approaches, to explain the bonding in these phases. Low-temperature magnetic-susceptibility studies, as well as electron-spin-resonance studies, are in progress to obtain more information about the low-temperature effects.

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Ferroelectric "Soft" Mode in $KTaO_3$†

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The far infrared reflectivity of $KTaO_3$ has been studied as a function of temperature from 12 to 463°K. The results have been analyzed by means of a Kramers-Kronig method, and indicate a "soft" mode, lowering its frequency as the temperature is lowered towards the "Curie" temperature. This is in accordance with the temperature dependence of the dielectric constant interpreted through Cochran's theory.

I. INTRODUCTION

THE high reflectivities in the long-wavelength infrared region, associated with the anomalously large dielectric constants, in materials with the TiO_6 and TaO_6 octahedral structure, have been observed by many recent workers.[1–6]

Far-infrared reflectance measurements have been made on single-crystal $KTaO_3$ from 40 to 1000 μ (250–10 cm^{-1}), over the temperature range 12–463°K. The reflectance data were analyzed using a Kramers-Kronig method to obtain the total conductivity σ from the imaginary part of the dielectric constant. The conductivity exhibits a very strong temperature-dependent low-frequency peak which moves from 106 cm^{-1} at 463°K, to 25 cm^{-1} at 12°K, and accounts for more than 90% of the static dielectric constant ϵ_0.

The results indicate a relationship between this low transverse optical mode ω_t for $k\simeq 0$, and the static dielectric constant, ϵ_0, such that

$$\omega_t^2(T)=A/\epsilon_0(T),$$

where $A=1.9\times10^6$ $(cm^{-1})^2$. This result can be related directly to the Curie-Weiss law behavior of ferroelectrics, and the associated implications have been derived and discussed by several authors.[7–9] Consequently, the experimental verification in the case of $KTaO_3$ helps confirm the theory of ferroelectricity in perovskite-type materials which indicate a soft mode lowering its frequency and becoming unstable as the temperature is lowered towards the Curie point. This phenomenon had previously only been observed with any certainty for $SrTiO_3$, using far infrared[1] and neutron techniques.[10]

II. EXPERIMENTAL PROCEDURE

The infrared-reflectance measurements at a 10° angle of incidence were performed on a Michelson spectrophotometer[11] using several beam splitters and a liquid-helium-cooled germanium detector. The sample was mounted in a separately evacuable chamber, and its temperature was measured with two calibrated thermocouples attached to the crystal. The complete temperature range could be accomplished without disturbing the sample and mount.

The total reflectivity curve from 10–4000 cm^{-1} was measured at 296°K, and also at 126°K, but very little temperature dependence of the modes at about 200

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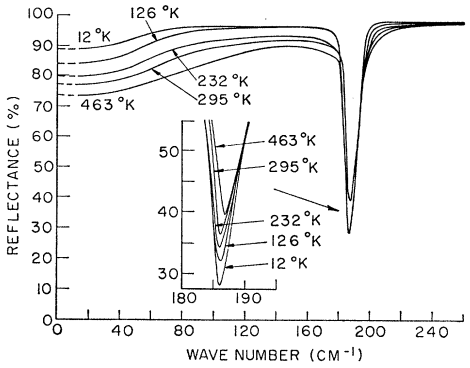

FIG. 1. Far infrared reflectivity of $KTaO_3$ as a function of temperature over the frequency range 10–250 cm^{-1}. The error in measurement is about ±2%.

cm^{-1}, 550 cm^{-1}, and the side band, at 760 cm^{-1} was observed. The results at room temperature agreed closely with those of Miller and Spitzer,[2] and reference should be made to their work for the complete spectrum. Between 0–10 cm^{-1}, the extrapolated curves were in good agreement with the reflectivity values calculated from the static dielectric constant measurements of Rupprecht and Bell,[12] and Davis.[13] Beyond 250 cm^{-1}, the reflectance curve measured at room temperature was used with the high-temperature and room-temperature data, while the 126°K curve was coupled with the measurements at other temperatures in order to evaluate the far infrared complex dielectric constant from the Kramers-Kronig analysis. The marked temperature-dependence of the reflectivity curve below 100 cm^{-1} can be clearly seen in Fig. 1, together with the weakly temperature-dependent mode at 200 cm^{-1}.

III. DISCUSSION

The frequencies of the normal optically active transverse modes were derived from peaks in the conductivity, $\sigma(\omega)$, where $\sigma_j=\epsilon_j''\omega/2$, and ϵ_j'' is the contribution of the jth resonance to the imaginary part of the dielectric constant.[14]

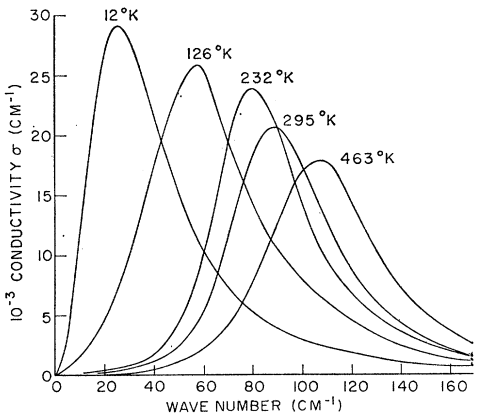

FIG. 2. The conductivity calculated from the reflectivity curves shown in Fig. 1 for the five different temperatures.

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TABLE I. The transverse optical modes in $KTaO_3$ as a function of temperature.

T°K	ω_{t_1}	ω_{t_2}	ω_{t_3}
12	25	196	...
126	58	198	551
232	79	198	551
295	88[a]	199[a]	550[a]
463	106	199	...

[a] See Ref. 7 for complete spectrum.

The frequency-dependence of the conductivity with temperature below 170 cm^{-1} is shown in Fig. 2, and the positions of the "soft" mode are estimated to be accurate to about ±5 cm^{-1}. This estimate was obtained by varying the low-frequency input data to the K-K analysis over the limit of the error (±2%) in the reflectance measurements.

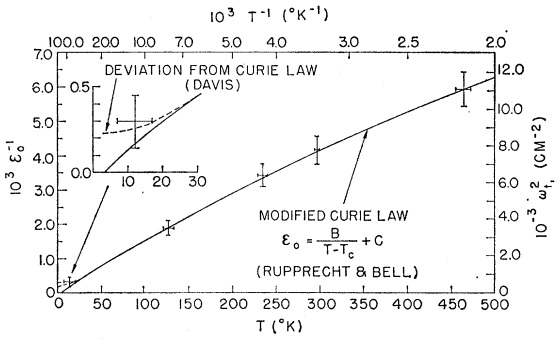

FIG. 3. The square of the frequency (in cm^{-1}) of the ferroelectric "soft" mode plotted as a function of temperature. Vertical lines indicate the $\omega_{t_1}^2$ error and horizontal lines show the temperature variation. The solid curve shows the reciprocal of the dielectric constant from the results of Rupprecht and Bell. The extrapolated curve gives a Curie temperature of 2.9°K. The dashed curve shows the low-temperature deviation (below 30°K) from the modified Curie law (Rupprecht and Bell) obtained by Davis.

The temperature dependence of the transverse optical modes is given in Table I.

The static dielectric constant ϵ_0 can be written in terms of the Curie law,

$$\epsilon_0 \propto 1/(T-T_c),$$

and consequently $\omega_{t_1}^2 \propto T-T_c$. However, measurements of ϵ_0 for $KTaO_3$ at microwave frequencies by Rupprecht and Bell,[12] from 80–300°K, have indicated a modified Curie-law behavior such that

$$\epsilon_0=B/(T-T_c)+C,$$

where $B=5.99\times10^4$°K, $C=39$, and the Curie temperature, $T_c=2.8$°K. This result is shown by the solid

[14] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, New York, 1940), Chap. 17, p. 635.

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.

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

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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

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