curve in Fig. 3, together with the temperature dependence of the low-frequency mode. The upper four points fall closely on the modified Curie law described by Rupprecht and Bell, but the experimental error in $\omega_{t_1}^2$ barely excludes normal Curie-law behavior. Davis[13] has recently measured the dielectric constant below 80°K, and has found deviations from the Curie law under 30°K. The one measured frequency in this region (∼12°K) also indicates a value corresponding to deviations found by Davis. The extremely low "Curie temperature" makes this crystal ideal for the investigation of the "soft" mode in the paraelectric cubic state. The temperature variation of this vibration is in good agreement with the temperature-dependence of the dielectric constant related by the Cochran-Cowley[7,15] theory of ferroelectricity in perovskite crystals.

ACKNOWLEDGMENTS

We would like to thank Prof. A. Smakula, Material Center for Science and Engineering, MIT, for the sample. All computations were performed on the IBM 7094 computer at the MIT Computation Center.

---

[15] W. Cochran and R. A. Cowley, J. Phys. Chem. Solids **23**, 447 (1962).

PHYSICAL REVIEW VOLUME 154, NUMBER 2 10 FEBRUARY 1967

Microscopic Theory of Far-Infrared 2-Magnon Absorption in Antiferromagnets. II. Second-Order Process and Application to MnF_2

J. Woods Halley[*][†]
Faculte des Sciences, Orsay, France

(Received 11 July 1966; revised manuscript received 28 September 1966)

A theory of a second-order mechanism giving two-magnon electric dipole absorption in rutile structure antiferromagnets is developed. In the mechanism, the absorption arises from indirect coupling of the spins to the field through the infrared-active optical phonons via the exchange-strictive part of the spin-phonon interaction. Detailed expressions are derived for the constants in the phenomenological Hamiltonian used by Allen *et al.* in interpreting experiments on a two-magnon electric dipole absorption recently observed in MnF_2 at 110 cm^{-1}. Thus, the frequency, temperature dependence, and electric dipole character of the observed line are predicted. To further compare the theory with the MnF_2 experiments, a model for the exchange interactions is postulated which gives an expected line shape and magnetic field dependence which are consistent with observations. A very imprecise intensity estimate is also consistent with experiment. The question of the choice between this mechanism and another proposed for the MnF_2 line and involving the interaction of the field with the exchange via the perturbation of the electronic orbitals is discussed.

I. INTRODUCTION

In recent experiments,[1–4] electric dipole absorption bands have been observed in the infrared in the antiferromagnets FeF_2, MnF_2, and CoF_2 at the frequencies 154.4, 110, and 120 cm^{-1}. In the first two cases, phenomenological theories[1,4] appear to have established that the bands, whose existence is correlated with the magnetic-ordering temperature, are due to absorption of photons with the production of two short-wavelength spin waves with wave vectors near the Brillouin-zone boundary. Two proposals[5,6] exist to explain the microscopic origin of the coupling between the electric field and the spin waves. One,[5] by the present author, (introduced for FeF_2 in the first paper of this series) depends on the existence of low-lying orbital electronic levels coupled to the ground state of the magnetic ion by the spin-orbit interaction. Such levels do not exist in the Mn^{2+} ion and a similar explanation cannot therefore account for the observations in MnF_2. The other proposal,[6] by Tanabe, Sugano, and Moriya, depends on that part of the dependence of the exchange constant

---

[*] National Science Foundation Postdoctoral Fellow.

[†] Present address: Department of Physics, University of California, Berkeley, California.

[1] I. Silvera and M. Tinkham, Bull. Am. Phys. Soc. **9**, 714 (1964).

[2] J. W. Halley and I. Silvera, Phys. Rev. Letters **15**, 654 (1965); I. Silvera and J. W. Halley, Phys. Rev. **149**, 415 (1966).

[3] P. L. Richards, Bull. Am. Phys. Soc. **10**, 33 (1965).

[4] S. J. Allen Jr., R. Loudon, and P. L. Richards, Phys. Rev. Letters **16**, 463 (1966).

[5] J. W. Halley, Phys. Rev. **149**, 423 (1966), and Ref. 2. The estimate of the absorption intensity from the TMS mechanism (Ref. 6) which is presented in this work omits some terms which may be important.

[6] Y. Tanabe, T. Moriya, and S. Sugano (hereinafter referred to as TMS), Phys. Rev. Letters **15**, 1023 (1965); T. Moriya, Institute of Solid State Physics, University of Tokyo Technical Report No. 188, Series A (unpublished). We have been informed that some errors in the ISSP report, which we discussed in Ref. 2, have been corrected in a revised edition.

on the electric field which arises from the interaction of the field with the electron orbitals. This second mechanism would be expected to give roughly the same absorption intensity in MnF_2 and FeF_2 as observed, and for this reason the MnF_2 experiments have been cited as evidence in favor of the Tanabe *et al.* mechanism for both materials. The following remarks, however, seem to indicate that another explanation of the MnF_2 line may be possible and necessary. (These remarks are not intended to disprove the TMS theory, but rather to motivate the present work by indicating that some doubt exists about certain aspects of the TMS theory and that another explanation may be possible.) (1) The experimental line shapes in the two materials are remarkably different. The contrast is shown in Fig. 1. To fit the MnF_2 line shape, it was necessary to postulate a coupling of the electric field to coupled neighboring spins with the coupling extending to several neighbors and depending exponentially on the distance between spins. The FeF_2 line is sharper and is better fit by the postulation of interactions between nearest neighbors. While it is possible that the differing electronic structures of the Fe^{2+} and Mn^{2+} ions (which do not dramatically affect the range of the exchange interaction itself), might nevertheless greatly affect the range of the TMS interaction, this does not seem obvious and has not been demonstrated. (2) The total integrated intensities differ by about a factor of 2, being larger for FeF_2. Because different numbers of neighbors appear to be involved in the two cases, the squares of the phenomenological couplings differ by more. (3) The polarization properties are different: The line shape does not change in FeF_2 for $E\perp c$ axis. This, together with the calculations of Allen *et al.*, seem to indicate that, as predicted by Ref. 5, the ratio of intensities with $E\|c$ axis and $E\perp c$ axis is effectively infinite. (The observed absorption with $E\perp c$ axis can be ascribed to experimental uncertainties arising from the spreadings of the light beam.[2] Another possible interpretation is mentioned in Sec. V of this paper.) In MnF_2 the line shape changes as theoretically predicted by Allen *et al.*, indicating a real absorption for $E\perp c$ axis. (4) Very rough estimates[5] have indicated that the intensity of the TMS process may be too small. (5) There exists another, second order, mechanism, considered briefly in Ref. 5, which should, according to the estimates presented there, dominate the two-magnon absorption in MnF_2.

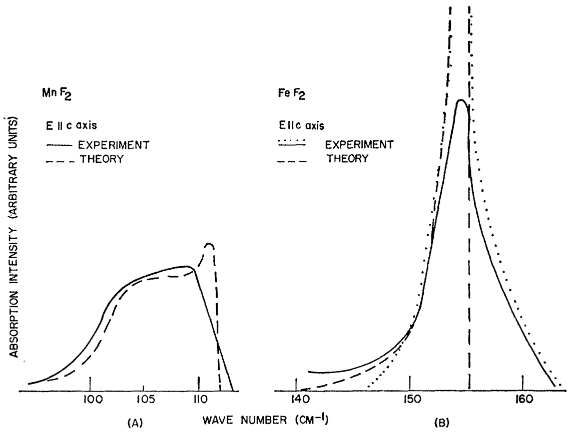

FIG. 1. Experimental line shapes for (A) MnF_2 and (B) FeF_2 lines. The theoretical curves are from the Allen *et al.* Hamiltonian including next-nearest neighbors only in the case (B) and many neighbors on the opposite sublattice with an exponential dependence on neighbor separation in the case (A). The two experimental curves in (B) result from different background subtraction procedures, see Ref. 2. The intensity scale is not the same in (A) and (B).

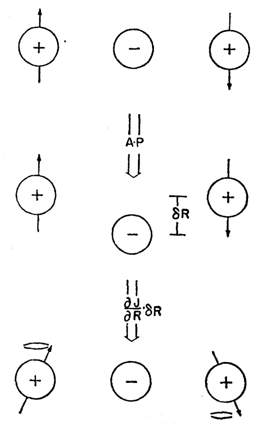

FIG. 2. Schematic illustration of physical origin of the effect. The three pictures represent, respectively, the initial, intermediate (virtual), and final states in one term of the perturbation theory calculation of the transition rate.

In the present paper, we develop the theory of the second-order mechanism last mentioned. We then consider its application to MnF_2 in as much detail as is presently permitted by the available knowledge of the needed parameters. The basic idea is simple (Fig. 2): The electric field couples to the optical phonon modes of the crystal and these modes couple in turn to the spin waves via the magnetoelastic interaction. We show in the following that the resultant indirect electric field-spin coupling leads to an effective spin–electric field Hamiltonian including terms of the form used by Allen, *et al.* in the phenomenological interpretation of their results. Detailed expressions for the constants involved in the effective Hamiltonian are derived. From these, the following additional results are obtained. (1) By postulating a model for the exchange mechanisms responsible for the spin-spin couplings in the usual spin Hamiltonian for MnF_2, we predict a dependence of the constants in the Hamiltonian of Allen *et al.* on the distance between spins which is close (within 1 to 20%) to the exponential dependence assumed by them for the first four neighbors on the opposite sublattice. (2) An extremely imprecise estimate of the intensity is consistent with experiment. (3) One expects finite absorption with $E\perp c$ axis, as observed. (4) On the basis of the model for the origin of the spin-spin couplings, the line shape is predicted to be very weakly dependent on the magnetic field. No magnetic field dependence is observed. (5) Those qualitative remarks which can be made on the intensity of the absorption due to the same mechanism in FeF_2 are consistent with the hypothesis that it is weaker there than in MnF_2.

These results are not as detailed as would be desirable because of lack of experimental and theoretical information on the magnitude of the relevant magnetoelastic coupling constant, lack of knowledge of the force constants of MnF_2 and the absence of infrared experimental data on the optical phonon modes of MnF_2. The precision of the intensity estimates suffers particularly of these deficiencies. The results nevertheless indicate that an explanation of the MnF_2 experiment which is free of the above mentioned difficulties may be possible on the basis of this mechanism.

In the following we present the Hamiltonian (which is the relevant part of a general Hamiltonian discussed in the first paper of this series with the addition of the magnetic dipole-dipole interaction) and then compute the effective electric field-spin Hamiltonian. Postulating a model for the origin of the exchange interactions in MnF_2, we then deduce experimental consequences and compare with experiment. A discussion points out areas for further work, discusses the relation of this kind of absorption to ordinary parallel pumping, and summarizes conclusions.

II. HAMILTONIAN

From the general Hamiltonian discussed in the first paper of this series we select those parts which are relevant to the second-order process (Fig. 6 of Ref. 5) considered there. To this we add the dipole-dipole interaction, which may be important because it determines the anisotropy field in MnF_2. We then have

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_I\,,$$

where

$$\mathcal{H}_0=\mathcal{H}_{\text{magnons}}+\mathcal{H}_{\text{photons}}+\mathcal{H}_{\text{phonons}}\,;$$

$$\mathcal{H}_I=\mathcal{H}_{\text{phot-phon}}+\mathcal{H}_{\text{phon-spin}}{}^{(\text{ex-st})}+\mathcal{H}_{\text{phon-spin}}{}^{(\text{di-di})}\,.$$

The terms in $\mathcal{H}_0$ are

$$\mathcal{H}_{\text{magnons}}=\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}{}^{m}(\alpha_{\mathbf{k}}{}^{\dagger}\alpha_{\mathbf{k}}+\beta_{\mathbf{k}}{}^{\dagger}\beta_{\mathbf{k}})\,;$$

$$\mathcal{H}_{\text{phonons}}=\sum_{\mathbf{k},\mu}\hbar\omega_{\mathbf{k}\mu}{}^{\text{ph}}A_{\mathbf{k}}{}^{(\mu)\dagger}A_{\mathbf{k}}{}^{(\mu)}\,;$$

$$\mathcal{H}_{\text{photons}}=\sum_{\mathbf{k},\lambda}\hbar c|\mathbf{k}|a_{\mathbf{k}\lambda}{}^{\dagger}a_{\mathbf{k}\lambda}\,.$$

In the first

$$\alpha_{\mathbf{k}}=u_{\mathbf{k}}c_{\mathbf{k}}-v_{\mathbf{k}}d_{\mathbf{k}}{}^{\dagger}\,;$$

$$\beta_{\mathbf{k}}=u_{\mathbf{k}}d_{\mathbf{k}}-v_{\mathbf{k}}c_{\mathbf{k}}{}^{\dagger}\,,$$

where $c_{\mathbf{k}}$ and $d_{\mathbf{k}}$ are related to the spin operators by relations given in Ref. 2 and $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are chosen to diagonalize the electric-field-independent part of the spin Hamiltonian which is quadratic in the operators $c_{\mathbf{k}}$, $d_{\mathbf{k}}$. The expression $\omega_{\mathbf{k}}{}^{m}$ is the spin-wave frequency.

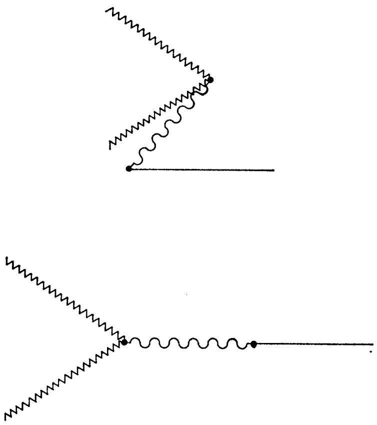

FIG. 3. Diagrams for the two terms in the sum over m for the transition rate [Eq. (1)]. Diagrams are defined in Ref. 5.

Because we are including the magnetic dipole-dipole interaction, $\omega_{\mathbf{k}}{}^{m}$ will depend on the direction of $\mathbf{k}$. In $\mathcal{H}_{\text{phonons}}$, $A_{\mathbf{k}}{}^{(\mu)}$ is a boson operator destroying a phonon of wave vector $\mathbf{k}$ and branch μ and is related to the displacement $\mathbf{X}_{l,b}$ of the bth atom in the lth cell by the relation

$$\mathbf{X}_{l,b}=\sum_{\mathbf{k}',\mu}[\mathbf{C}^{(b)}(\mu,\mathbf{k}')e^{-i\mathbf{k}'\cdot\mathbf{X}_{l,b}{}^{(0)}}A_{\mathbf{k}'}{}^{(\mu)}+\text{H.c.}]\,,$$

where $\mathbf{X}_{l,b}{}^{(0)}$ is the equilibrium position of the bth atom in the lth unit cell and $\mathbf{C}^{(b)}(\mu,\mathbf{k}')$ are constants determined from the diagonalization of the Hamiltonian

$$\mathcal{H}=\tfrac{1}{2}\sum_{l,b}\frac{1}{M_b}\mathbf{P}_{l,b}\cdot\mathbf{P}_{l,b}+\tfrac{1}{2}\sum_{l,b;l'b'}\mathbf{X}_{l,b}\cdot\mathbf{G}_{l,b;l'b'}\cdot\mathbf{X}_{l',b'}\,,$$

where M_b is the mass of the bth atom in the cell, $\mathbf{G}_{l,b;l'b'}$ is the tensor describing the elastic interactions and $\mathbf{P}_{l,b}$ is the momentum of the bth atom of the lth unit cell. In $C^{(b)}(\mu,\mathbf{k})$, μ labels the branch of the phonon spectrum to which $A_{\mathbf{k}'}{}^{(\mu)}$ refers. For the rutile structure, there are 6 atoms per unit cell, hence $3\times6=18$ modes of which 3 are acoustic for each value of $\mathbf{k}'$. The general problem of the determination of the $C^{(b)}(\mu,\mathbf{k})$ is considered in Ref. 7. In the present problem, we only need their values for infrared active optical phonons with $\mathbf{k}'=0$. [The reason that these phonons are the only ones relevant to the process under consideration becomes evident in the sequel. See, for example, Eq. (1) below: The intermediate state $|m\rangle$ contains one $\mathbf{k}=0$ phonon mode and the part of the interaction $\mathcal{H}_I$ coupling $|i\rangle$ to $|m\rangle$ (in the first term of Fig. 3) or $|m\rangle$ to $|f\rangle$ (in the second term of Fig. 3) is the electric-dipole interaction between the external field and the phonon field. Thus, the relevant phonons are infrared active.] Standard group-theoretical arguments[8] show that the

---

[7] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962), pp. 27–31.

[8] G. Parisot, thesis, Faculte des Sciences de l'Universite de Paris, 1963 (unpublished).

infrared-active optical phonons have point-group symmetry A_{2u} (one mode) or E_u (three doubly degenerate modes). For the A_{2u} mode, symmetry restrictions completely determine the $C^{(b)}(\mu,\mathbf{k})$ which are written down in Appendix A. The problem of determining the $C^{(b)}(\mu,\mathbf{k})$ for the E_u modes, which are not completely determined by symmetry, is discussed there.

In the photon term of the zero-order Hamiltonian, $a_{\mathbf{k}\lambda}$ is a photon destruction operator related to the vector potential $\mathbf{A}$ of the electromagnetic field at the position $\mathbf{X}$; by

$$\mathbf{A}(\mathbf{X}_j)=\frac{1}{\sqrt{V}}\sum_{\mathbf{k},\lambda}\left(\frac{2\pi\hbar c}{k}\right)^{1/2}\hat{\epsilon}_{\mathbf{k}\lambda}(a_{\mathbf{k}\lambda}e^{-i\mathbf{k}\cdot\mathbf{X}_j}+a_{\mathbf{k}\lambda}{}^{\dagger}e^{i\mathbf{k}\cdot\mathbf{X}_j}).$$

The first term in the interaction Hamiltonian is the photon-phonon interaction arising from the electromagnetic interaction

$$\mathcal{H}_{\text{phot-phon}}=\sum_{l,b}\left(\frac{Z_b}{M_bc}\right)\mathbf{P}_{l,b}\cdot\mathbf{A}(\mathbf{X}_{l,b}{}^{(0)}+\mathbf{X}_{l,b}),$$

in which Z_b is the change of the bth ion of the unit cell. Supposing $|\mathbf{X}_{l,b}|/|\mathbf{X}_{l,b}{}^{(0)}|\ll 1$, this leads to

$$\mathcal{H}_{\text{phot-phon}}=i\left(\frac{2\pi N}{\hbar\omega_{\mathbf{k}\lambda}\Omega}\right)^{1/2}\sum_{\mathbf{k},\lambda,\mu}\hbar\omega_{\mathbf{k}\mu}\Big[\sum_b Z_b(\mathbf{C}^{(b)}(\mu,-\mathbf{k})\cdot\hat{\epsilon}_{\mathbf{k}\lambda})a_{\mathbf{k}\lambda}A_{-\mathbf{k}}{}^{(\mu)}+\sum_b Z_b(\mathbf{C}^{(b)}(\mu,\mathbf{k})\cdot\hat{\epsilon}_{\mathbf{k}\lambda})a_{\mathbf{k}\lambda}{}^{\dagger}A_{\mathbf{k}}{}^{(\mu)}$$
$$-\sum_b Z_b(\mathbf{C}^{(b)*}(\mu,\mathbf{k})\cdot\hat{\epsilon}_{\mathbf{k}\lambda})a_{\mathbf{k}\lambda}A_{\mathbf{k}}{}^{(\mu)\dagger}-\sum_b Z_b(\mathbf{C}^{(b)}(\mu,-\mathbf{k})\cdot\hat{\epsilon}_{\mathbf{k}\lambda})a_{\mathbf{k}\lambda}{}^{\dagger}A_{-\mathbf{k}}{}^{(\mu)\dagger}\Big].$$

Because this is quadratic in $A_{\mathbf{k}}{}^{(\mu)}$ and $a_{\mathbf{k}\lambda}$, it can be diagonalized exactly with $\mathcal{H}_{\text{phon}}+\mathcal{H}_{\text{phot}}$. This procedure is necessary when considering photons with $\omega_{\mathbf{k}\lambda}\simeq\omega_{\mathbf{k}\mu}$ for some $\mathbf{k}$ and μ, as was first pointed out by Hopfield.[9] In the present case, the photons considered have $\omega_{k\lambda}<\omega_{\mathbf{k}\mu}$ for the optical phonons of interest and the term $\mathcal{H}_{\text{phot-phon}}$ can be treated in perturbation theory at least without qualitative error.

As discussed above and shown in the sequel, for the present problem we need only the part of $\mathcal{H}_{\text{phot-phon}}$ corresponding to coupling of $\mathbf{k}=0$ photons to the phonon fields. The only phonons which couple are those with symmetry A_{2u} and E_u. We thus have, displaying only the relevant parts

$$\mathcal{H}_{\text{phot-phon}}=i\left(\frac{2\pi N}{\hbar\omega_{\mathbf{k}\lambda}\Omega}\right)^{1/2}\Big(\hbar\omega_{A_{2u}}\Big[\sum_b Z_b(C_z{}^{(b)}(A_{2u},0))a_{\mathbf{k}z}A_{-\mathbf{k}=0}{}^{(A_{2u})}+\sum_b Z_b(C_z{}^{(b)}(A_{2u},0))a_{\mathbf{k}z}{}^{\dagger}A_{\mathbf{k}=0}{}^{(A_{2u})}$$
$$-\sum_b Z_b(C_z{}^{(b)*}(A_{2u},0))a_{\mathbf{k}z}A_{\mathbf{k}=0}{}^{(A_{2u})\dagger}-\sum_b Z_b(C_z{}^{(b)*}(A_{2u},0))a_{\mathbf{k}z}{}^{\dagger}A_{-\mathbf{k}=0}{}^{(A_{2u})\dagger}\Big]$$
$$+\sum_{i=1}^{6}\hbar\omega_{E_u{}^{(i)}}\Big[\sum_b Z_b(C_x{}^{(b)}(E_u{}^{(i)},0))a_{\mathbf{k}x}A_{-u=0}{}^{(E_u{}^{(i)})}+\sum_b Z_b(C_x{}^{(b)}(E_u{}^{(i)},0))a_{\mathbf{k}x}{}^{\dagger}A_{\mathbf{k}=0}{}^{(E_u{}^{(i)})}$$
$$-\sum_b Z_b(C_x{}^{(b)*}(E_u{}^{(i)},0))a_{\mathbf{k}x}A_{\mathbf{k}=0}{}^{(E_u{}^{(i)})\dagger}-\sum_b Z_b(C_x{}^{(b)*}(E_u{}^{(i)},0))a_{\mathbf{k}x}{}^{\dagger}A_{-\mathbf{k}=0}{}^{(E_u{}^{(i)})\dagger}$$
$$+\sum_b Z_b(C_y{}^{(b)}(E_u{}^{(i)},0))a_{\mathbf{k}y}A_{-\mathbf{k}=0}{}^{(E_u{}^{(i)})}+\sum_b Z_b(C_y{}^{(b)}(E_u{}^{(i)},0))a_{\mathbf{k}y}{}^{\dagger}A_{\mathbf{k}=0}{}^{(E_u{}^{(i)})}$$
$$-\sum_b Z_b(C_y{}^{(b)*}(E_u{}^{(i)},0))a_{\mathbf{k}y}A_{\mathbf{k}=0}{}^{(E_u{}^{(i)}\dagger}-\sum_b Z_b(C_y{}^{(b)}(E_u{}^{(i)},0))a_{\mathbf{k}y}{}^{\dagger}A_{-\mathbf{k}=0}{}^{(E_u{}^{(i)})\dagger}\Big]\Big)+\cdots.$$

To derive the phonon-spin term, we consider both the terms arising from exchange striction and from the dipole-dipole interaction. To derive the former, consider the Heisenberg exchange Hamiltonian

$$\mathcal{H}_{\text{ex}}=\sum_{l,l'}\sum_{b,b'}{}'J_{l,b;l',b'}\mathbf{S}_{l,b}\cdot\mathbf{S}_{l'b'}.$$

Here the prime on the sum over b, b' restricts the sum to the magnetic ions in the unit cell. We suppose that $J_{l,b\,l',b'}$ depends analytically on the displacements of the ions. Then expanding $J_{l,b\,l',b'}$ in a Taylor series and keeping only the zero-order and linear terms gives

$$\mathcal{H}_{\text{phon-spin}}{}^{(\text{ex-st})}=\sum_{l,l'}\sum_{b,b'}{}'\sum_{l''}\sum_{b''}\mathbf{X}_{l'',b''}\cdot(\nabla_{\mathbf{X}_{l''b''}}J_{l,b;l',b'})_0\mathbf{S}_{l,b}\cdot\mathbf{S}_{l'b'}$$
$$=\sum_{l,l',l''}\sum_{b,b'}{}'\sum_{b''}\sum_{\mathbf{k}'\mu,}[\mathbf{C}^{(b'')}(\mu,\mathbf{k}')[\exp(-i\mathbf{k}'\cdot\mathbf{X}_{l'',b''}{}^{(0)})]A_{\mathbf{k}'}{}^{(\mu)}+\text{H.c.}]\cdot(\nabla_{\mathbf{X}_{l''b''}}J_{l,b;l',b'})_0\mathbf{S}_{l,b}\cdot\mathbf{S}_{l',b'}.$$

---

[9] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

At the Brillouin-zone boundary, the only two-magnon absorption coming from this will come from the part $S_{l,b}{}^{x}S_{l',b'}{}^{x}+S_{l,b}{}^{y}S_{l',b'}{}^{y}$ of the dot product.[10] Displaying only the terms referring to the $\mathbf{k}=0$ phonons of interest

$$\mathcal{H}_{\text{phon-spin}}{}^{(\text{ex-st})}=\sum_{l,l'}\sum_{b,b'}{}'\Bigg[\bigg(\sum_{l'',b''}C_{z}{}^{(b'')}(A_{2u},0)\frac{\partial J_{l,b,l',b'}}{\partial z_{l'',b''}}\bigg)A_{\mathbf{k}'=0}{}^{(A_{2u})}+\bigg(\sum_{l'',b''}C_{z}{}^{(b'')*}(A_{2u},0)\frac{\partial J_{l,b;l',b'}}{\partial z_{l'',b''}}\bigg)A_{\mathbf{k}'=0}{}^{(A_{2u})\dagger}$$

$$+\sum_{i=1}^{6}\Bigg\{\bigg(\sum_{l'',b''}C_{x}{}^{(b'')}(E_{u}{}^{(i)},0)\frac{\partial J_{l,b;l',b'}}{\partial x_{l'',b''}}\bigg)A_{\mathbf{k}'=0}{}^{(E_{u}{}^{(i)})}+\bigg(\sum_{l'',b''}C_{x}{}^{(b'')*}(E_{u}{}^{(i)},0)\frac{\partial J_{l,b;l',b'}}{\partial x_{l'',b''}}\bigg)A_{\mathbf{k}'=0}{}^{(E_{u}{}^{(i)})\dagger}$$

$$+\bigg(\sum_{l'',b''}C_{y}{}^{(b'')}(E_{u}{}^{(i)},0)\frac{\partial J_{l,b;l',b'}}{\partial y_{l'',b''}}\bigg)A_{\mathbf{k}'=0}{}^{(E_{u}{}^{(i)})}+\bigg(\sum_{l'',b''}C_{y}{}^{(b'')*}(E_{u}{}^{(i)},0)\frac{\partial J_{l,b;l',b'}}{\partial y_{l'',b''}}\bigg)A_{\mathbf{k}'=0}{}^{(E_{u}{}^{(i)})\dagger}\Bigg]\Bigg\}$$

$$\times(S_{l,b}{}^{x}S_{l',b'}{}^{x}+S_{l,b}{}^{y}S_{l',b'}{}^{y})+\cdots.$$

The part of the phonon-spin Hamiltonian which arises from the dipole-dipole interaction is derived from

$$\mathcal{H}_{\text{dip-dip}}=\tfrac{1}{2}\sum_{l,b;l',b'}{}'\frac{4\mu_{B}{}^{2}}{R_{l,b;l',b'}{}^{5}}[R_{l,b;l',b'}{}^{2}(\mathbf{S}_{l,b}\cdot\mathbf{S}_{l',b'})-3(\mathbf{R}_{l,b;l',b'}\cdot\mathbf{S}_{l,b})(\mathbf{R}_{l,b;l',b'}\cdot\mathbf{S}_{l',b'})]$$

by expanding in a Taylor series for small displacements giving

$$\mathcal{H}_{\text{phon-spin}}{}^{(\text{di-di})}=(-3\mu_{B}{}^{2})\sum_{i=1}^{6}\sum_{l,b;l',b'}{}'\frac{1}{R_{l,b;l',b'}{}^{5}}\Bigg[(S_{l,b}{}^{x}S_{l',b'}{}^{x}+S_{l,b}{}^{y}S_{l',b'}{}^{y})$$

$$\times[(C_{x}{}^{(b)}(E_{u}{}^{(i)},0)-C_{x}{}^{(b')}(E_{u}{}^{(i)},0))X_{l,b;l',b'}+(C_{y}{}^{(b)}(E_{u}{}^{(i)},0)-C_{y}{}^{(b')}(E_{u}{}^{(i)},0))Y_{l,b;l',b'}]$$

$$\times\bigg(4-\frac{5(X_{l,b;l',b'}{}^{2}+Y_{l,b;l',b'}{}^{2})}{R_{l,b;l',b'}{}^{2}}\bigg)A_{k'=0}{}^{(E_{u}{}^{(i)})}+\text{H.c.}+(S_{l,b}{}^{x}S_{l',b'}{}^{x}-S_{l,b}{}^{y}S_{l',b'}{}^{y})$$

$$\times\bigg[(C_{x}{}^{(b)}(E_{u}{}^{(i)},0)-C_{x}{}^{(b')}(E_{u}{}^{(i)},0))X_{l,b;l',b'}\bigg(2-\frac{5(X_{l,b;l',b'}{}^{2}-Y_{l,b;l',b'}{}^{2})}{R_{l,b;l',b'}{}^{2}}\bigg)$$

$$+(C_{y}{}^{(b)}(E_{u}{}^{(i)},0)-C_{y}{}^{(b')}(E_{u}{}^{(i)},0))Y_{l,b;l',b'}\bigg(-2+\frac{5(-Y_{l,b;l',b'}{}^{2}+X_{l,b;l',b'}{}^{2})}{R_{l,b;l',b'}{}^{2}}\bigg)\bigg]A_{k'=0}{}^{(E_{u}{}^{(i)})}$$

$$+\text{H.c.}+2(S_{l,b}{}^{y}S_{l',b'}{}^{x}+S_{l,b}{}^{x}S_{l',b'}{}^{y})\bigg[(C_{x}{}^{(b)}(E_{u}{}^{(i)},0)-C_{x}{}^{(b')}(E_{u}{}^{(i)},0))Y_{l,b;l',b'}\bigg(1-\frac{5X_{l,b;l',b'}{}^{2}}{R_{l,b;l',b'}{}^{2}}\bigg)$$

$$+(C_{y}{}^{(b)}(E_{u}{}^{(i)},0)-C_{y}{}^{(b')}(E_{u}{}^{(i)},0))X_{l,b;l',b'}\bigg(1-\frac{5Y_{l,b;l',b'}{}^{2}}{R_{l,b;l',b'}{}^{2}}\bigg)\bigg]A_{k'=0}{}^{(E_{u}{}^{(i)})}+\text{H.c.}\Bigg].$$

Here $\mathbf{R}_{l,b\ l'b'}=\mathbf{X}_{l,b}{}^{(0)}-\mathbf{X}_{l',b'}{}^{(0)}$ is the vector between ions l, b and l', b'. The terms in $\mathcal{H}_{\text{phon-spin}}{}^{(\text{di-di})}$ involving the A_{2u} mode vanish when the fact that all the magnetic ions are in phase in this mode (Appendix A) is taken into account.

III. EFFECTIVE-SPIN HAMILTONIAN

We calculate the two-spin wave absorption rate with this Hamiltonian taking as initial and final states

$$|i\rangle=|1\text{ photon with }\mathbf{k}=0\rangle;\quad|f\rangle=|2\text{ spin waves with }\mathbf{k}\text{ and }-\mathbf{k}\rangle.$$

The first nonvanishing term in the absorption is in second order

$$W(i\rightarrow f)=\frac{2\pi}{\hbar}\bigg|\sum_{m}\frac{\langle i|\mathcal{H}_{I}|m\rangle\langle m|\mathcal{H}_{I}|f\rangle}{\hbar\omega_{im}}\bigg|^{2}\delta(\hbar\omega_{i}-\hbar\omega_{f}).\tag{1}$$

---

[10] This follows from the fact that v_k in the relation between c_k, $d_k{}^{\dagger}$, and α_k given after $\mathcal{H}_{\text{photon}}$ at the beginning of this section vanishes near the Brillouin-zone boundary. See, e.g., C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), pp. 58–61.

There are two terms in the sum, corresponding to the two diagrams shown in Fig. 3. Denoting the absorption for the E field of the radiation parallel to the c axis of the crystal by $W_{\parallel}(i \rightarrow f)$:

$$W_{\parallel}(i\rightarrow f)=\frac{2\pi}{\hbar}\left| i\left(\frac{2\pi N}{\hbar\omega_{\mathbf{k}\lambda}\Omega}\right)^{1/2}\left(\frac{\omega_{\mathbf{k}\lambda}}{\omega_{A_{2u}}-\omega_{\mathbf{k}\lambda}}\right)\sum_{l,l'}\sum_{b,b'}{}'\left(\sum_{b''}C_z^{(b'')*}(A_{2u},0)\sum_{l'',b''}C_z^{(b'')}(A_{2u},0)\frac{\partial J_{l,b;l',b'}}{\partial z_{l'',b''}}\right)\right.$$
$$\left.\times\langle\text{ground spin state}|(S_{l,b}^xS_{l'b'}^x+S_{lb}^yS_{l'b'}^y)|2\text{ spin waves}\rangle\right|^2\delta(\hbar\omega_i-\hbar\omega_f).$$

For the E field parallel to the x axis, the absorption, labeled $W_{\perp}^{(x)}(i \rightarrow f)$ is

$$\frac{2\pi}{\hbar}\left| i\left(\frac{2\pi N}{\hbar\omega_{\mathbf{k}\lambda}\Omega}\right)^{1/2}\sum_{i=1}^{6}\sum_{l,l'}\sum_{b,b'}{}'\left(\frac{\omega_{\mathbf{k}x}}{\omega_{\mathbf{k}x}-\omega_{E_u^{(i)}}}\right)\sum_{b''}Z_{b''}C_x^{(b'')}(E_u^{(i)},0)\right.$$
$$\times\Bigg[\left\{\sum_{l'',b''}C_x^{(b'')*}(E_u^{(i)},0)\frac{\partial J_{l,b;l',b'}}{\partial x_{l'',b''}}+\sum_{l'',b''}C_y^{(b'')*}(E_u^{(i)},0)\frac{\partial J_{l,b;l',b'}}{\partial y_{l'',b''}}\right\}+\left(\frac{-3\mu_B^2}{R_{l,b;l',b'}^5}\right)$$
$$\times[(C_x^{(b)*}(E_u^{(i)},0)-C_x^{(b')*}(E_u^{(i)},0)X_{l,b;l',b'}+(C_y^{(b)*}(E_u^{(i)},0)-C_y^{(b)*}(E_u^{(i)},0))Y_{l,b;l',b'}]$$
$$\times\left(4-\frac{5(Y_{l,b;l',b'}^2+X_{l,b;l',b'}^2)}{R_{l,b;l',b'}^2}\right)\Bigg\}\langle\text{ground spin}|(S_{l,b}^xS_{l',b'}^x+S_{l,b}^yS_{l',b'}^y)|2\text{ spin waves}\rangle$$
$$\left.+\left\{\begin{matrix}\text{terms involving the dipole dipole interaction and }\langle\text{ground spin}|(S_{l,b}^xS_{l',b'}^x-S_{l,b}^yS_{l',b'}^y)|2\text{ spin waves}\rangle\\ \text{or}\langle\text{ground spin}|(S_{l,b}^xS_{l',b'}^y+S_{l,b}^yS_{l',b'}^x)|2\text{ spin waves}\rangle\end{matrix}\right\}\Bigg]\right|^2$$
$$\times\delta(\hbar\omega_i-\hbar\omega_f).$$

The matrix elements of $S_{l,b}^xS_{l'b'}^x-S_{l,b}^yS_{l',b'}^y$ and $S_{l,b}^xS_{l'b'}^y+S_{l,b}^yS_{l',b'}^x$ in this expression will vanish in the case in which the sums over l, b; l', b' are confined to pairs on opposite sublattices (in lowest nonvanishing order in the Holstein-Primakoff transformation). This is the reason that the corresponding terms appearing in the effective-spin Hamiltonian written down below do not appear in the effective spin Hamiltonian of Ref. 4 which is confined to pairs on opposite sublattices and displays only terms contributing to two magnon absorption.

The preceding results show that an equivalent absorption is obtained from the effective-spin Hamiltonian

$$\mathcal{H}_{\text{eff}}=\sum_{l,l'}\sum_{b,b'}{}'\{(\mathbf{E}\cdot\mathbf{\Pi}_{l,b;l',b'})(S_{l,b}^xS_{l',b'}^x+S_{l,b}^yS_{l',b'}^y)+(\mathbf{E}\cdot\mathbf{\Pi}_{l,b;l',b'}{}')(S_{l,b}^xS_{l',b'}^x-S_{l,b}^yS_{l',b'}^y)$$
$$+(\mathbf{E}\cdot\mathbf{\Pi}_{l,b;l',b'}{}'')(S_{l,b}^xS_{l'b'}^y+S_{l,b}^yS_{l',b'}^x)\}. \quad (2)$$

Here only the $\mathbf{\Pi}_{l,b\;l',b'}$ involve exchange-striction, whereas $\mathbf{\Pi}_{l,b\;l'b'}{}'$ and $\Pi_{l,b\;l',b'}{}''$ arise from the magnetic dipole-dipole interaction. We show the explicit expressions only for a few representative terms:

$$\Pi_{l,b;l',b'}{}^{(z)}=\frac{N}{\hbar(\omega_{\text{phot}}-\omega_{A_{2u}})}\sum_{b''',i}Z_{b'''}C_x^{(b''')}(E_u^{(i)},0)\sum_{l'',b''}C_z^{(b'')*}(A_{2u},0)\frac{\partial J_{l,b;l'b'}}{\partial z_{l''b''}};$$

$$\Pi_{l,b;l',b'}{}^{(x)}=\sum_{i=1}^{6}\frac{N}{\hbar(\omega_{\text{phot}}-\omega_{E_u^{(i)}})}\sum_{b'''}Z_{b'''}C_x^{(b''')}(E_u^{(i)},0)P_{l,b;l',b'}{}^{(i)};$$

$$\Pi_{l,b;l',b'}{}^{(x)\prime}=\sum_{i=1}^{6}\frac{N}{\hbar(\omega_{\text{phot}}-\omega_{E_u^{(i)}})}\sum_{b'''}Z_{b'''}C_x^{(b''')}(E_u^{(i)},0)P_{l,b;l',b'}{}^{(i)\prime}; \quad (3)$$

$$\Pi_{l,b;l',b'}{}^{(x)\prime\prime}=\sum_{i=1}^{6}\frac{N}{\hbar(\omega_{\text{phot}}-\omega_{E_u^{(i)}})}\sum_{b'''}Z_{b'''}C_x^{(b''')}(E_u^{(i)},0)P_{l,b;l',b'}{}^{(i)\prime\prime};$$

$$\Pi_{l,b;l',b'}{}^{(z)\prime}=\Pi_{l,b;l',b'}{}^{(z)\prime\prime}=0;$$

in which

$$P_{l,b;l',b'}{}^{(i)}=\sum_{l'',b''}C_x{}^{(b'')*}(E_u{}^{(i)},0)\frac{\partial J_{l,b;l'b'}}{\partial x_{l'',b''}}+\sum_{l'',b''}C_y{}^{(b'')*}(E_u{}^{(i)},0)\frac{\partial J_{l,b;l'b'}}{\partial y_{l'',b''}}+\left(\frac{-3\mu_B{}^2}{R_{l,b;l',b'}{}^5}\right)$$
$$\times[(C_x{}^{(b)*}(E_u{}^{(i)},0)-C_x{}^{(b')*}(E_u{}^{(i)},0))X_{l,b;l',b'}+(C_y{}^{(b)*}(E_u{}^{(i)},0)-C_y{}^{(b')*}(E_u{}^{(i)},0))Y_{l,b;l',b'}]$$
$$\times\left(4-5\left(\frac{Y_{l,b;l',b'}{}^2+X_{l,b;l',b'}{}^2}{R_{l,b;l',b'}{}^2}\right)\right)$$

with similar expressions not, however, involving $\nabla_{\mathbf{R}_{c''b''}}J_{l,b;l'b'}$ for $P_{l,b;l',b'}{}^{(i)'}$ and $P_{l,b;l'b'}{}^{(i)''}$. The expressions for $\Pi_{l,b;l'b'}{}^{(y)}$, $\Pi_{l,b;l'b'}{}^{(y)'}$, $\Pi_{l,b;l'b'}{}^{(y)''}$ are obtained from those for $\Pi_{l,b;l',b'}{}^{(x)}$, $\Pi_{l,b;l'b'}{}^{(x)'}$, $\Pi_{l,b;l',b'}{}^{(x)''}$ in (3) by the replacement of the subscript x by y. The first term in the expression (2) has the form given by Allen *et al.*, if $\Pi_2=0$. The absence of the Π_2 term arises from the fact that the symmetry of the spin-spin interactions considered (isotropic exchange and the dipole-dipole interaction) is higher than that of the magnetic crystal. The last two terms in (2) arise from the dipole-dipole interaction only and do not contribute to two-magnon absorption if the sums are restricted to spin pairs on opposite sublattices. These last two terms contribute only to the absorption for $E\perp c$ axis. In Appendix B we show explicitly how the geometry of the crystal structure gives $\Pi_{l,bl;',b'}{}^{(z)}$ the transformation properties cited by Allen *et al.*

IV. MODEL FOR EXCHANGE MECHANISMS IN MnF$_2$ AND EXPERIMENTAL CONSEQUENCES

In MnF$_2$, the anisotropy field, which arises from the dipole-dipole interaction, is about one-fifth of the exchange field. Further, the relevant contribution of the dipole-dipole interaction to the spin-phonon interaction arises from the phase differences between the displacements of the magnetic ions in the unit cell when an optical phonon is excited. Even when, in the case of $E\perp c$ axis, these phase differences can be nonzero, they can be expected to be small compared to the phase differences between the magnetic and fluorine ions when an optical phonon is excited. On the other hand, the exchange interaction, being dominated in many cases by superexchange, will depend strongly on the difference between the displacements of the fluorine and magnetic ions. We thus anticipate that the important contributions to the Π's in Eq. (2) will come from the exchange-strictive and not the dipole-dipole terms and we will concentrate attention on the exchange strictive terms in the sequel.

The magnitude of the derivative $J_{l,b;l'b'}$ will depend strongly on which neighbor is being considered. To establish a simple model which will permit semiquantitative predictions of the behavior of the derivatives of $J_{l,b;l'b'}$ we consider the neighbors of the spin on site 9 of Fig. 4(a). The first 7 magnetic neighbors are represented by that labeled 12 (2 in all; 1 kind), that labeled 5 (8 in all; 2 kinds), that labeled 18 (4 in all; 2 kinds; the label on 18 in fig. 4a is illegible: 17 is to 18 as 5 is to 6), that labeled 11 (8 in all; 2 kinds); that labeled 28 (8 in all; 2 kinds); that labeled 17 (16 in all; 4 kinds) and that labeled 23 (32 in all; 4 kinds). Of these, 5, 11, 17, and 23 are on the opposite sublattice and 8, 18, and 24 are on the same sublattice as the spin on site 6. To fit the spin-wave dispersion relation,[11] one includes the neighbors 12, 5, and 18 of which 5 contributes the largest exchange. We note from the scale drawings of Fig. 4(b) that (i) no fluorine ion lies close to the line between 12 and 6; (ii) the fluorine ion labeled 1 is on the line between 6 and 11; (iii) no fluorine ion is collinear or near collinear with 6 and 18; (iv) the fluorine ion 14 is nearly collinear with 17 and 6; (v) the fluorine ion 1 is more nearly collinear with 6-24 than with 6-12 but less than with 6-11; (vi) the fluorine ion 20 is nearly collinear with 6-23. Finally we know that 5-6 exchange is usually attributed to superexchange. On the basis of these facts we postulate that the neighbors 5, 11, 17, and 23 are magnetically coupled to 6 via superexchange through the fluorine[12] ions 1, 1, 14, and 20, respectively, whereas the magnetic coupling between 12 and 6 and 18 and 6 arises from direct wave-function overlap.[13] Concerning neighbor-type 24 we can make no plausible assumption about the total exchange, but we suppose that part of the 6-24 coupling coming from superexchange arises from superexchange through the fluorine ions 1 and 15.

Specializing to the case of $E\|c$ axis, we consider the effects of these postulates on the predicted magnitudes of $\Pi_{l,b;l',b'}{}^{(z)}$. We note that, with the excitation of an A_{2u} phonon, the magnetic neighbors remain in phase and oscillate against the fluorine ions (Appendix A). Thus, the exchange depending on direct overlap will be unaffected, but that depending on superexchange will

---

[11] G. G. Low, A. Okazaki, R. W. H. Stevenson, and G. Turberfield, J. Appl. Phys. 35, 998 (1964).

[12] A corresponding intervening fluorine is found for all equidistant neighbors, but the derivatives have different signs, depending on the position of the neighbor. See Appendix B.

[13] The postulate concerning the neighbor 12-6 is certainly too simple. However, the existing theoretical studies (Ref. 14) of the angular dependence of the superexchange interaction indicate a large antiferromagnetic exchange between these ions, while a small and ferromagnetic interaction is observed. It has been suggested for this reason that there may be a large ferromagnetic contribution from direct overlap.

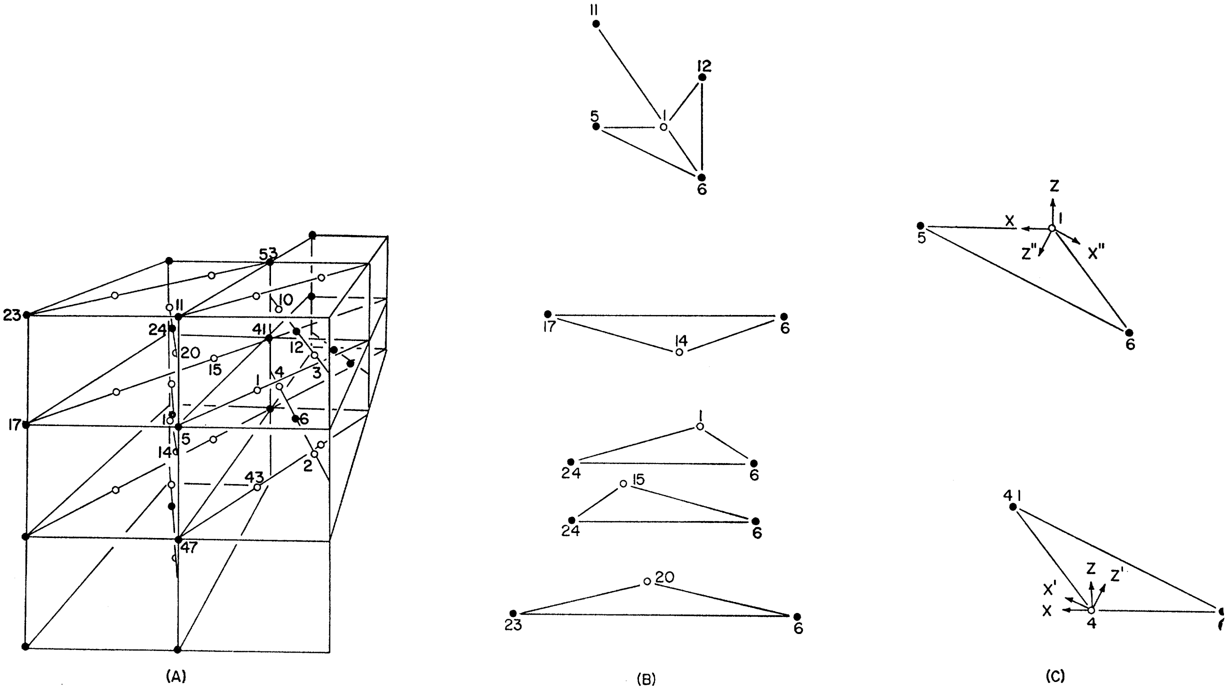

FIG. 4. (A) Neighbors in the rutile structure. In the text, neighbors of the ion labeled 6 are considered. Ions in each unit cell are labeled in the same order. The numbering of the ions in the unit cell containing 6 is the same as that employed in Ref. 8 and elsewhere. (B) Sketches (to scale) of the first four neighbor positions. (C) Coordinate systems used in Appendix B.

be strongly affected. On the basis of the preceding paragraph, one then expects large $\Pi_{l,b;l',b'}^{(z)}$ for neighbors of the types 5, 11, 17, and 23, zero $\Pi_{l,b;l',b'}^{(z)}$ for neighbors of types 12 and 18 and a $\Pi_{l,b;l',b'}^{(z)}$ somewhere between these two extremes for neighbors of type 24.

A rough idea of the relative magnitudes of the $\Pi_{l,b;l',b'}^{(z)}$ for the neighbors of types 5, 11, 17, and 23 can then be obtained by the assumption

$$\Pi_{l,b,l'b'}^{(z)} \propto \exp[-\{|\mathbf{X}_{l,b}^{(0)}-\mathbf{X}_F^{(0)}| + |\mathbf{X}_{l',b'}^{(0)}-\mathbf{X}_F^{(0)}|\}k], \quad (4)$$

where $\mathbf{X}_F^{(0)}$ is the position of the fluorine contributing to the superexchange. This is consistent with established ideas of superexchange[14] except that it neglects the dependence of the superexchange constant on the angles between the three participating ions. On the basis of the foregoing, the obvious extension of (3) will probably overestimate the $\Pi_{l,b;l'b'}^{(z)}$ for the neighbor type 24, while setting the $\Pi_{l,b;l',b'}^{(z)}$ for neighbor type 12 equal to zero is probably an underestimate.

The fact that the neighbors of types 5, 11, 17, and 23 are on the sublattice opposite to that of the ion 6 means that the only dependence of the line shape on the magnetic field in lowest order will arise, in this model, from neighbors of the type 24. A very rough upper limit on the importance of this effect is obtained by estimating the relative contribution of the type 24 neighbors to the total line intensity via the relation

$$\frac{N_{24}^2[e^{-k(|\mathbf{X}_{24}-\mathbf{X}_{15}|+|\mathbf{X}_6-\mathbf{X}_{15}|)}+e^{-k(|\mathbf{X}_{24}-\mathbf{X}_1|+|\mathbf{X}_6-\mathbf{X}_1|)}]^2}{\sum_n N_n^2(e^{-k(R_{6,F}+R_{n,F})})^2} \sim 0.05,$$

where N_n is the number of neighbors of type n. (Table I. The k used here is discussed in the next section.) The effect of a magnetic field of 50 kG will be to broaden that part of the absorption contributed by the type 24 neighbors by about 20 cm^{-1}. Since this contribution is expected to be broad in no magnetic field, a small effect is expected.

For $E\perp c$ axis, the Π's involve sums over 6 modes, instead of one, and the dipole-dipole terms in Eq. (2) contribute. The symmetry does not require, however, that the Mn^{2+} and F^- ions move precisely out of phase in this case. The first two facts are likely to increase the $E\perp c$ axis absorption relative to that with $E\| c$ axis and the last is likely to reduce it, but no quantitative con-

---

[14] P. W. Anderson, Phys. Rev. **79**, 350 (1950); P. W. Anderson, in *Magnetism*, edited by G. T. Walker and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, p. 25. There is, however, some experimental evidence that, for small pressure-induced changes in the lattice constant, T_N and hence the exchange interaction varies as $1/|\mathbf{X}_{l,b}^{(0)}-\mathbf{X}_{l',b'}^{(0)}|^{10}$ [D. Bloch (private communication)]. This is not necessarily in contradiction with the hypothesis (4) if, as has been suggested, the $1/R^{10}$ variation arises from shifts in the ionic energy level structure with lattice constant, since the energy level structure does not change in going from one neighbor to another. In other words, if we write $J\propto b^2(E_p-E_d)^2/U$, then $(E_p-E_d)^2$ changes with pressure (possibly as $1/R^{10}$) whereas b^2 changes in going from one pair to another (probably exponentially).

TABLE I. Comparison of dependence on position of $\Pi_{l,b;l',b'}{}^{(z)}$ in various theories.

Neighbor type	No. of neighbors	Allen *et al.*[a]	This theory[b]	Coupling from mechanism of Ref. 5[c]
12	2	0	0	1.82
5	8	1.00	1.00	1.00
18	4	0	0	0.387
11	8	0.323	0.332	0.164
24	8	0	0.254	0.182
17	16	0.126	0.094	0.057
23	16	0.063	0.080	0.031

[a] Reference 4.
[b] With model described in Sec. III for $J_{l,b;l',b'}$.
[c] An estimate like that of Sec. IV indicates that the contributions from 12, 18, and 24 in this column will make ~14% of the absorption intensity magnetic-field-dependent.

clusions can be drawn because of lack of detailed information about the E_u modes.

The order of magnitude of the absorption intensity is easily related to a spin-phonon coupling constant defined by

$$G'=(\sqrt{N})\left[\sum_{l'',b''}C_z{}^{(b'')}(A_{2u},0)\frac{\partial J_{l,b;l',b'}}{\partial z_{l'',b''}}\right]\frac{1}{|e|},$$

where $|e|$ is the strain involved in the optical phonon mode. Taking $|e|\simeq 10^{-2}$ we find that in order to produce the experimental result

$$\frac{\text{Absorption Intensity}}{\text{AFMR}}\sim 1$$

where AFMR is the antiferromagnetic resonance absorption intensity, we would need $G'\sim 10^{-15}$ or 10^{-14} erg. Unfortunately, no experimental numbers for this G' are available. The sums of the form

$$\sum_{l'',b''}C_z{}^{(b'')}(A_{2u},0)\frac{\partial J_{l,b;l',b'}}{\partial z_{l'',b''}}$$

which are involved are not the same as those involved in measurements of the variation of T_N with pressure[14] or of the variation of J with lattice constant. Though some of the former measurements do give variations of J with separation of the magnetic ions, the perturbation of the crystal structure involved is a homogeneous one and therefore the change in J is expected to be much smaller than in the present case, where the distortion (an optical phonon) moves the positions of the ions within the unit cell with respect to one another. Similarly, all the other numbers which are available for the spin-phonon coupling constant G refer to a homogeneous distortion or to an acoustic phonon and not to an A_{2u} optical phonon. As discussed above, G' is expected to be larger than such a G. It is perhaps worth noting, however, that the estimates of G are in the range[15,16]

$$10^{-17}\ \text{erg}\lesssim G\lesssim 10^{-13}\ \text{erg}$$

within which the needed G' lies. A slightly better estimate of the intensity is possible from the work of Benedek and Kushida on the observed pressure dependence of the covalency mixing coefficients f via NMR on the F^{19} nuclei and leads to[17]

$$\frac{\text{Absorption Intensity}}{\text{AFMR}}\sim 10^{\pm 2}. \tag{5}$$

Clearly, no firm conclusions about the intensity can be drawn. One possible way to improve this situation is discussed in the last section.

V. COMPARISON WITH EXPERIMENT

Allen *et al.* showed that the MnF_2 line shape could be approximately fitted with Eq. (1), restricting the sums on $l,b;l'b'$ to spin pairs on opposite sublattices and taking

$$\Pi_{l,b;l',b'}\propto e^{-R_{l,b;l',b'}k'}. \tag{6}$$

[The last two terms in (2) give no two magnon absorption for pairs of spins on opposite sublattices.] Allen *et al.* used $k'=1/0.4a$. This relation is compared with that of Eq. (3) for neighbors of types 5, 11, 17, and 23 in Table I, where we take $k=1/0.33a$. We predict zero $\Pi_{l,b;l'b'}{}^{(z)}$ for neighbor types 12 and 18 in agreement with Allen *et al.* but a finite $\Pi_{l,b;l',b'}{}^{(z)}$ for neighbor type 24. The k used was chosen by averaging the three k values found by matching the two expressions (4) and (3) for the neighbor types 11, 17, and 23. The difference between (3) and (4) is seen from Table I is seen to alternate in sign and thus the discrepancies appear to compensate. As an indication of the importance of this effect

---

[15] P. Pincus and J. Winter, Phys. Rev. Letters **7**, 269 (1961). G is estimated from nuclear spin-lattice relaxation times and the temperature dependence of the electronic magnetization.

[16] M. Papoular (private communication), from ultrasonic attenuation experiments. Estimates of spin-lattice couplings from ultrasonic attenuation in similar materials give the same order of magnitude and are consistent with estimates from effects of uniaxial stress on the paramagnetic resonance frequency. See E. B. Tucker, Phys. Rev. **143**, 264 (1966), and references cited there.

[17] G. B. Benedek and T. Kushida, Phys. Rev. **118**, 46 (1960). Two difficulties attend the deduction of the parameters needed in the present paper from the Benedek-Kushida results: (1) Uncertainties in the covalency formulation of the superexchange theory (Ref. 14) make the J's deduced from the observed f's unreliable. (2) The dependence of the f's on the various nuclear coordinates cannot be separated, since the only stress applied was isotropic pressure. We can deduce from the Benedek Kushida results that the approximation $\partial f/\partial r\simeq f/a$ is roughly correct with $a\simeq 0.5$ Å. Then with

$$\frac{1}{J}\frac{\partial J}{\partial R}=\frac{\partial}{f}\frac{\partial f}{\partial r}$$

or

$$\frac{\partial J}{\partial r}\sim\frac{2J}{a}$$

we find Eq. (5).

we note that

$$\frac{\left|\sum_n N_n{}^2(\Pi_n(\text{Allen})^2-\Pi_n(\text{this theory})^2)\right|}{\left|\sum_n N_n{}^2\Pi_n(\text{this theory})^2\right|}\sim 0.07\,.$$

Most of the discrepancy comes from neighbor type 24, where we have overestimated $\Pi_{l,b,l',b'}{}^{(z)}$. The Allen *et al.* theoretical line shape fits the experimental data to within about 20%. On the basis of the foregoing, one can expect a fit using the relation (3) to work as well.[18]

No change in the line is observed in a magnetic field of 50 kG and the observed intensity falls within the estimated limits. The shift in the line for $E\perp c$ axis indicates a real absorption.

In FeF_2, the mechanism considered here would be expected to contribute to the two-magnon absorption intensity, in addition to the contribution from the mechanism considered in detail in Ref. 5. No detailed theoretical comparison of the absorption intensity due to the mechanism considered in this paper in the two materials is presently possible due to lack of experimental information. The following remarks can be made, however: (1) The exchange interaction will have longer range than the coupling arising from the Coulomb interaction which gives rise to the absorption mechanism considered in Ref. 5. Even without considering screening effects, the $1/|\mathbf{X}_{l,b}{}^{(0)}-\mathbf{X}_{l',b'}{}^{(0)}|^4$ dependence of the interaction arising from the process proposed by us for FeF_2 in Ref. 5 leads to a more rapidly decreasing coupling for the first four neighbors on the opposite sublattice (Table I). Thus a sharper line is anticipated if the mechanism proposed by us for FeF_2 dominates the mechanism considered here in FeF_2. A sharper line is observed in FeF_2. (2) The Van Vleck spin-phonon interaction contributes weakly (of order λ/Δ less than to $1/T_1$) to the present absorption mechanism and hence certain estimates[15] of the spin-phonon coupling constant which include the Van Vleck contribution (which will be larger in FeF_2) cannot be used in comparing the intensities in this case. (3) Inspection of Eqs. (2) shows that if $\omega_{k\lambda}$ lies near $\omega_{A_{2u}}$, a large absorption intensity will be found. Some observed frequencies $\omega_{A_{2u}}$ for other fluorides of the rutile crystal structure are shown in Table II along with lattice constants for the corresponding materials. We note, however, that as expected physically and with the exception of FeF_2, $\omega_{A_{2u}}$ is decreasing with increasing lattice constant and that MnF_2 has the largest lattice constants of the materials listed. Thus it seems quite possible that $\omega_{A_{2u}}$ lies closer to $\omega_{k\lambda}$ in MnF_2 than in FeF_2, resulting in a larger contribution for the mechanism in MnF_2. Since $\omega_{A_{2u}}$ and $\omega_{k\lambda}$ are of the same order of magnitude and the factor $1/(\omega_{A_{2u}}-\omega_{\mathbf{k}\lambda})$ enters the intensity as the square, it is possible that such an effect could result in a difference of as much as an order of magnitude in the intensities. (4) In FeF_2, the relative position of the fluorine ions is somewhat different with respect to the magnetic pairs than it is in MnF_2. This will lead to a different dependence of $J_{l,b;l'b'}$ on the fluorine displacements. (5) It is experimentally possible that a broad line of the sort observed in MnF_2 lies under the sharp peak observed in FeF_2. (6) The experimental arrangement[2] in the FeF_2 experiment allowed the possibility that a substantial portion of the absorption labeled $E\perp c$ axis came from radiation with $E\|c$ axis. That being the case, a small, shifted absorption with $E\perp c$ axis in FeF_2 arising from the mechanism described in the present paper would be masked by the large, unshifted absorption due to the mechanisms described in both papers with $E\|c$ axis. Finally, because of differences in lattice constants, the peak in the $E\perp c$ axis absorption may be closer to that for $E\|c$ axis in FeF_2 than in MnF_2. It is to be emphasized that remarks (3), (5), and (6) are speculative and that the question of the relative intensities due to the mechanism described here in the two materials is important and unresolved.

TABLE II. A_{2u} phonon frequencies and lattice constants for various materials.

Material	c (Å)[a]	a (Å)[a]	$\omega_{A_{2u}}$ (cm^{-1})
NiF_2	3.0836	4.6506	372±3[b]
CoF_2	3.1769	4.6951	350±10[b]
ZnF_2	3.1335	4.7034	294[c]
FeF_2	3.3091	4.6966	440[d]
MnF_2	3.3099	4.8734	...

[a] J. W. Stout and S. A. Reed, J. Am. Phys. Soc. **76**, 5279 (1954).
[b] Reference 8.
[c] A. S. Baker, Phys. Rev. **136**, A1290 (1964).
[d] M. Balkanski *et al.*, J. Chem. Phys. **44**, 940 (1966).

VI. DISCUSSION

There has been some confusion about the relation of the coupling mechanism and absorption process considered here to the usual amplitude-dependent parallel pumping absorption[19] which has long been observed and understood in ferromagnetic insulators like yttrium iron garnet. The only thing which the two absorption processes have in common is the same final state, containing two magnons. There is no amplitude dependence or threshold power for any of the three proposals so far advanced for the coupling mechanism in the rutile antiferromagnets. This is because the threshold behavior of the ordinary parallel pumping absorption is a consequence of the magnetic dipole character of the field-spin coupling. As a consequence of this magnetic dipole character, an rf magnetic field parallel to the $T=0$

---

[18] Considering superexchange in the TMS theory would also predict a more complicated behavior of the $\Pi_{l,b;l',b'}{}^{(z)}$ than that postulated by Allen *et al.*

[19] M. Sparks, *Ferromagnetic Relaxation Theory* (McGraw-Hill Book Company, Inc., New York, 1964) ,p. 166.

magnetization cannot couple to the spins unless there is already some magnetization normal to this saturization magnetization. Thus a large increase in absorption is expected when the rf field feeds this perpendicular magnetization faster than it leaks away through magnon relaxation and a threshold results. In the two-magnon experiments considered here, the absorption is electric dipole and the coupling mechanism is (in each proposal) not dependent on the existence of any magnetization normal to the saturization magnetization. Thus the superficial similarity of Fig. 3 to diagrams arising in Suhl instability studies (with a phonon substituted for a magnon in the intermediate state) does not mean that a threshold behavior is expected. Another important difference is that the phonon considered here is virtual (its energy is not the same as that of the incoming photon) whereas the $\mathbf{k}=0$ magnon involved in the usual Suhl instability study is real.

Though giving results consistent with the MnF_2 experiment, the considerations presented in this paper suffer at several points from inadequate knowledge of the parameters involved The model chosen in Sec. III for the exchange interactions is certainly too simple. Despite extensive[18,20] experimental studies of the exchange interactions in MnF_2, the required information, that of the variation of the exchange constants $J_{l,b;l',b'}$ with the excitation of an infrared optical phonon, does not appear to be deduceable in any reliable way from the available results. It is possible that the needed numbers can be more directly measured by epr experiments in $Mn{:}ZnF_2$ and $Fe{:}ZnF_2$ under uniaxial stress in various directions.[21] Such information would, in particular, make possible a more detailed consideration of the important question of the relation of the absorption intensities due to this mechanism in FeF_2 and MnF_2.

In conclusion, the theory presented here is consistent with the MnF_2 experiment insofar as a comparison can presently be made. The strongest qualitative evidence favoring our picture over that proposed by TMS lies in the contrasting line shapes of the MnF_2 and FeF_2 lines. We suggest that the picture suggested here is compelling enough so that further work on two-magnon absorption in rutile structure antiferromagnets should take into account the possibility that this mechanism may play an important or dominant role.

ACKNOWLEDGMENTS

J. Owen, D. Bloch, D. Mills, F. Hartmann, and M. Papoular are thanked for discussions. P. L. Richards and T. Moriya provided preliminary accounts of their work. Professor J. Friedel and his group at Orsay are thanked for hospitality while this work was done.

APPENDIX A: LONG-WAVELENGTH OPTICAL PHONONS

From Ref. 7, the displacement $\mathbf{X}_{l,b}$ is related to the phonon destruction and annihilation operators via the relations

$$\mathbf{X}_{l,b}=\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\mathbf{X}_{\mathbf{q},b}\exp[-i\mathbf{q}\cdot\mathbf{X}_l^{(0)}];$$

$$\mathbf{P}_{l,b}=\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\mathbf{P}_{\mathbf{q},b}\exp[i\mathbf{q}\cdot\mathbf{X}_l^{(0)}];$$

$$P_{\mathbf{q},\mu}=\sum_b\frac{1}{(M_b)^{1/2}}(\hat{e}_{\mathbf{q},b,\mu}{}^*\cdot\mathbf{P}_{\mathbf{q},b});$$

$$X_{\mathbf{q},\mu}=\sum_b(M_b)^{1/2}(\hat{e}_{\mathbf{q},b,\mu}\cdot\mathbf{X}_{\mathbf{q},b});$$

$$A_{\mathbf{q}}{}^{(\mu)}=\frac{1}{(2\hbar\omega_{\mathbf{q}\mu})^{1/2}}P_{\mathbf{q}\mu}-i\left(\frac{\omega_{\mathbf{q}\mu}}{2\hbar}\right)^{1/2}X_{\mathbf{q}\mu}{}^*;$$

$$A_{\mathbf{q}}{}^{(\mu)\dagger}=\frac{1}{(2\hbar\omega_{\mathbf{q}\mu})^{1/2}}P_{\mathbf{q}\mu}{}^*+i\left(\frac{\omega_{\mathbf{q}\mu}}{2\hbar}\right)^{1/2}X_{\mathbf{q},\mu}.$$

Here $\hat{e}_{\mathbf{q},b,\mu}$ is defined so that the value of $\mathbf{X}_{\mathbf{q},b}$ when the μth mode of wave vector $\mathbf{q}$ is excited is

$$\mathbf{X}_{\mathbf{q},b}{}^{(\mu)}=\frac{1}{(M_b)^{1/2}}\hat{e}_{\mathbf{q},\mu,b}\exp[i\omega_{\mathbf{q},\mu}t].$$

$\omega_{\mathbf{q}\mu}$ is the phonon frequency. The problem of diagonalizing $\mathcal{H}$ is reduced to an eigenvalue problem in which the eigenvalues are the $\omega_{\mathbf{q}\mu}$ and the eigenvectors are the $\hat{e}_{\mathbf{q},\mu,b}$. The normalization condition on the $\hat{e}_{\mathbf{q},\mu,b}$'s is

$$\sum_b\hat{e}_{\mathbf{q},\mu,b}{}^*\cdot\hat{e}_{\mathbf{q},\mu',b}=\delta_{\mu,\mu'}.$$

At the point $\mathbf{q}=0$, decomposition of the representation of the point group which is provided by the nuclear coordinates shows that there are 7 infrared active modes transforming as the representations A_{2u} (1 mode) and E_u (3 doubly degenerate modes). In the case of the A_{2u} mode, the form of the normal coordinate $X_{q=0(A_{2u},0)}$ is found by use of the Van Vleck basis generator, the point group character table and the normalization condition, together with the requirement that the center of mass of the unit cell be stationary for an optical mode. One finds

$$X_{\mathbf{q}=0,(A_{2u},0)}=\frac{(NM)^{1/2}m}{(Mm+2m^2)^{1/2}}\times\{\tfrac{1}{2}(z_1+z_2+z_3+z_4)-(z_5+z_6)\}.$$

The other normal-mode coordinates involving the z_i's are those transforming as E_g (doubly degenerate), B_{1u}

---

[20] J. Owen *et al.*, Phys. Rev. Letters **7**, 246 (1961).

[21] Similar measurements have recently been reported for gadolinium iron garnet by T. G. Phillips and R. L. White, Phys. Rev. Letters **16**, 650 (1965).

(doubly degenerate) and the uniform A_{2u} mode. By the same procedure

$$X_{q=0,(A_{2u},u)}=\left(\frac{N}{(4m+2M)}\right)^{1/2}\times(m(z_1+z_2+z_3+z_4)+M(z_5+z_6));$$

$$X_{q=0,(E_g,1)}=\left(\frac{mN}{2}\right)^{1/2}(z_1-z_3);$$

$$X_{q=0,(E_g,2)}=\left(\frac{mN}{2}\right)^{1/2}(z_2-z_4);$$

$$X_{q=0,(B_{1u},1)}=\left(\frac{mN}{2}\right)^{1/2}(z_1+z_3-z_2-z_4);$$

$$X_{q=0,(B_{1u},2)}=\left(\frac{MN}{2}\right)^{1/2}(z_5-z_6).$$

Here z_i is the z component (taken along the c axis) of the ith ion in the unit cell as numbered in Fig. 4(a) (ions labeled 1 through 6). m and M are the masses of the fluorine and magnetic ions, respectively.

Inverting these gives

$$z_1=X_{(E_g,1)}\left(\frac{1}{2mN}\right)^{1/2}+X_{(B_{1u},1)}\frac{1}{(4mN)^{1/2}}+\frac{1}{(2+4m/M)}\left(X_{(A_{2u},0)}\left(\frac{(Mm+2m^2)}{m^2MN}\right)^{1/2}+X_{(A_{2u},u)}\left(\frac{(4m+2M)}{NM^2}\right)^{1/2}\right);$$

$$z_2=X_{(E_g,2)}\left(\frac{1}{2mN}\right)^{1/2}-X_{(B_{1u},1)}\left(\frac{1}{4mN}\right)^{1/2}+\frac{1}{(2+4m/M)}\left(X_{(A_{2u},0)}\left(\frac{(Mm+2m^2)}{m^2MN}\right)^{1/2}+X_{(A_u,u)}\left(\frac{(4m+2M)}{NM^2}\right)^{1/2}\right);$$

$$z_3=-X_{(E_g,1)}\left(\frac{1}{2mN}\right)^{1/2}+X_{(B_{1u},1)}\frac{1}{(4mN)^{1/2}}+\frac{1}{(2+4m/M)}\left(X_{(A_{2u},0)}\left(\frac{Mm+2m^2}{m^2MN}\right)^{1/2}+X_{(A_{2u},u)}\left(\frac{4m+2M}{NM^2}\right)^{1/2}\right);$$

$$z_4=-X_{(E_g,2)}\left(\frac{1}{2mN}\right)^{1/2}-X_{(B_{1u},1)}\left(\frac{1}{4mN}\right)^{1/2}+\frac{1}{(2+4m/M)}\left(X_{(A_{2u},0)}\left(\frac{Mm+2m^2}{m^2MN}\right)^{1/2}+X_{(A_{2u},u)}\left(\frac{4m+2M}{NM^2}\right)^{1/2}\right);$$

$$z_5=X_{(B_{1u},2)}\left(\frac{1}{2MN}\right)^{1/2}-\frac{1}{(2+M/m)}\times\left[X_{(A_{2u},0)}\left(\frac{M+2m}{mMN}\right)^{1/2}-\tfrac{1}{2}X_{(A_{2u},u)}\left(\frac{4M+2m}{Nm^2}\right)^{1/2}\right];$$

$$z_6=-X_{(B_{1u},2)}\left(\frac{1}{2MN}\right)^{1/2}-\frac{1}{(2+M/m)}\times\left[X_{(A_{2u},0)}\left(\frac{M+2m}{mMN}\right)^{1/2}-\tfrac{1}{2}X_{(A_{2u},u)}\left(\frac{(4M+2m)}{Nm^2}\right)^{1/2}\right].$$

Together with the relation

$$X_{q=0,\mu}=-i\left(\frac{\hbar}{2\omega_{q=0,\mu}}\right)^{1/2}(A_{q=0}{}^{(\mu)\dagger}-A_{q=0}{}^{(\mu)}).$$

These give the $C_z{}^{(b)}(A_{2u},0)$ which are needed for evaluation of the absorption intensity with $E\|c$ axis:

$$C_z{}^{(1)}(A_{2u},0)=\frac{1}{(2+4m/M)}\left(\frac{Mm+2m^2}{m^2MN}\right)^{1/2}\times\left(i\left(\frac{\hbar}{2\omega_{A_{2u}}}\right)^{1/2}\right);$$

$$C_z{}^{(1)}(A_{2u},0)=C_z{}^{(2)}(A_{2u},0)=C_z{}^{(3)}(A_{2u},0)=C_z{}^{(4)}(A_{2u},0);$$

$$C_z{}^{(5)}(A_{2u},0)=\frac{-1}{(2+M/m)}\left(\frac{Mm+2m^2}{m^2MN}\right)^{1/2}\times\left(i\left(\frac{\hbar}{2\omega_{A_{2u}}}\right)^{1/2}\right);$$

$$C_z{}^{(5)}(A_{2u},0)=C_z{}^{(6)}(A_{2u},0).$$

Note that, as stated in the text, the fluorine ions oscillate against the magnetic ions in this mode.

No comparably simple solution is available for the modes $E_u{}^{(i)}$ ($i=1,\cdots,6$) which appear in the expression for the absorption with $E\perp c$ axis. In that case, 8 simultaneous equations involving the unknown force constants in the tensor $\mathbf{G}_{l,b;l',b'}$ must be solved for the $\hat{e}_{\mathbf{q},\mu,b}$, since the form of the normal coordinates is not fully determined by symmetry. (Two equations are eliminated by removing the uniform modes.) From symmetry, one can only conclude that the $\binom{x}{y}$ components of ions (2 and 4) and (1 and 3) are always in phase for these modes.

APPENDIX B: SYMMETRY PROPERTIES OF THE $\pi_{l,b;l',b'}^{(z)}$

The result of Allen *et al.* shows that the only parts of the $\Pi_{l,b;l',b'}^{(i)}$ which do not vanish when the sums in Eq. (2) are done are those having the following transformation properties

$$\Pi_{l,b;l',b'}^{(z)}=\Pi^{(\parallel)}(|\mathbf{X}_{l,b}^{(0)}-\mathbf{X}_{l',b'}^{(0)}|)\times\sigma_x^{(l,b;l',b')}\sigma_y^{(l,b;l',b')}\sigma_z^{(l,b;l',b')};$$

$$\Pi_{l,b;l',b'}^{(x)}=\Pi^{(\perp)}(|\mathbf{X}_{l,b}^{(0)}-\mathbf{X}_{l',b'}^{(0)}|)\sigma_y^{(l,b;l',b')};\qquad\text{(B-1)}$$

$$\Pi_{l,b;l',b'}^{(y)}=\Pi^{(\perp)}(|\mathbf{X}_{l,b}^{(0)}-\mathbf{X}_{l',b'}^{(0)}|)\sigma_x^{(l,b;l',b')},$$

where

$$\sigma_x^{(l,b;l',b')}=\operatorname{sgn}(\mathbf{X}_{l,b}^{(0)}-\mathbf{X}_{l',b'}^{(0)}),\text{ etc.}$$

For $E\|c$ axis, we show explicitly how the nature of the A_{2u} mode and the geometry of the crystal give $\Pi_{l,b,l',b'}^{(z)}$ the right properties for the first four neighbors on the opposite sublattice under the assumption that the exchange interaction is entirely due to superexchange with the fluorine ion lying nearest the line between the two magnetic ions. The demonstration is essentially the same for each set of neighbors. We show the required change in sign in detail for the pairs 6-5 and 6-41. The relevant factors in $\Pi_{l,b,l',b'}^{(z)}$ are

$$\sum_{l'',b''}C_z^{(b'')}(A_{2u},0)\frac{\partial}{\partial z_{l'',b''}}[J_{l,5\;l,6}]=\frac{-1}{(2+M/m)}\left(\frac{(Mm+m^2)}{m^2MN}\right)^{1/2}\left(i\left(\frac{\hbar}{2\omega_{A_{2u}}}\right)^{1/2}\right)\times\left(\frac{\partial}{\partial z_5}J_{56}+\frac{\partial}{\partial z_6}J_{56}-\frac{1}{2}\frac{M}{m}\frac{\partial J_{56}}{\partial z_2}\right);$$

$$\sum_{l'',b''}C_z^{(b'')}(A_{2u},0)\frac{\partial}{\partial z_{l'',b''}}J_{6,41}=\frac{-1}{(2+M/m)}\left(\frac{(Mm+2m^2)}{m^2MN}\right)^{1/2}\left(i\left(\frac{\hbar}{2\omega_{A_{2u}}}\right)^{1/2}\right)\times\left(\frac{\partial}{\partial z_{41}}J_{41,6}+\frac{\partial}{\partial z_6}J_{41,6}-\frac{1}{2}\frac{M}{m}\frac{\partial}{\partial z_4}J_{41,6}\right)$$

under the assumptions indicated and using the expressions for the $C_z^{(b)}(A_{2u},0)$'s derived in the preceding appendix. Transforming the derivatives to the two coordinate systems indicated in Fig. 4(c), we have

$$\frac{\partial}{\partial z_4}=\cos\theta\frac{\partial}{\partial z_4'}+\sin\theta\frac{\partial}{\partial x_4'};$$

$$\frac{\partial}{\partial z_6}=\cos\theta\frac{\partial}{\partial z_6'}+\sin\theta\frac{\partial}{\partial x_6'};$$

$$\frac{\partial}{\partial z_{41}}=\cos\theta\frac{\partial}{\partial z_{41}'}+\sin\theta\frac{\partial}{\partial x_{41}'};$$

$$\frac{\partial}{\partial z_1}=-\cos\theta\frac{\partial}{\partial z_1''}-\sin\theta\frac{\partial}{\partial x_1''};$$

$$\frac{\partial}{\partial z_6}=-\cos\theta\frac{\partial}{\partial z_6''}-\sin\theta\frac{\partial}{\partial x_6''};$$

$$\frac{\partial}{\partial z_5}=-\cos\theta\frac{\partial}{\partial z_5''}-\sin\theta\frac{\partial}{\partial x_5''}.$$

From the geometry it is clear that

$$\frac{\partial J_{41}}{\partial z_4'}=\frac{\partial J_{5,6}}{\partial z_1'};\quad\frac{\partial J_{41,6}}{\partial x_4'}=\frac{\partial J_{5,6}}{\partial x_1'};$$

$$\frac{\partial J_{41,6}}{\partial x_6'}=\frac{\partial J_{5,6}}{\partial z_5''};\quad\frac{\partial J_{41,6}}{\partial x_6'}=\frac{\partial J_{5,6}}{\partial x_5''};$$

$$\frac{\partial J_{41,6}}{\partial z_{41}'}=\frac{\partial J_{5,6}}{\partial z_6''};\quad\frac{\partial J_{41,6}}{\partial x_{41}'}=\frac{\partial J_{5,6}}{\partial x_6''}.$$

Combining these results, one has

$$\Pi_{6,5}^{(z)}=-\Pi_{6,41}^{(z)}$$

as required by the relation (B1). Physically, the result is seen more clearly by sketching the two pairs in motion when the A_{2u} mode is excited. The relative phase of the fluorine ion and the magnetic ions is opposite in the two cases when the motion is decomposed into a component along the line between the magnetic ions and another normal to it. By similar sketches for the other relevant pairs, identical proofs of all the special cases of relation (B1) can be constructed for the first four neighbors.