr}) \tag{8}$$

where $\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1\rangle$ is the n.n. spin correlation.

Let us first consider a uniform expansion [7] of the lattice. In this case $d_1^{nr} = d_2^{nr} = (a_0 + \Delta a)/2$ (the interatomic distance is $a/2$) and $x^{nr} = 0$. The dependence of the lattice constant on the magnetic state is found from the Gibbs thermodynamic potential for zero pressure

$$G = \frac{N}{2}\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1\rangle \sum_{n,r} J(d_1^{nr}, d_2^{nr}, x^{nr}) + \frac{9 N a_0^3}{8 K_l}\left(\frac{\Delta a}{a_0}\right)^2 - T S(\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1\rangle) \tag{9}$$

where K_l is the lattice compressibility (without magnetic contributions [2]) and $a_0^3/4$ the volume per unit cell. We consider Δa and $\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1\rangle$ as parameters with respect to which G is a minimum. From $\partial G/\partial \Delta a = 0$ we have

$$\frac{\Delta a}{a_0} = -\frac{16}{3}\frac{K_l J_d}{a_0^2}\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1\rangle \tag{10}$$

where the subindex of J denotes a partial derivative. From symmetry $J_{d_1} = J_{d_2} = J_d$. All functions are taken at $a_0/2, a_0/2, 0$. The frequency shift due to the lattice expansion follows from (5) and (10).

Let us now consider a relative displacement $\boldsymbol{u}$ of the non-magnetic sublattice with respect to the magnetic one and develop (8) up to order u^2. To that end we have to know the quantities d_1^{nr}, d_2^{nr} and x^{nr} as functions of the components u_μ ($\mu = 1, 2, 3$) of $\boldsymbol{u}$. We shall demonstrate the calculation for a given pair of magnetic ions (o and

$n = 1$) and one non-magnetic ion $r = 1$. We choose a coordinate system with the magnetic ion o at the origin and the three orthogonal axis in the directions of the equilibrium positions of the n.n. non-magnetic ions. With the arrangement shown in Figure 2 we have

$$\boldsymbol{d}_1^{11} = \left(\frac{a}{2} + u_1, u_2, u_3\right) \qquad \boldsymbol{d}_2^{11} = \left(-u_1, \frac{a}{2} - u_2, -u_3\right)$$

and then

$$d_1^{11} = |\boldsymbol{d}_1^{11}| = \frac{a}{2}\left(1 + \frac{u_1}{a/2} + \frac{1}{2}\frac{u^2}{a^2/4} - \frac{1}{2}\frac{u_1^2}{a^2/4}\right)$$

$$d_2^{11} = |\boldsymbol{d}_2^{11}| = \frac{a}{2}\left(1 - \frac{u_2}{a/2} + \frac{1}{2}\frac{u^2}{a^2/4} - \frac{1}{2}\frac{u_2^2}{a^2/4}\right)$$

$$x^{11} = -\frac{\boldsymbol{d}_1^{11} \cdot \boldsymbol{d}_2^{11}}{d_1^{11}\, d_2^{11}} = \frac{u_1}{a/2} - \frac{u_2}{a/2} + \frac{u_3^2}{a^2/4} + 2\frac{u_1 u_2}{a^2/4}. \tag{11}$$

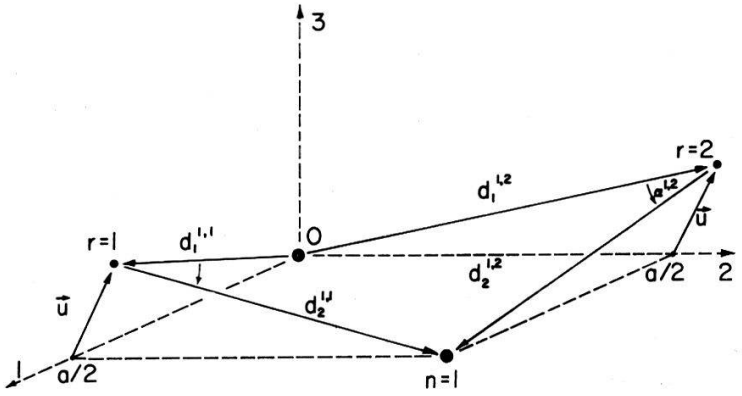

Figure 2

Symbols and coordinate system used in the development of the superexchange coupling constant I_{on} in terms of the relative sublattice displacement $\boldsymbol{u}$.

Analogous calculations have to be made for the second path of interaction $r = 2$ and for the twelve n.n. magnetic ions ($n = 1, \ldots, 12$). All these expressions are used in the series development of (8)

$$\begin{aligned} U^m = \frac{N}{2} \langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1 \rangle \sum_{n,r} \Bigg\{ & J + \left(J_{d_1} \frac{\partial d_1^{nr}}{\partial u_\mu} \frac{\partial u_\mu}{\partial u} + J_{d_2} \frac{\partial d_2^{nr}}{\partial u_\mu} \frac{\partial u_\mu}{\partial u} \right. \\ & \left. + J_x \frac{\partial x^{nr}}{\partial u_\mu} \frac{\partial u_\mu}{\partial u} \right) u + \left[J_{d_1 d_1} \left(\frac{\partial d_1^{nr}}{\partial u_\mu} \frac{\partial u_\mu}{\partial u} \right)^2 + J_{d_2 d_2} \left(\frac{\partial d_2^{nr}}{\partial u_\mu} \frac{\partial u_\mu}{\partial u} \right)^2 \right. \\ & + J_{xx} \left(\frac{\partial x^{nr}}{\partial u^\mu} \frac{\partial u^\mu}{\partial u} \right)^2 + 2 J_{d_1 d_2} \frac{\partial d_1^{nr}}{\partial u_\mu} \frac{\partial d_2^{nr}}{\partial u_\nu} \frac{\partial u_\mu}{\partial u} \frac{\partial u_\nu}{\partial u} \\ & + 2 J_{d_1 x} \frac{\partial d_1^{nr}}{\partial u_\mu} \frac{\partial x^{nr}}{\partial u_\nu} \frac{\partial u_\mu}{\partial u} \frac{\partial u_\nu}{\partial u} + 2 J_{d_2 x} \frac{\partial d_2^{nr}}{\partial u_\mu} \frac{\partial x^{nr}}{\partial u_\nu} \frac{\partial u_\mu}{\partial u} \frac{\partial u_\nu}{\partial u} \\ & + J_{d_1} \frac{\partial^2 d_1^{nr}}{\partial u_\mu \partial u_\nu} \frac{\partial u_\mu}{\partial u} \frac{\partial u_\nu}{\partial u} + J_{d_2} \frac{\partial^2 d_2^{nr}}{\partial u_\mu \partial u_\nu} \frac{\partial u_\mu}{\partial u} \frac{\partial u_\nu}{\partial u} \\ & \left. + J_x \frac{\partial^2 x^{nr}}{\partial u_\mu \partial u_\nu} \frac{\partial u_\mu}{\partial u} \frac{\partial u_\nu}{\partial u} \right] \frac{1}{2} u^2 \Bigg\}. \end{aligned}$$

The coefficients of products of the direction cosines $(\partial u_\mu/\partial u)\,(\partial u_\nu/\partial u)$ vanish when $\mu \neq \nu$, and the sum of the remaining terms becomes independent of the direction of $\boldsymbol{u}$. Finally we obtain, using the symmetry properties of J,

$$U^m = \frac{N}{2} \langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1 \rangle \left\{ 24\, J + \left[16\, J_{dd} + 32\, (J_d + J_{dx})\, \frac{2}{a} + 16\, (J_x + J_{xx}) \left(\frac{2}{a}\right)^2 \right] \frac{1}{2}\, u^2 \right\}. \tag{12}$$

The spin correlation has been assumed independent of u, since the spins do not reach equilibrium during the time of a lattice vibration. The linear term in u vanishes because of the inversion symmetry of the crystal. From (12) and (4) we identify

$$V_2^m = \frac{8\,N}{a_0^2} \langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1 \rangle \left[a_0^2\, J_{dd} + 4\, a_0\, (J_d + J_{dx}) + 4\, (J_x + J_{xx}) \right]. \tag{13}$$

Up to terms linear in the derivatives of J we can replace a by a_0.

Results

Replacing (5), (10) and (13) in (7) we finally obtain for the relative frequency shift

$$\frac{\omega - \omega_0}{\omega_0} = \frac{4 \langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1 \rangle}{\mu_0\, a_0^2\, \omega_0^2} \left\{ 4\, a_0 \left[\left(1 + \frac{\gamma_l\, K_l\, \mu_0\, \omega_0^2}{a_0} \right) J_d + J_{dx} \right] + 4\, (J_x + J_{xx}) + a_0^2\, J_{dd} \right\} \tag{14}$$

with $\mu_0 = \mu/N$ the reduced mass per unit cell. As expected, the result does not only depend on J_d and J_{dd}, which can be measured through the pressure dependence of the Curie temperature [3], but also on the angular derivatives in the combination $a_0\, J_{dx} + J_x + J_{xx}$.

Numerical Estimate

To estimate the order of magnitude of $\Delta\omega/\omega_0$ we disregard the angular derivatives of J since we have no information about them. For the remaining terms we use typical values for EuO: $\mu_0 = 2.4 \cdot 10^{-23}$ g, $\omega_0 \approx 3.15 \cdot 10^{13}$ sec^{-1} (transverse optical phonon frequency), $a_0 = 5.14$ Å. The values $K_l = 0.94 \cdot 10^{-12}$ erg^{-1} cm^3 and $\gamma_l = 1.9$ are taken from Reference [2]. Using the experimental curve T_C vs. $\Delta\Omega/\Omega$ of Reference [3] we obtain $dT_C/da = -2.9 \cdot 10^{10}$ °K cm^{-1} and $d^2T_C/da^2 = 7 \cdot 10^{18}$ °K cm^{-2}. From the relation $I_{on} = -3\, k_0\, T_C/z\, S\,(S+1)$ given by the molecular field theory, with $z = 12$ and $S = 7/2$, we deduce $J = -0.75 \cdot 10^{-16}$ erg, $J_d = 3.15 \cdot 10^{-8}$ erg cm^{-1} and $J_{dd} = -16.2$ erg cm^{-2}.

Replacing in (14) the above numerical values we get

$$\frac{\omega - \omega_0}{\omega_0} \approx -2 \cdot 10^{-3} \langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1 \rangle. \tag{15}$$

The spin correlation function is well known theoretically at very low temperatures $T \ll T_C$ (spin wave region) and also for $T \gg T_C$. In the temperature range in which we are interested, namely $0 < T \approx T_C$, only approximate theoretical results exist (molecular field theory, Cluster expansion [8]). We can also obtain this function empirically for EuO from measurements of the magnetic specific heat which give the

relative change of the magnetic energy with temperature [2]. Within the n.n. interaction it follows from (8) and (10) that

$$\frac{U^m(T)}{U^m(0)} = \frac{\langle \boldsymbol{S}_0 \cdot \boldsymbol{S}_1 \rangle}{S^2} + 0(J_d) \,. \tag{16}$$

Based on the values of the specific heat of Reference [2], Figure 3 shows the relative frequency shift (15) and also the partial contributions due to the thermal expansion (5) and to the harmonic terms of the magnetic potential.

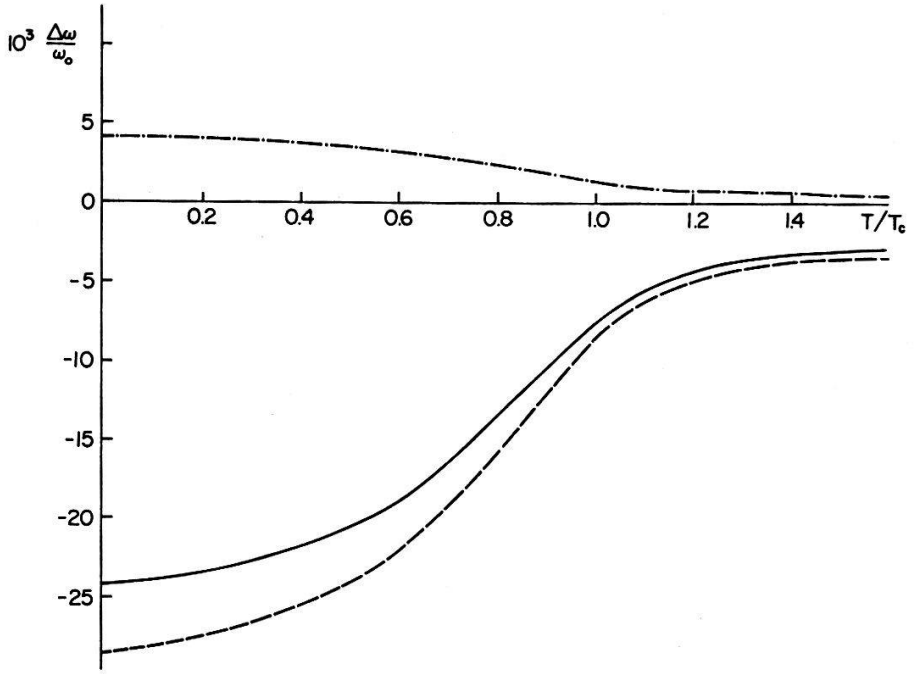

Figure 3

Estimated relative frequency shift of a transverse long wavelength optical phonon vs temperature in EuO.
—·—·— Contribution due to the thermal expansion. — — — — Contribution due to the harmonic terms of the magnetic potential. ——— Total shift.

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References

[1] P. W. ANDERSON, *Magnetism*, Ed. by G. T. RADO and H. SUHL (Academic Press Inc., New York 1963), Vol. 1, Chap. 2.
[2] B. E. ARGYLE, N. MIYATA and T. D. SCHULTZ, Phys. Rev. *160*, 413 (1967).
[3] D. B. MCWHAN, P. C. SOUERS and G. JURA, Phys. Rev. *143*, 385 (1966).
[4] E. CALLEN and H. B. CALLEN, Phys. Rev. *139*, A455 (1965).
[5] C. KITTEL, *Quantum Theory of Solids* (John Wiley and Sons, Inc., New York 1963), p. 37.
[6] J. M. ZIMAN, *Electrons and Phonons* (Oxford University Press, London 1963), p. 153.
[7] C. P. BEAN and D. S. RODBELL, Phys. Rev. *126*, 104 (1962).
[8] E. CALLEN and H. B. CALLEN, Phys. Rev. *136*, A1675 (1964).