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# Complex Dielectric Constant of $KH_2PO_4$ at 9.2 Gc/sec

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The temperature dependence of the dielectric constant and loss tangent in potassium dihydrogen phosphate along and normal to the optic axis has been measured by a cavity perturbation method at 9.2 Gc/sec. The dielectric constants agree with earlier low-frequency measurements. The parallel dielectric constant exhibits a modified Curie-Weiss behavior which may be described by $(T-T_c)\epsilon_c'=A'+BT$, with $T_c=119°\text{K}$, $A'=2.27\times10^3°\text{K}$, $B=4.7$. The parallel loss tangent also has an approximate Curie-Weiss dependence which may be described by $(T-T_c)\tan\delta_c=\alpha+\beta T+\gamma T^2$, with $\alpha=8.42\times10^{-1}°\text{K}$, $\beta=-9.49\times10^{-4}$, and $\gamma=8.49\times10^{-6}(°\text{K})^{-1}$. This result is discussed in terms of Silverman's treatment of the microwave loss in strontium titanate. The implications of these measurements for microwave light modulation are also discussed.

## INTRODUCTION

POTASSIUM dihydrogen phosphate (KDP) is a piezoelectric crystal with tetragonal symmetry at room temperature. At its Curie temperature of −150°C it becomes ferroelectric and orthorhombic with its $c$ axis as the polar direction.[1] In the paraelectric region, above −150°C, the dielectric properties may be described by two complex dielectric constants, one for fields along the $c$ axis, and the other for fields perpendicular to that direction. The real part of the relative dielectric constant is designated $\epsilon'$, the imaginary part $\epsilon''$, and the loss tangent $\epsilon''/\epsilon'$ or $\tan\delta$. The quantities measured with the field along the $c$ axis are denoted by a subscript $c$. Measurements normal to the $c$ axis, along an $a$ axis, are denoted by the subscript $a$. In general these quantities will be temperature and frequency dependent. Measurements of their temperature dependence in the paraelectric region at 9.2 Gc/sec are reported here. Since the measuring frequency is much greater than the frequencies of the macroscopic mechanical resonances which may be induced by the piezoelectric effect, the measurements lead to constant strain or "clamped" values.[1]

Measurements of the constant stress or "free" dielectric constant at low frequencies have been made by several workers.[2-6] The temperature dependence of $\tan\delta_c$ at $10^3$ cps has been reported by von Hippel.[4] Comparing measurements of $\epsilon_c'$ at $10^3$ and $10^7$ cps close to the Curie point, Baumgartner[6] found a shift in the apparent Curie temperature from −150°C for the free crystal to −154°C for the clamped case. A similar result has been calculated by Mason.[3] The region below the Curie temperature has been investigated by Barkla and Finlayson.[5] Previous microwave measurements consist of values for $\epsilon_c'$, $\epsilon_a'$, $\tan\delta_c$, and $\tan\delta_a$ at 8.8 Gc/sec,[7] and for $\epsilon_c'$ and $\tan\delta_c$ at 25 Gc/sec[8] all at room temperature. Measurements of $\epsilon_c'$, $\epsilon_a'$, $\epsilon_c''$, and $\epsilon_a''$ by Barker and Tinkham[9] indicate strong absorptions for $a$- and $c$-axis fields in the far infrared.

Our results for $\epsilon_c'$ and $\epsilon_a'$ agree closely with the low-frequency measurements, and there is no evidence of dispersion. However, our results for $\tan\delta_c$ are considerably higher than von Hippel's[4] at $10^3$ cps, but are somewhat lower than the room temperature results at 8.8 and 25 Gc/sec.

## EXPERIMENT

The complex dielectric constant may be measured by observing the change in resonant frequency and $Q$ of a resonant cavity when a small sample is inserted. For a rod parallel to the electric field the perturbation formula is[10]

$$(\delta\omega/\omega)-j\delta(1/2Q) = (\epsilon'-1-j\epsilon'')\int_{\Delta V} E^2dv \Big/ 2\int_V E^2dv, \quad (1)$$

in which $\omega$ is the resonant frequency, $Q$ the quality factor, and $V$ the volume of the cavity. $E$ is the field in the empty cavity, and $\Delta V$ the volume of the sample. The variations $\delta\omega$ and $\delta(1/2Q)$ represent shifts resulting from insertion of the sample. For small perturbations, it may be assumed that the change in loaded $Q$ is due to dielectric losses alone.

The apparatus for measuring $\omega$ and the width of the cavity resonance is shown schematically in Fig. 1. Klystron 1 was swept through the cavity resonance and the result displayed on an oscilloscope. The repeller of

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[1] W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

[2] G. Busch, Helv. Phys. Acta. **11**, 269 (1938).

[3] W. P. Mason, Phys. Rev. **69**, 173 (1946).

[4] *Dielectric Materials and Applications*, edited by A. R. von Hippel (John Wiley & Sons, Inc., New York, 1954).

[5] H. M. Barkla and D. M. Finlayson, Phil. Mag. **44**, 349 (1953).

[6] H. Baumgartner, Helv. Phys. Acta **24**, 326 (1951).

[7] H. Granicher and W. Shurter, Z. angew. Math. Phys. **8**, 382 (1957).

[8] W. A. Yager, mentioned in W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 258.

[9] A. S. Barker and M. Tinkham, Bull. Am. Phys. Soc. **7**, 439 (1962).

[10] See e.g. K. S. Champlin and R. R. Krongard, IRE Trans. **MTT-9**, 545 (1961); also F. E. Borgnis and C. H. Papas, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 16, and references.

klystron 2 was modulated at a few megacycles by a variable frequency oscillator (VFO) and its output mixed with a sample from klystron 1. The mode of klystron 1 with zero-beat marker pips was displayed on the oscilloscope. The width of the cavity response at the 3-dB points was measured by adjusting the VFO and measuring its frequency using a frequency counter. With no modulation on klystron 2, the zero beat pip was set at the peak of the cavity response and the resonant frequency, measured by means of a transfer oscillator (TO) and counter.

Changing the power level in the cavity had no appreciable effect at temperatures above the Curie point indicating that the quantities measured were the small signal values. The field strength was typically ~20 V/cm.

A thermocouple was attached to the cavity near the sample, and the cavity was enclosed in a massive copper can maintained at an overpressure of dry nitrogen.[11] The temperature was varied slowly by adjusting the height of the can above the liquid-nitrogen level in the Dewar. In practice, a temperature run was made with the sample in place. The sample was then removed without opening the cavity, and an empty cavity run was made. Data from smoothed curves for the two runs were then used to compute $\epsilon'$ and tan$\delta$ at regular temperature intervals.

Cavities were constructed from standard waveguide and operated in the $TE_{102}$ or $TE_{105}$ mode. They could be opened along a current null to insert the sample. Small holes were provided at this junction, in the centers of the broad walls, in order that rods could be removed without opening the cavity. The rods were roughly 0.020 in. square and 0.5 in. or more in length. Since the rod cross section was irregular owing to a tendency for KDP to chip, the mean cross section was obtained from measurements of the length and weight, the density of KDP being taken as 2.345. The cross section could be determined to within 3%.

The rods were oriented optically to within about 1° of the *a* or *c* axis. Three rods for the *a*-axis experiment were cut from the same crystal[12] along the same axis. Three *c*-axis rods were cut from three different crystals.[13]

The perturbation method is not suitable from either the experimental or computational standpoint for measuring large complex dielectric constants. For this reason, the measurements along the *c* axis were taken only to within 20°C of the Curie temperature. The perturbation formula (1) is valid when[10]

$$(\Gamma b)^2 = (2\pi b/\lambda)^2(\epsilon' - j\epsilon'') \ll 1, \tag{2}$$

where $\Gamma$ is the complex propagation constant in the sample, $2b$, the rod thickness, and $\lambda$, the vacuum wavelength. A first-order correction to (1) may be obtained by multiplying the right side by $[1+(\Gamma b)^2/6]$. For $b = 0.010$ in., the correction is 6% when $\epsilon'$ is 150 and tan$\delta \ll 1$, and is smaller at lower values of $\epsilon'$. This correction has not been applied to our results.

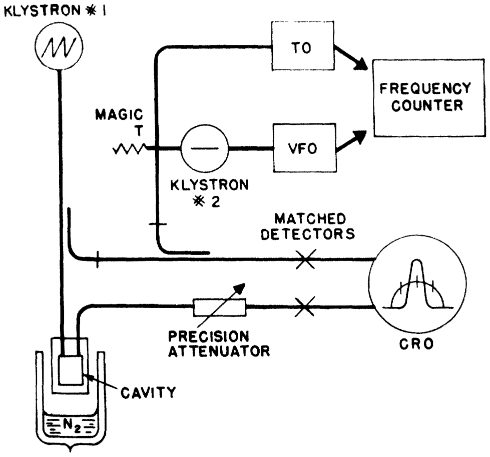

FIG. 1. Microwave dielectric constant measuring apparatus (VFO is variable frequency oscillator and TO is transfer oscillator).

While the error due to the perturbation approximation decreases as $\epsilon'$ and $\epsilon''$ decrease, the precision of measurement becomes poorer because of the reduced magnitudes of the shifts in $\omega$ and $Q$. Further, although certain errors resulting from the perturbation approximation and uncertainty in sample dimensions cancel in the calculation of tan$\delta$, $\epsilon''$ is somewhat more difficult to measure precisely than $\epsilon'$. Thus, the over-all error for both $\epsilon'$ and tan$\delta$ was about the same, namely ~10%, and was independent of temperature.

The loss measurements *below* the Curie temperature were not reproducible and were sensitive to power-level variations. These difficulties presumably are a result of saturation effects and domain formation.[5]

## RESULTS

Smooth curves of the several runs on various samples were plotted, and the most reliable curve, drawn through them. With the exception of the loss measurements below the Curie temperature, the results of individual runs agreed within 10%. The final curves for $\epsilon'$ and tan$\delta$, derived from the individual runs, are given in Figs. 2 and 3. The tan$\delta$ results for individual runs below the Curie point are shown dashed in Fig. 3.

Both $\epsilon_c'$ and tan$\delta_c$ increase hyperbolically in the neighborhood of the Curie temperature in the paraelectric region. On the other hand $\epsilon_a'$ increases slowly and tan$\delta_a$ decreases slowly as the temperature is reduced. It should be noted here that two constants are required to determine the dielectric constant or loss in the transverse plane at temperatures below the Curie point where the crystal becomes orthorhombic.

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[11] It was discovered that moisture in the cavity could be readily detected by an abrupt peak in the loss near 0°C.

[12] Obtained from H. Jaffe of Clevite Corporation.

[13] Two crystals came from Clevite, one of which was also used for the *a*-axis measurements, and the third was grown at Bell Telephone Laboratories several years ago.

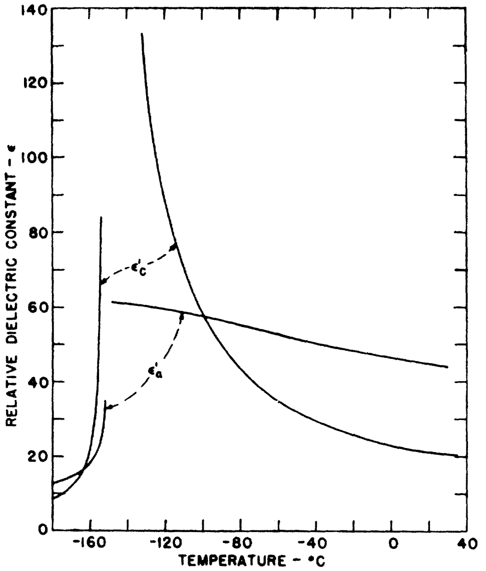

FIG. 2. Relative dielectric constant of $KH_2PO_4$ at 9.2 Gc/sec for fields along the $a$ axis, $\epsilon_a'$, and along the $c$ axis, $\epsilon_c'$. The curves are derived from several runs on various samples.

The $a$ axis in the tetragonal system used here is at 45° to the principal axes in the orthorhombic system.[1]

The constant stress Curie temperature[1] may be determined from the sharp break in the $a$-axis measurements and is at $-150\pm1$°C. The constant strain value, determined by extrapolating a plot of $1/\epsilon_c'$ versus temperature, occurs at $-154.5\pm2$°C.

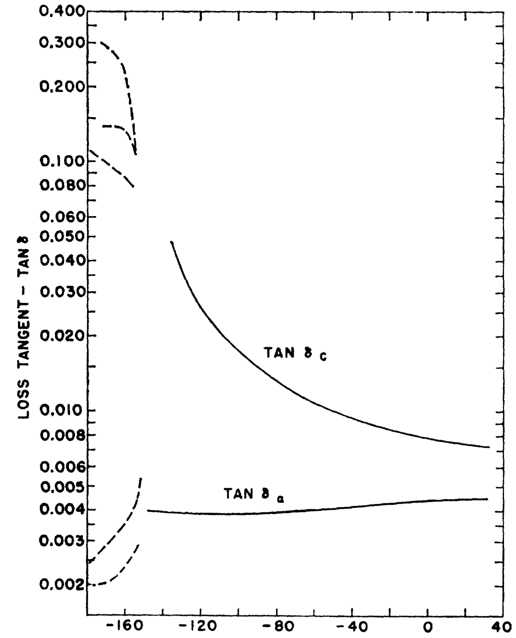

FIG. 3. Loss tangent of $KH_2PO_4$ at 9.2 Gc/sec for fields along the $a$ axis, $\tan\delta_a$, and along the $c$ axis, $\tan\delta_c$. The curves are derived from several runs on various samples.

In order to determine a functional relation for $\epsilon_c'$, we have plotted $(T-T_c)\epsilon_c'$ as a function of temperature in Fig. 4. The points are obtained with the aid of the curve of $\epsilon_c'$ (Fig. 2) taking 119°K (−154°C) as the appropriate Curie temperature. The straight line through these points gives

$$\epsilon_c'=(A'+BT)/(T-T_c) \tag{3}$$

or, equivalently,

$$\epsilon_c'=A/(T-T_c)+B \tag{4}$$

with temperature in degrees Kelvin and $A'=2.27\times10^3$°K, $A=2.82\times10^3$°K, $B=4.7$. A similar result is given by Mason.[3] The constant $B$ may be taken as that portion of the dielectric constant which does not depend on the ferroelectric nature of the crystal.[3]

In a similar way, $\tan\delta_c$ may be fitted to the function

$$\tan\delta_c=(\alpha+\beta T+\gamma T^2)/(T-T_c). \tag{5}$$

The points in Fig. 5 for $(T-T_C)\tan\delta_c$ are obtained with the aid of Fig. 3. The coefficients in (5) which give the best fit are $\alpha=8.42\times10^{-1}$°K, $\beta=-9.49\times10^{-4}$, and $\gamma=8.49\times10^{-6}$(°K)$^{-1}$.

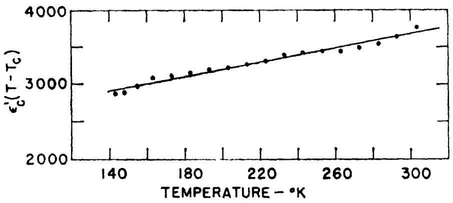

FIG. 4. $(T-T_C)\epsilon_c'$ vs $T$. Points are obtained with the aid of Fig. 2 with $T_c=119$°K. The fitted curve is $(T-T_c)\epsilon_c'=2.27\times10^3T+4.7$.

## DISCUSSION

### Microwave Absorption

Cochran[14,15] and others[16] have proposed a model of ferroelectricity which has been useful in accounting for certain properties of strontium titanate and related materials. In particular, Silverman[17] has used this model to show that a temperature dependence of the form (5) is reasonable for the microwave loss tangent.

According to the theory, the vibrational frequency of a particular long-wavelength transverse optical mode becomes small as the temperature is reduced toward the Curie point. Energy from the microwave field is coupled into this unstable mode and from it into other

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[14] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.

[15] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 401.

[16] P. Anderson, in *Fizika dielektrikov*, edited by G. I. Skanavi (P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R., Moscow, 1960).

[17] B. D. Silverman, Phys. Rev. **125**, 1921 (1962).

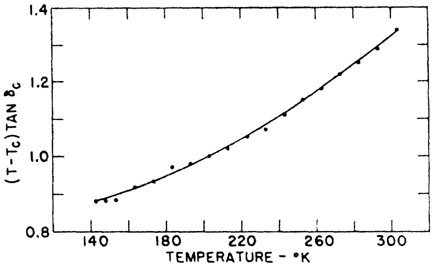

FIG. 5. $(T-T_C)\tan\delta_c$ vs. $T$. Points are obtained with the aid of Fig. 3 with $T_c=119$°K. The fitted curve is $(T-T_C)\tan\delta_c = 8.42\times10^{-1}-9.49\times10^{-4}T+8.49\times10^{-6}T^2$.

vibrational modes. The efficiency of this process increases rapidly as the frequency of the unstable mode, $\omega_0$, approaches the microwave frequency, $\omega$. The temperature dependence of $\omega_0$ is taken to be

$$\omega_0^2 \approx g(T-T_c), \tag{6}$$

in which $g$ is a constant that measures the temperature sensitivity of $\omega_0$. Silverman shows that

$$(T-T_c)\tan\delta \approx \omega\gamma'/g, \tag{7}$$

where $\gamma'$ is a damping constant which is a measure of the width of the unstable mode resonance, and identifies the right-hand side of (7) with the polynomial in (5). The temperature-independent part of the polynomial, $\alpha$, is attributed to a temperature-independent coupling between the unstable mode and the other lattice modes by lattice imperfections, impurities, or other temperature-independent processes. The remaining terms are thought to be the result of anharmonicity and are intrinsic to the crystal. The theory provides a satisfactory explanation of microwave experiments on strontium titanate by Rupprecht and Bell.[18]

Although it is not at all clear that the preceding picture is valid for KDP,[9,15] it is interesting to compare the values of $\alpha$, $\beta$, and $\gamma$ in (5) for KDP with the measurements on strontium titanate. For strontium titanate at 22 Gc/sec $\beta$ and $\gamma$ are roughly $7\times10^{-4}$ and $3\times10^{-6}$(°K)$^{-1}$, respectively. (Note that the sign of $\beta$ is reversed in the two substances.) After accounting for the difference in frequency of the measurements, the strontium titanate coefficients $\beta$ and $\gamma$ are about one third the KDP values.

For pure single-crystal strontium titanate, $\alpha$ vanishes. With the addition of 0.03% $Fe^{3+}$ Rupprecht and Bell[18] find a value of roughly $0.4\times10^{-1}$°K, which is about $2\times10^{-2}$ the KDP value when the frequency difference is taken into account. If the model used by Silverman were applicable to KDP, the relatively large observed value of $\alpha$ would suggest that the loss tangent in our samples can be reduced by improving the quality of the crystal. A spectroscopic analysis of the three crystals used indicated only slight traces (less than 0.005%) of impurities. However, other elements, not sensitive to this type of analysis, as well as lattice imperfections may be present in significant concentrations.

Since KDP differs in several respects from strontium titanate,[9,13] entirely different mechanisms may contribute to the loss. For example, the effects of piezoelectrically excited phonons, the tunneling of protons, or the hopping of protons between sites might be considered in this regard.

## Microwave Light Modulation

The electro-optic effect in KDP is intimately related to the dielectric constant. Zwicker and Sherrer[1,19] found that the low-frequency electro-optic coefficient, $f_{63}$, is nearly proportional to the dielectric constant, $\epsilon_c'$, and approximates a Curie-Weiss law as a function of temperature. A similar result was found in $RbH_2PO_4$.[20] Since $\epsilon_c'$ shows no sign of dispersion at microwave frequencies, it had been predicted[21] and was later demonstrated experimentally at room temperature[22] that $f_{63}$ also maintains its low-frequency clamped value at 9 Gc/sec. Thus, one may also expect the electro-optic coefficient to increase according to a Curie-Weiss law as the temperature is reduced at microwave frequencies, an inference which is of interest in the design of microwave light modulators.

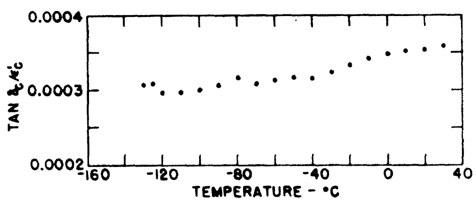

FIG. 6. $\tan\delta_c/\epsilon_c'$ vs $T$. Points are obtained from Figs. 2 and 3.

One may distinguish two types of microwave light modulator. In the cavity type,[22] most of the input power is dissipated in the crystal, while in a broad-band traveling wave-type[23,24] it may be that only a small fraction of the power is lost in the crystal. In the cavity-type modulator, the ratio of input power to peak phase retardation (modulation index) is proportional to $\epsilon_c''/\epsilon_c'^2$ or $(\tan\delta_c)/\epsilon_c'$, assuming $\epsilon_c'$ proportional to the electro-optic coefficient and neglecting losses other than the dielectric loss.[22] This ratio is plotted in Fig. 6 where it may be seen that very little improvement in efficiency can be expected at reduced temperature. On the other hand, in a pure traveling wave device, in

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[18] G. Rupprecht and R. O. Bell, Phys. Rev. **125**, 1915 (1962).

[19] B. Zwicker and P. Scherrer, Helv. Phys. Acta **17**, 346 (1944).

[20] M. Beck and H. Granicher, Helv. Acta Phys. **23**, 522 (1950).

[21] W. P. Mason, Bell System Tech. J. **29**, 161 (1950).

[22] I. P. Kaminow, Phys. Rev. Letters **6**, 528 (1961).

[23] I. P. Kaminow, R. Kompfner, and W. H. Louisell, IRE Trans. **MTT**. MTT-10,311 (1962). W. W. Rigrod and I. P. Kaminow, Proc. Inst. Radio Engrs. (to be published).

[24] I. P. Kaminow and Julia Liu, Proc. Inst. Radio Engrs. (to be published).

which the KDP loss is not significant, there may be some advantage in operating at reduced temperature. However, thermal strain and the higher dielectric constant may prove troublesome[24] at low temperature.

There are at least two KDP isomorphs—KD$_2$PO$_4$ and KH$_2$AsO$_4$—that require less dc voltage than KDP to produce a given phase retardation at room temperature.[25] If the microwave loss in these materials is sufficiently low, and if the microwave dielectric constant does not indicate any dispersion, these substances may provide a means for avoiding some of the problems involved in operating at reduced temperature.

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[25] *American Institute of Physics Handbook*, edited by Dwight E. Gray (McGraw-Hill Book Company, New York, 1957).

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# Far Infrared Antiferromagnetic Resonance in MnO and NiO†

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The uniaxial dipolar anisotropy in antiferromagnetic MnO and NiO aligns the two opposing sublattice moments in an easy (111) plane. The two normal modes for small oscillations of the sublattice magnetizations about a preferred direction within this plane are both nondegenerate and linearly polarized. The high-frequency mode has been observed at low temperatures (2°K) at 27.5 and 36.6 cm$^{-1}$ in MnO and NiO, respectively. In agreement with the unobservably small second-order Zeeman shift expected for these nondegenerate modes, a 10.7-kOe field was found to have no effect on the observed resonance frequencies. Increasing the sample temperature decreases the frequency of the mode in each case. The experimental temperature dependence of the antiferromagnetic resonance frequency can be accounted for by present theories only if an anomalous temperature dependence, previously found from neutron-diffraction data, is assumed for the temperature dependence of the sublattice magnetization.

## I. INTRODUCTION

Because coherent sources at present do not extend through the far infrared region of the electromagnetic spectrum, two very different experimental methods are used to examine the high-frequency properties of magnetic compounds. They consist of tuning the magnetic absorption to another frequency region with large magnetic fields[1] or using incoherent sources.[2] We have used the second method, namely, incoherent sources and optical techniques, to obtain transmission measurements on the antiferromagnetic resonances in manganese oxide[3] (MnO) and nickel oxide (NiO) under different experimental conditions.

In antiferromagnetic MnO and NiO, the most important source of anisotropy energy is the long-range magnetic-dipole interaction. Because $L=0$ in Mn$^{2+}$ and because the lowest level of Ni$^{2+}$ in NiO is an orbital singlet, the interaction of individual magnetic ions with the crystalline electric field from the slightly distorted octahedron of oxygen ions is of far lesser importance than the dipolar anisotropy.

The anisotropy energy from dipolar interactions has been calculated by Kaplan[4] for magnetic ions in a two-sublattice NaCl structure. Keffer and O'Sullivan[5] have computed the dipolar anisotropy for the general case of ordering of the second kind, but they suggest that, due to lattice distortion, the general eight-sublattice model can be replaced by a two-sublattice one, in which the spins are constrained by dipolar and exchange forces to point parallel to the (111) planes and constrained by weaker anisotropy to a threefold set of axes within these planes. It is the Keffer and O'Sullivan two-sublattice model using the Kaplan dipolar computation that we have compared with our experimental results.

## II. INFRARED PROPERTIES OF MnO AND NiO

The magnetic dipole-dipole interaction in NaCl-structure antiferromagnets, such as MnO and NiO, produces an unusual uniaxial anisotropy energy in which the uniaxis is the hard axis.[4] This easy plane anisotropy causes the uniform precession modes to be very different from those for oscillations about an easy uniaxis. The two modes in MnO and NiO are found to be nondegenerate and linearly polarized, whereas the two normal modes are degenerate and circularly polarized for the case of an easy-uniaxis antiferromagnet. Let us consider these nondegenerate modes in more detail. Since the dipolar anisotropy only determines a plane, the actual easy direction within the plane is determined by higher-order anisotropy terms. Thus for small oscillations at $k=0$, the sublattices appear to move in the exchange field, plus an anisotropy

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[1] S. Foner, J. Phys. Radium **20**, 336 (1959).

[2] R. C. Ohlmann and M. Tinkham, Phys. Rev. **123**, 425 (1961).

[3] A preliminary report of these results has been given: F. Keffer, A. J. Sievers, III, and M. Tinkham, J. Appl. Phys. **32**, 65S (1961).

[4] J. Kaplan, J. Chem. Phys. **22**, 1709 (1954).

[5] F. Keffer and W. O'Sullivan, Phys. Rev. **108**, 637 (1957).