L-phonon spectrum at $\bar{\omega}$. The intrinsic lattice absorption from the transverse optic branch of the L system is far removed from the low-frequency region considered here. As the temperature of the system increases from absolute zero, the absorption strength is transferred from the frequency region around ω_0 to the frequency region around $\bar{\omega}$, and the center of gravity of the total absorption strength shifts with temperature. As long as the center of gravity of the low-frequency impurity-induced absorption strength is temperature dependent, Eq. (6) guarantees that the static dielectric constant is also temperature dependent. An interesting consequence of this temperature dependence is that a characteristic electrocaloric effect[10] should occur for this system. This effect should be quite modest for $KI:Ag^+$ and $KBr:Li^+$ but should become measurable for systems with lower frequency impurity modes.[11]

In summary, then we conclude that the Debye-Waller factor, which appears in the zero-phonon lines of neutron diffraction, x-ray diffraction, the Mössbauer effect,[8] and optical absorption of some defects in solids,[12] also exists for the zero–L-phonon line of impurity-activated infrared absorption in alkali-halide crystals. The appearance of the Debye-Waller factor in this latter problem arises from random thermal modulation of impurity modes by lattice phonon modes. The low frequency of the resonant mode insures that the influence of this modulation can also be seen as a temperature-dependent contribution to the static di-

electric constant.

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MAGNON-INDUCED ELECTRIC DIPOLE TRANSITION MOMENT*

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Recently Halley and Silvera[1] suggested a mechanism of inducing the electric dipole transition moment at an ion site in a magnetic material by magnon excitation. Assuming this mechanism, they interpreted the far-infrared absorption peak of FeF_2 at 154 cm^{-1}. The same mechansim was assumed by Greene et al.[2] in the interpretation of the magnon side band in the

visible absorption spectrum of MnF_2.

In this Letter we will point out that these spectra as well as the far-infrared absorption[3] of CoF_2 should be, as shown at the end of this Letter, interpreted by another mechanism, which was originally considered to explain[4] the magnon side band of the $^3A_2 \rightarrow {}^1E$ line in $KNiF_3$ and was successfully applied to the Mn-

Mn and Mn-Ni pair spectra in $KZnF_3$:Mn[5] and $KZnF_3$:Mn, Ni[6] in order to explain the observed spectral structure and the intensity enhancement.

Our mechanism can be explained as follows:

For simplicity, let us consider a pair of ions a and b where an up and a down spin are accommodated in orbitals φ_a and φ_b, respectively, in the ground state. The transition electric dipole moment accompanying the flip of both spins, $\langle \varphi_{a\uparrow}\varphi_{b\downarrow} | \vec{P}_{eff} | \varphi_{b\uparrow}\varphi_{a\downarrow} \rangle$, is given as

$$\langle \varphi_{a\uparrow}\varphi_{b\downarrow} | \vec{P}_{eff} | \varphi_{b\uparrow}\varphi_{a\downarrow} \rangle = \sum_\mu \langle \varphi_{a\uparrow}\varphi_{b\downarrow} | \vec{P} | \varphi_{\mu\uparrow}\varphi_{b\downarrow} \rangle \langle \varphi_{\mu\uparrow}\varphi_{b\downarrow} | V | \varphi_{b\uparrow}\varphi_{a\downarrow} \rangle /\Delta E(\varphi_\mu - \varphi_a)$$

$$+ (\text{expression obtained interchanging } \vec{P} \text{ and } V)$$

$$+ \sum_\nu \langle \varphi_{a\uparrow}\varphi_{b\downarrow} | \vec{P} | \varphi_{a\uparrow}\varphi_{\nu\downarrow} \rangle \langle \varphi_{a\uparrow}\varphi_{\nu\downarrow} | V | \varphi_{b\uparrow}\varphi_{a\downarrow} \rangle /\Delta E(\varphi_\nu - \varphi_b)$$

$$+ (\text{expression obtained interchanging } \vec{P} \text{ and } V), \qquad (1)$$

where $\vec{P}$ is the electric dipole moment operator, $\Delta E(\varphi_\mu - \varphi)$ the energy required in transferring an electron from φ to φ_μ, and φ_μ and φ_ν any orbital of ions a and b [φ_μ (or φ_ν) is an odd-parity excited orbital when φ_μ (or φ_ν) is the orbital of ion a (or b)]. The nonvanishing interaction operator V should be the two-electron Coulomb operator r_{12}^{-1} when $\varphi_\mu \neq \varphi_b$ ($\varphi_\nu \neq \varphi_a$), but it could also be the kinetic plus the crystalline field operator when $\varphi_\mu = \varphi_b$ ($\varphi_\nu = \varphi_a$). In the former case the matrix elements of V are the hybrid or nondiagonal exchange integrals, and in the latter they are the so-called transfer integrals. The matrix elements are defined as

$$\langle \varphi_\mu \varphi_b | V | \varphi_b \varphi_a \rangle$$

$$= \int d\tau_1 d\tau_2 \, \varphi_\mu{}^*(1)\varphi_b{}^*(2) V \varphi_b(1)\varphi_a(2).$$

We have neglected the contribution from the charge transfer effect where ligand electrons are involved.[7] This may be more important as in the theory of superexchange interaction.[8] By using spin operators $\vec{s}_a$ and $\vec{s}_b$ of electrons in φ_a and φ_b, respectively, the operator equivalent of Eq. (1) may be expressed as follows,

$$\vec{P}_{eff} = \vec{\Pi}_{ab}(\vec{s}_a \cdot \vec{s}_b). \qquad (2)$$

It should be noted that, if the arrangement of the pair of orbitals, φ_a and φ_b, has a center of symmetry, the first two lines in Eq. (1) cancel the last two lines leading to a vanishing electric dipole transition moment. However, if the pair has no center of symmetry, as Fe-F-Fe in rutile crystals, $\vec{P}_{eff}$ is nonvanishing, even if the metal ion is at the center of symmetry.

For periodic crystals Eq. (1) may be easily extended. For example, in a one-dimensional antiferromagnet, in which metal ions are at the center of symmetry but no center of symmetry is found between two neighboring metal ions, the effective transition dipole moment is given by

$$\vec{P}_{eff} = \vec{\Pi} \sum_{j = \text{even}} (\vec{s}_j \cdot \vec{s}_{j+1} - \vec{s}_j \cdot \vec{s}_{j-1}), \qquad (3)$$

where only the nearest-neighbor interaction is assumed. The minus sign of $\vec{s}_j \cdot \vec{s}_{j-1}$ comes from the fact that $\vec{\Pi}$ transforms like a vector and the jth ion is at the center of symmetry. Eq. (3) indeed leads to the excitation of a very short spin wave.

Similarly a transition moment accompanying an electronic excitation, $\varphi_a \rightarrow \varphi_a'$ (in the case of MnF_2, $^6A_1 \rightarrow {}^4T_1$), is given as

$$\vec{P}_{eff}(\varphi_a' - \varphi_a) = \vec{\Pi}_{a'a,b}(\vec{s}_{a'a} \cdot \vec{s}_b), \qquad (4)$$

for the ion pair $a-b$, where

$$\vec{s}_{a'a} = \sum_{m,m'} c_{a'm'}{}^* c_{am} \langle m' | \vec{s} | m \rangle,$$

and c_{am} is the annihilation operator of the electron in the orbital φ_a with spin m. Even if the pair has a center of symmetry ($\varphi_a = \varphi_b$), we obtain in this case a nonvanishing $\vec{P}_{eff}$,

$$\vec{P}_{eff}(\varphi_a' - \varphi_a) = \vec{\Pi}_{a'a,b}(\vec{s}_{a'a} \cdot \vec{s}_b - \vec{s}_a \cdot \vec{s}_{b'b}). \qquad (5)$$

It will not be difficult to understand that our mechanism will lead for the FeF_2 and MnF_2 spectra of interest to a result qualitatively similar to those mentioned by the authors cited in the beginning. The observed intensity of the magnon side band of MnF_2 can be explained if the matrix elements of V are of the order

of 1-10 cm^{-1} which seems reasonable. More detailed studies of our mechanism[8] and its application will be published elsewhere in the future.

Halley and Silvera's mechanism seems to us to be ineffective. If their first expression is correctly written, it is

$$Q = [\lambda\sum_m \langle\Gamma_1|Q^{(op)}|\Gamma_m\rangle\langle\Gamma_m|\vec{L}|\Gamma_1\rangle/(E_1-E_m) + \lambda\sum_m\langle\Gamma_1|\vec{L}|\Gamma_m\rangle\langle\Gamma_m|Q^{(op)}|\Gamma_1\rangle/(E_1-E_m)]\cdot\vec{S}. \qquad (6)$$

Considering the fact that the orbital functions appearing in Eq. (6) can be chosen to be real, we see that the matrix elements of $\vec{L}$ are pure imaginary while those of $Q^{(op)}$ are real. This immediately leads to a vanishing Q because of the Hermitean nature of $\vec{L}$. Putting it in a more sophisticated way, the quadrupole moment, which is Hermitean and invariant with respect to time reversal, cannot be represented by a Hermitean operator proportional to $\vec{S}$ which changes its sign upon time reversal.

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STRUCTURE OF THE ORDERED STATE OF ORTHO-HYDROGEN AT ABSOLUTE ZERO

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It is known that solid hydrogen has a specific-heat anomaly at about 1.6°K at high ortho-hydrogen concentrations (>60%).[1-3] This anomaly is accompanied by a change in the nuclear magnetic resonance line shape.[4-7] It has been shown that solid hydrogen undergoes an order-disorder transition at this temperature which could be caused by the quadrupole-quadrupole interaction between the ortho-molecules.[8-10] Further, Nakamura[8] has shown that this quadrupole-quadrupole interaction is the most important contribution to the energy of ordering. Below the transition temperature an ordered state is formed to give minimum interaction energy. Recently, the infrared-absorption spectrum of solid hydrogen has been measured by Clouter and Gush[11] near 1.5°K. They observed a change in the spectrum at the same temperature, which can only be explained if we assume that the crystal structure changes from one without inversion symmetry above the transition temperature to one with inversion symmetry below it.

The purpose of this note is to suggest a lowest energy configuration of pure ortho-hydrogen and to show that the minimum quadrupolar energy in the face-centered cubic lattice is lower than that in the hexagonal close-packed lattice, a result in accord with the measurements of Clouter and Gush.[11] This is done by the classical method of Luttinger and Tisza[12] for minimizing the dipole-dipole interaction energy which has been generalized by Nagai and Nakamura[13] for quadrupole interaction.

The interaction energy between two quadrupoles, each of quadrupole moment Q, is given by

$$\tfrac{3}{4}e^2Q^2\left\{\frac{1+2(\vec{S}_1\cdot\vec{S}_2)^2}{r^5} - 5\frac{(\vec{S}_1\cdot\vec{r})^2+(\vec{S}_2\cdot\vec{r})^2+4(\vec{S}_1\cdot\vec{r})(\vec{S}_2\cdot\vec{r})(\vec{S}_1\cdot\vec{S}_2)}{r^7} + 35\frac{(\vec{S}_1\cdot\vec{r})^2(\vec{S}_2\cdot\vec{r})^2}{r^9}\right\},$$