EFFECTS OF MAGNON-ACOUSTICAL PHONON HYBRIDIZATION IN THE FAR-INFRARED ABSORPTION SPECTRUM OF FeF_2*

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It is shown theoretically that, if a strong magnetic field H is applied, effects due to magnon–acoustical phonon hybridization should be apparent in the far-infrared absorption spectrum of FeF_2 consisting in a splitting and displacement of the two-magnon absorption line when H approaches a value of the order of 200 kGs. The extinction coefficient for absorption processes with creation of one magnon and one hybridized magnon-acoustical phonon excitation, and its dependence on the field H, are calculated.

1. Introduction

Ferrous fluoride FeF_2 is a collinear, two-sublattice antiferromagnet which orders at 78.4° K and has the rutile crystal structure. The unit cell of this compound with magnetic structure is shown in Fig. 1. Infrared, Raman and neutron spectroscopies have been used to study the elementary magnetic excitations (magnons) and crystal lattice excitations (phonons). The neutron spectroscopy data prove the existence of strong coupling between acoustical phonons and magnons, which leads to neutron scattering from hybridized magnon–acoustical phonon excitations rather than from pure magnons or phonons. In experiment this is apparent by a "repulsion" of the dispersion curves in a frequency range in which the frequencies of the interacting excitations lie close or are equal to one another [1–3].

Since the magnon frequency (without an external magnetic field) in the Brillouin zone centre (i. e. in the region accessible to investigation by first order Raman scattering) is 52.7 cm^{-1}, the acoustical phonon frequency is practically equal to zero and the lowest optical phonon (the B_{1g} symmetry phonon) frequency is 73 cm^{-1}, one can obtain B_{1g}-optical phonon–two magnons resonance interaction by applying an external magnetic field [4–6].

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However, the frequency of the magnon is too low to observe magnon–B_{1g}-optical phonon resonance interaction in the magnetic fields now available.

In this paper we show that magnon–acoustical phonon interaction can be observed by the method of far-infrared spectroscopy. It is well known that, in the FeF_2-absorption spectrum, with the incident beam polarization vector ε parallel to the c-axis ($\varepsilon || c$), the

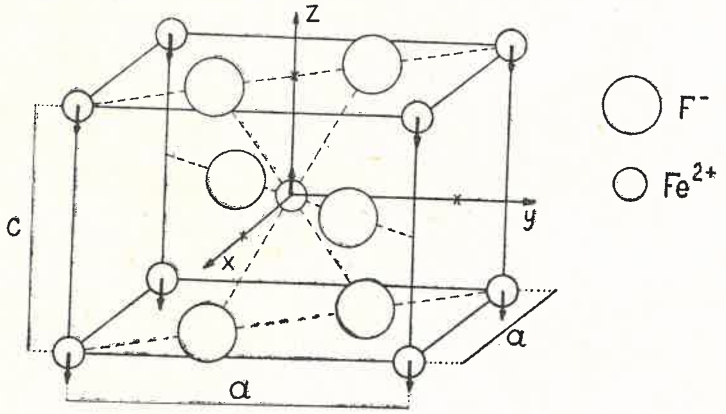

Fig. 1. Crystal structure in the antiferromagnetic state (Lovesey [3]) and coordinate system xyz used in this paper

154.4 cm^{-1} spectral line occurs, whereas if the vector ε is perpendicular to the c-axis ($\varepsilon \perp c$) a much weaker spectral line occurs at 154 cm^{-1} [7, 8]. It is moreover known that the occurrence of these spectral lines is related with the simultaneous excitation of two magnons approximately with the wave vectors $\boldsymbol{k}$ and $-\boldsymbol{k}$. Parity conservation causes that in absorption processes only states of negative parity, i. e. states $|\boldsymbol{k}\rangle = (1/\sqrt{2})(|\uparrow \boldsymbol{k}, \downarrow -\boldsymbol{k}\rangle - |\uparrow -\boldsymbol{k}, \downarrow \boldsymbol{k}\rangle)$ can be excited. The symbols "$\uparrow$" and "$\downarrow$" distinguish the two kinds of magnons possible in an antiferromagnet. Taking into account that the density of one-magnon states exhibits a sharp maxima in the points X, M, A and R of the Brillouin zone [9, 10] and the selection rules for quantum transitions in the absorption processes [9], one finds that for $\varepsilon || c$ and $\varepsilon \perp c$ the two-magnon states $|\boldsymbol{k}\rangle$ are excited from the point A and X, respectively. Neutron spectroscopy data [1] give the energy of the magnon from the point X as equal to about 80.7 cm^{-1} whereas that of the TA$\perp$ phonon (the one interacting with the magnons) as about 98.4 cm^{-1}. Thus it is possible, by applying a magnetic field, to reach the resonance interaction between these excitations from the point X. The symbol TA$\perp$ stands for the transversal acoustical phonon for which the unit vector e_k in the direction of the lattice atom displacements from their equilibrium position is perpendicular to the xy-plane if the wave vector $\boldsymbol{k}$ lies in this plane. No interaction occurs between the two remaining acoustical phonons and magnons for reasons of symmetry.

From the above experimental data it is easy to note that the energy of the state $|\boldsymbol{k}\rangle$ is smaller than the sum of the energies of the states $|\uparrow \boldsymbol{k}\rangle$ and $|\downarrow \boldsymbol{k}\rangle$. The difference is due to magnon–magnon interaction [11] which we take into consideration approximately.

In Section 2 we give the Hamiltonian of the magnon–phonon system in FeF_2 and discuss the hybridization problem. The absorption phenomenon with simultaneous creation of one "pure" magnon and one hybridized magnon–acoustical phonon excitation is discussed in Section 3. In Section 4 are drawn and discussed some essential conclusions.

2. *Hamiltonian of the magnon–phonon system in FeF_2*

Let us consider FeF_2 at sufficiently low temperature when the spin wave approximation is valid. For the reasons given in the Introduction, we restrict ourselves to but one phonon branch i.e. to the TA⊥ phonons neglecting the existence of the two remaining acoustical phonon branches. The Hamiltonian H of the magnon and phonon systems of FeF_2, coupled by magnon–phonon interaction described by a Hamiltonian H_{m-ph}, is of the form [2, 10, 12];

$$H = \sum_k E_{\uparrow k}\alpha^+_{\uparrow k}\alpha_{\uparrow k} + \sum_k E_{\downarrow k}\alpha^+_{\downarrow k}\alpha_{\downarrow k} + \sum_k E_k a^+_k a_k + H_{m-ph}, \quad (1)$$

where $E_{\uparrow k}$ and $E_{\downarrow k}$ are the energies of both kinds of antiferromagnons, E_k is the energy of the TA⊥ phonon whereas $\alpha^+_{\uparrow k}$, $\alpha^+_{\downarrow k}$ and a^+_k ($\alpha_{\uparrow k}$, $\alpha_{\downarrow k}$ and a_k) are the creation (annihilation) operators of these elementary excitations, respectively. If the external magnetic field is directed along the negative z-axis, the magnon energies are given by the following expression

$$E_{\uparrow(\downarrow)k} = E^0_k \mp g\mu_B H_z, \quad (2)$$

where the upper (lower) sign refers to the symbol ↑ (↓), E^0_k denotes the magnon energy at zero external magnetic field, μ_B — the Bohr magneton, and g — Lande's factor. According to Eq. (2), it is possible to vary the magnon energies in experiment and, in this way, to achieve magnon–phonon resonance interaction.

The model of magnon–phonon interaction Hamiltonian consisting in a phonon modulation of the crystal field transferred to the spin system by way of spin-orbit coupling is due to Lovesey [2]. This Hamiltonian is given by the following expression [2]

$$H_{m-ph} = \sum_k (V_k\alpha^+_{\downarrow k} + V^*_{-k}\alpha_{\uparrow -k})(a_k + a^+_{-k}), \quad (3)$$

where V_k is a coupling constant dependent on k and $0 = V_{k=0} \leqslant V_k \leqslant V_{k_B} = 1.6\ \text{cm}^{-1}$ (k_B is certain vector from Brillouin zone boundary). Taking into account that photon absorption at $\varepsilon \perp c$ occurs mainly with excitation of magnons from the point X, we are interested in the nearest surroundings of this Brillouin zone point. Thus we have neglected in Eq. (3) the interaction of the "↑"-magnons with the phonons since the crossing point of the appriopriate dispersion curves lies far from the point X. In Eq. (3) we have omitted as well the terms containing $a^+_k\alpha^+_{\downarrow -k}$ and $a_k\alpha_{\downarrow -k}$, related with the simultaneous creation and annihilation of a magnon–phonon pair; in the first order of perturbation treatment they do not contribute to magnon–phonon hybridization.

Performing the diagonalizing transformation;

$$\alpha_{\downarrow k} = e^{-i\varphi_k} \cos\frac{\beta_k}{2} c_{1k} + e^{-i\varphi_k} \sin\frac{\beta_k}{2} c_{2k} \tag{4a}$$

$$a_k = -e^{i\varphi_k} \sin\frac{\beta_k}{2} c_{1k} + e^{i\varphi_k} \cos\frac{\beta_k}{2} c_{2k} \tag{4b}$$

(and similar expressions for $\alpha^+_{\downarrow k}$ and a^+_k obtained by taking a Hermitian conjugation of (4a) and (4b), respectively) where β_k is given in a first approximation by the equation

$$\tan\beta_k = \frac{2|V_k|}{E_{\downarrow k} - E_k}, \tag{5}$$

we obtain the Hamiltonian in the following form

$$H = \sum_k E_{\uparrow k}\alpha^+_{\uparrow k}\alpha_{\uparrow k} + \sum_k E_{1k}c^+_{1k}c_{1k} + \sum_k E_{2k}c^+_{2k}c_{2k}, \tag{6}$$

where the energies of the two hybridized modes are given, in the same approximation, by the following expressions

$$E_{1(2)k} = \tfrac{1}{2}(E_{\downarrow k} + E_k) \mp \tfrac{1}{2}\left[4|V_k|^2 + (E_{\downarrow k} - E_k)^2\right]^{\frac{1}{2}}. \tag{7}$$

In Eq. (7), the upper sign refers to the energy E_{1k} and lower sign to E_{2k}, and the phase coefficient φ_k is defined as $V_k = |V_k| \exp(2i\varphi_k)$.

3. Far-infrared absorption

Two different mechanisms of photon–two magnons coupling have been suggested. The photon induced exchange mechanism proposed by Tanabe, Moriya and Sugano [13] is the more effective one. However, we are not interested in a microscopic model of the Hamiltonian, and thus consider the spin Hamiltonian H_s derived from the theory of crystal symmetry. This Hamiltonian, invariant under all operations of the magnetic space group of FeF_2, is of the form [14];

$$H_S = \sum_{\langle ij \rangle} \{D_1(S^x_iS^x_j + S^y_iS^y_j)(\varepsilon_x\sigma_y + \varepsilon_y\sigma_x) + D_2(S^x_iS^y_j - S^y_iS^x_j)(\varepsilon_x\sigma_y - \varepsilon_y\sigma_x)$$
$$+ D_3(S^x_iS^x_j + S^y_iS^y_j)\varepsilon_z\sigma_x\sigma_y\sigma_z\}, \tag{8}$$

where D_1, D_2 and D_3 are coupling constants involving the matrix elements of electric dipole and exchange interactions [10, 13, 14], σ_x is defined as $\sigma_x = \text{sign}\,(r_i - r_j)_x$ i. e. $\sigma_x = 1$ at $(r_i - r_j)_x > 0$ and $\sigma_x = -1$ at $(r_i - r_j)_x < 0$, etc.; and summation runs over all pairs of nearest neighbour spins.

The extinction coefficient h is defined as

$$h = \frac{\partial}{\partial L}\left(\frac{N_2}{N_1}\right), \tag{9}$$

where N_1 and N_2 are the numbers of incident and respectively scattered photons per unit time per unit cross-sectional area of the crystal, and L is the width of the crystal sample. The ratio N_2/N_1 can be written as [15]

$$\frac{N_2}{N_1} = \frac{W(t)L\varepsilon^{1/2}}{tn_1c}, \tag{10}$$

where $W(t)$ is the probability of annihilation up to the moment of time t of an incident photon possessing a given polarization and wave vector, ε is the dielectric constant for the incident light, and n_1 is the number of photons in the crystal sample. We neglect, for the time being, the magnon–phonon coupling. In first order of the time dependent perturbation theory we obtain the extinction coefficient $h_\perp$, at $\varepsilon \perp c$, for photon absorption with excitation of a pair of magnons in the following form

$$h_\perp = \frac{32\pi S^2\varepsilon^{1/2}}{\hbar c}\sum_k (n_{\uparrow k}+1)(n_{\downarrow k}+1)\left[D_1^2+D_2^2(u_k^2+v_k^2)^2\right]\cos^2\frac{k_zc}{2}$$
$$\times\left[\sin^2\frac{k_xa}{2}\cos^2\frac{k_ya}{2}\varepsilon_y^2+\cos^2\frac{k_xa}{2}\sin^2\frac{k_ya}{2}\varepsilon_x^2\right]\delta(\hbar\omega-E_{\downarrow k}-E_{\uparrow k}) \tag{11}$$

where ω is the frequency of the incident photon, and $n_{\uparrow k}$ and $n_{\downarrow k}$ are the population numbers of the magnons. Equation (11) can be simplified by taking into account that the excited magnons have wave vectors from the nearest surroundings of the point X. Thus we can put $u_k^2 = 1$, $v_k^2 = 0$, $n_{\uparrow k} = n_{\downarrow x}$, $n_{\downarrow k} = n_{\uparrow x}$ (x denotes $\boldsymbol{k}$ from the point X). Obviously such an approximation provides no possibility for a discussion of the line-shape which, in two--magnon absorption processes, is determined by two elements: the finite life-time of magnons defined by the relaxation processes, and the circumstance that magnons are excited from the whole Brillouin zone and not only from the point X (the appearance of a sharp maximum in the absorption spectrum is due to the high density of magnon states in the point X). We can include approximately both sources of the half-width Γ of the spectral line by performing the mathematical substitution

$$\delta(\hbar\omega-E_{\uparrow k}-E_{\downarrow k}) \to \frac{1}{\pi}\frac{\Gamma}{(\hbar\omega-E_{\uparrow k}-E_{\downarrow k})^2+\Gamma^2} \tag{12}$$

treating Γ as a phenomenological parameter. Finally, we obtain $h_\perp$ in the following form:

$$h_\perp = \frac{4NS^2\varepsilon^{1/2}}{\hbar c}(n_{\uparrow x}+1)(n_{\downarrow x}+1)(D_1^2+D_2^2)\frac{\Gamma_0}{(\hbar\omega-E_{\uparrow x}-E_{\downarrow x})^2+\Gamma_0^2}, \tag{13}$$

where N is the number of unit cells of the crystal.

Returning to the case of magnon–phonon interaction and taking into account Eqs (4), (6), (11–13), we obtain the extinction coefficient for absorption processes with creation of one "↑"-magnon and one hybridized "↓"-magnon–TA⊥–phonon excitation in the form

$$h_{\perp} = \frac{32\pi S^2 \varepsilon^{1/2}}{\hbar c} \sum_{k} (n_{\uparrow k}+1)\,[D_1^2 + D_2^2 (u_k^2 + v_k^2)^2]$$

$$\times \cos^2 \frac{k_z c}{2} \left(\sin^2 \frac{k_x a}{2} \cos^2 \frac{k_y a}{2}\, \varepsilon_y^2 + \cos^2 \frac{k_x a}{2} \sin^2 \frac{k_y a}{2}\, \varepsilon_x^2 \right)$$

$$\times \left[(N_{1k}+1) \cos^2 \frac{\beta_k}{2}\, \delta(\hbar\omega - E_{\uparrow k} - E_{1k}) + (N_{2k}+1) \sin^2 \frac{\beta_k}{2}\, \delta(\hbar\omega - E_{\uparrow k} - E_{2k}) \right] \qquad (14)$$

or

$$h_{\perp} = \frac{4NS^2 \varepsilon^{1/2}}{\hbar c} (n_{\uparrow x}+1)\,(D_1^2 + D_2^2) \left\{ \cos^2 \frac{\beta_x}{2} (N_{1x}+1) \right.$$

$$\left. \times \frac{\Gamma_1}{(\hbar\omega - E_{\uparrow x} - E_{1x})^2 + \Gamma_1^2} + \sin^2 \frac{\beta_x}{2} (N_{2x}+1) \frac{\Gamma_2}{(\hbar\omega - E_{\uparrow x} - E_{2x})^2 + \Gamma_2^2} \right\}. \qquad (15)$$

Eqs (14) and (15) are the counterparts of our preceding expressions for non-hybridized magnons i. e. Eqs (11) and (13), respectively. It should be stated that the parameters Γ_0, Γ_1 and Γ_2 which occur in Eqs (12) and (14) are in general different.

4. *Conclusions and discussion*

Halley and Silvera [7, 8] have found that an external magnetic field of 26 kGs has no influence on the two-magnon absorption spectral line of FeF_2. The available literature reports no experiment on this line in a strong magnetic field e. g. of the order of 200 kGs. We assume that such strong field has no influence on the two-magnon line as well, if the hybridization does not exist. It is equivalent to the assumption that the magnon–magnon coupling, which participates in determination of the position and line–shape of the two-magnon absorption spectral line [11], does not depend on an external magnetic field and that such strong magnetic field does not cause any structural transitions, which could change the structure of elementary excitations in FeF_2. Although there is no experimental data, the second assumption seems to be reasonable because of existence of high anisotropy field in FeF_2.

In the present paper we have shown that in magnetic field of the order of 200 kGs effects due to magnon–TA⊥–phonon hybridization can become observable. These effects show up in the experiment as a specific behaviour of the two-magnon absorption line in the external magnetic field. This behaviour is described by Eq. (15) from which one can draw the conclusion that, when H increases up to a value $H_{res} = 190$ kGs at which $E_{\downarrow x} = E_x$, a new line should appear corresponding to an absorbed energy equal to $E_{2x} + E_{\uparrow x}$, and the initial line should gradually lose its intensity on behalf of this new line. At resonance, when $E_{\downarrow x} = E_x$, both lines should have the same intensity, equal to one half of the initial line intensity. As H further increases, the total intensity should be taken over by the new line, which now becomes identical to the initial line.

Obviously Eqs (13, 14) were derived neglecting the magnon–magnon coupling. It is known that the energy reduction ΔE of the two-magnon state $|\boldsymbol{k}\rangle$ is due to this interaction [11]. In the case of FeF_2 $\Delta E \equiv \Delta E_0 \cong 7.4\ \mathrm{cm}^{-1}$ what is the conclusion from the experimental data given in the Introduction. Thus, the effects due to the magnon–magnon coupling can be taken into account by suitable displacement ΔE of the extinction coefficient peak, which is calculated according to Eq. (13) or Eq. (14), in the lower energy direction. In the case when the absorption is related with the simultaneous creation of one magnon and one hybridized magnon–phonon excitation the problem is more complicated. It is due to the fact that now the interaction causing the energy reduction has more

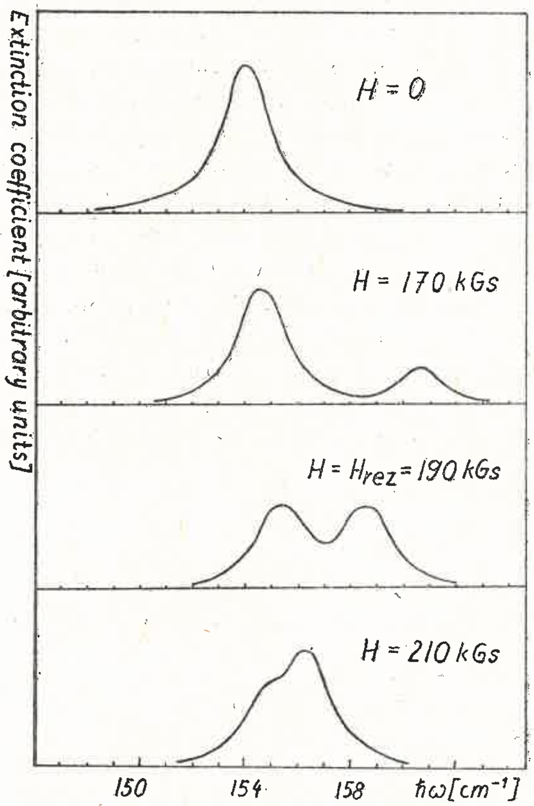

Fig. 2. Two-magnon absorption line-shape for fourth values of the external magnetic field. Here $\Gamma_1 = \Gamma_2 = 1\ \mathrm{cm}^{-1}$ is taken

complex form. Since the hybridized magnon–phonon excitation $|\psi\rangle$ is a superposition of the magnon $|\psi_m\rangle$ and the phonon $|\psi_{ph}\rangle$ i. e. $|\psi\rangle = c_1|\psi_m\rangle + c_2|\psi_{ph}\rangle$, its interaction with the magnon results from the magnon–magnon and magnon–phonon interactions. Usually the magnon–phonon interaction is weaker than the magnon–magnon one (as is the case for FeF_2) and we can omit it. Under this assumption the interaction between magnon and hybridized magnon–phonon excitation has the same structure as the magnon–magnon interaction and is proportional to it with c_1 as a proportionality coefficient. All results of Ref. [11] are then valid in the case of the magnon–hybridized magnon–phonon excitation interaction, on condition that the magnon–magnon interaction is replaced by this one multiplied by c_1.

For our further discussion we write the energy reduction in the form $\Delta E = \Delta E_0(a_2 c_1^2 + a_3 c_1^3 + \ldots)$where $a_i(i = 2,3, \ldots)$ are certain coefficients. For simplicity we restrict ourselves to the term $\Delta E_0 a_2 c_1^2$ giving the main contribution (in perturbation treatment this term contains second order contribution) and neglect all higher terms putting $a_2 = 1$ ($\Delta E = \Delta E_0$ for $c_1 = 1$).

The two-magnon absorption line-shape calculated under above described assumptions for several values of the magnetic field is shown in Fig. 2 where $\Gamma_1 = \Gamma_2 = 1\ \mathrm{cm}^{-1}$ is taken. It should be noted that experimental data concerning the line half-width are scarce. Nonetheless the value $\Gamma = 1\ \mathrm{cm}^{-1}$ seems to be reasonable for sufficiently low temperatures. So far as can be seen from Fig. 2 the two-magnon spectral line should be split in experiment in which the external magnetic field of the order of 200 kGs is applied. Another effects which should be observable in the two-magnon absorption spectrum consist in existence of a spectrum "mass centre" displacement and asymmetric behaviour of the spectral line with regard to the sign change of the difference $H - H_{\mathrm{res}}$. These effects are due to the "↓"-magnon–TA⊥–phonon hybridization and magnon–magnon coupling. Although the effects predicted by us require the application of a strong magnetic field, they can nonetheless serve as a criterion for the assessment of the microscopic model of magnon–magnon interaction. The suggested experiments consisting in a splitting and displacement of the two-magnon absorption spectral line in a strong magnetic field can provide interesting information about the magnon-phonon and magnon-magnon interactions.

REFERENCES

[1] B. D. Rainford, J. G. Houmann, H. J. Guggenheim, 5th I.A.E.A. Symposium on Neutron Inelastic Scattering, Grenoble 1972, France, p. 655.

[2] S. W. Lovesey, *J. Phys.* **C5**, 2769 (1972).

[3] S. W. Lovesey, *Comments Solid State Phys.* **7**, 117 (1976).

[4] E. N. Economou, K. L. Ngai, T. L. Reinecke, J. Ruvalds, R. Silberglitt, *Phys. Rev.* **B13**, 3135 (1976).

[5] A. Stasch, Wissenschaftlicher Tätigkeitsbericht, Max-Planck Institut für Festkörperforschung, Stuttgart–Grenoble, Project III-57 (1976).

[6] A. Stasch, *Verhandlungen der Deutschen Physikalischen Gesellschaft* **1**, 83 (1977); Frühjahrstagung Münster 1977.

[7] J. W. Halley, I. Silvera, *Phys. Rev. Lett.* **15**, 654 (1965).

[8] J. W. Halley, I. Silvera, *Phys. Rev.* **149**, 415 (1966).

[9] V. V. Eremenko, *Vvedenye v opticheskuyu spektroskopiyu magnetikov*, Naukova Dumka, Kiev 1975, p. 143.

[10] P. A. Fleury, R. Loudon, *Phys. Rev.* **166**, 514 (1968).

[11] C. R. Natoli, J. Ranninger, *J. Phys.* **C6**, 345 (1973); **C6**, 386 (1973).
[12] C. Kittel, *Quantum Theory of Solids*, Wiley, New York 1966.
[13] Y. Tanabe, T. Moriya, S. Sugano, *Phys. Rev. Lett.* **15**, 1023 (1965).
[14] S. J. Allen, R. Loudon, P. L. Richards, *Phys. Rev. Lett.* **16**, 463 (1966).
[15] R. Loudon, *Proc. R. Soc.* **275**, 218 (1963).
[16] R. C. Ohlmann, M. Tinkham, *Phys. Rev.* **123**, 425 (1961).