ance radiation. Thus the same sense of signal is observed as when the light was collinear with the magnetic field.

It is easily shown that no alignment can be produced when the light beam makes an angle of $\cos^{-1}(\frac{1}{3})^{1/2} \cong 55°$ with the field axis. This follows from a consideration of the sum rules[3] and is independent of the values for the transition matrix elements. This prediction has been verified with the described experimental arrangement.

The effect of relaxation processes is to decrease the alignment and hence the resonance signal. We believe the relaxation time is of the order of one millisecond for our systems and is due to a quenching of the metastable states by impurities, including electrons, that are present in the discharge. Thus the resonance should exhibit a width of $\sim 10^{-4}$ gauss in a perfectly homogeneous magnetic field. We have observed line widths of $\sim 6 \times 10^{-3}$ gauss, which is consistent with the measured inhomogenieties of the earth's magnetic field presented by the Randall Laboratories. We have moved the apparatus into an adjacent parking area and observed line widths of $\sim 10^{-3}$ gauss, which appears consistent with the inhomogenieties of that area.

The helium pressure in the discharge tube may be varied over a range of about $10^2$. The design of the discharge tube is not critical to the experiment. We have used dc excitation and rf excitation applied either to the electrodes or externally to the glass envelope.

The analysis outlined above assumed a dilute sea of metastable atoms—specifically, one in which the optical mean free path for the resonance radiation was large compared to the dimensions of the discharge tube. The dense-sea case is very complicated and gives rise to novel experimental effects such as a total inversion of the resonance line. The discussion of these effects is elaborate and will be presented in later papers together with a detailed discussion of the simple effects and their applications.

*This work was supported in part by the Faculty Research Fund of the Horace H. Rackham School of Graduate Studies of The University of Michigan, and the U. S. Atomic Energy Commission.

[1] See, for example, A. Kastler, J. Opt. Soc. Am. 47, 460 (1957), and H. G. Dehmelt, Phys. Rev. 105, 1487 (1957).

[2] The Osram Helium Spectroscopic Lamp with rf excitation has been used for much of this work. However, it exhibits the disadvantage of low-frequency noise. We have recently developed helium lamps with superior noise characteristics which will be described in a later paper.

[3] E. U. Condon and G. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, 1957), Chap. 3.

## FAR INFRARED ENERGY GAP MEASUREMENTS IN BULK SUPERCONDUCTORS*

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Several measurements[1] of the surface resistance of superconductors have been made at microwave frequencies with photon energies comparable with $kT_c$. In these experiments the surface resistance has generally approached zero for temperatures much less than $T_c$, showing that the photons used were not energetic enough to excite electrons across the absolute zero energy gap of $\sim 3.5\ kT_c$.[2,3] Using far infrared techniques, we have measured the onset of absorption in superconducting tin and lead for $T \ll T_c$ over the quantum energy ranges of (1 to 13)$kT_c$ for lead and (2 to 18)$kT_c$ for tin, corresponding to a wavelength range of ~0.15 to 2 mm. For both lead and tin these energy ranges span the transition from essentially lossless reflection to absorption indistinguishable from that of the metal in the normal state.

The output of a far infrared grating monochromator was conveyed through a brass light pipe to a cast nonresonant superconducting cavity immersed in liquid helium at 1.55°K. After making many reflections to build up the metallic absorption to a measurable amount, the radiation was absorbed in a carbon resistance bolometer mounted on a wall of the cavity. The power ($P_S$) reaching the bolometer when the cavity was superconducting was compared to that ($P_N$) when it was held normal by a magnetic field. The percentage change of the bolometer signal $[(P_S - P_N)/P_N]$ for tin and lead is plotted against photon energy in units of $kT_c$ in Fig. 1.

For quantum energies below the energy gap these curves show the difference between the nearly perfect reflection of the superconducting state and the frequency-dependent reflection of the normal state. At quantum energies high enough to excite electrons across the energy

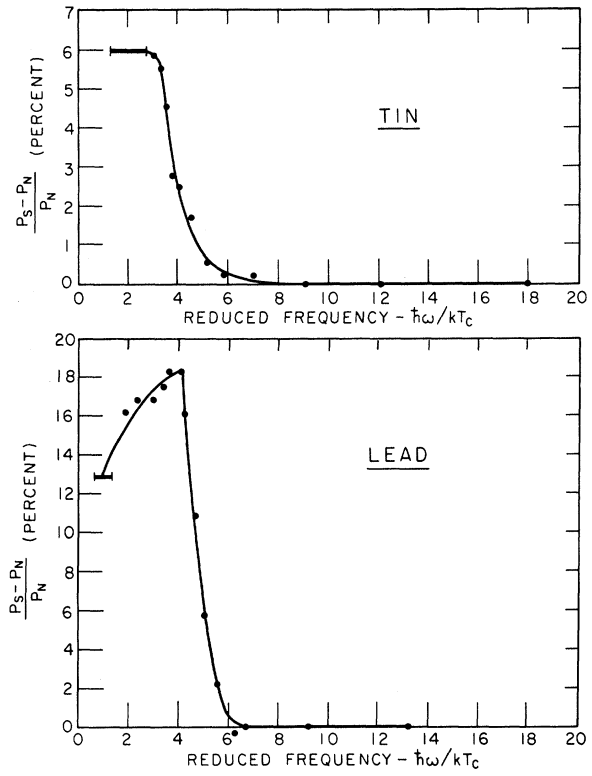


FIG. 1. Observed differences between the power reaching the bolometer in the normal and superconducting states as a function of frequency in lead and tin. Note that the sudden onset of absorption in the superconductor that marks the energy gap occurs at a slightly higher value of the reduced frequency in lead than in tin.

gap there is a sudden onset of absorption in the superconductor, and as the absorption approaches that in the normal state, $[(P_S - P_N)/P_N]$ falls rapidly to zero. The observed onset of absorption in the superconductor is qualitatively similar to that predicted by the BCS theory,[4] but is about twice as fast. This rapid approach to the normal-state value of the absorption makes it clear why earlier measurements[5] with room-temperature black-body radiation peaked at 0.014 mm revealed no change in absorption between the superconducting and normal states.

The scale of the ordinates is governed by the value of the normal-state reflectivity and by the amount of flux trapping. Trapped flux keeps $\frac{1}{4}$ to $\frac{1}{2}$ of the cavity in the normal state at all times after the magnet is first turned on. This normal fraction remains constant throughout a run. The presence of trapped flux in the cavity indicates that large amounts of the surface are subjected to fields of the order of $H_c$. Thus the sharpness of the absorption edge indicates that the energy gap width is not a sensitive function of such fields. If the law of corresponding states between superconductors were obeyed exactly, the tin and lead curves would be identical except for the above mentioned differences in flux trapping and normal state reflectivity.

The frequencies of interest for the determination of the energy gap in lead lie entirely within the range available from the monochromator. For tin, the required frequencies are reduced by the ratio of the transition temperatures (3.7/7.2 ~0.5), and the points at $3.0kT_c$ and $3.25kT_c$ were measured only with a sacrifice in radiation purity. Any admixture of higher-order radiation depresses these points, and this effect probably accounts for the difference between the two curves near $E_g$. The lowest frequency point on each curve was measured using broad-band radiation from a zero-order filter grating with the approximate spread of frequencies indicated by the horizontal bars. The frequency band width (~10%) used on all other points was not large enough to broaden the absorption edge appreciably. The accuracy in the vertical direction is limited by random noise (each point is an average of 8 to 10 readings) and by radiation impurity.

If one assumes that the sudden onset of absorption occurs at the gap energy $E_g$, then the widths of the energy gap in lead and tin at 1.55°K may be deduced to be $(4.1 \pm 0.1)kT_c$ and $(3.3 \pm 0.3)kT_c$, respectively. Extrapolating these results to 0°K using the BCS temperature dependence, and noting that 1.55°K is $0.22T_c$ for lead and $0.42T_c$ for tin, we find the widths of the energy gap at absolute zero, $E_g(0)$, to be $(4.1 \pm 0.2)kT_c$ for lead and $(3.4 \pm 0.3)kT_c$ for tin. These results may be compared with the BCS value of $3.5kT_c$, which should hold for all superconductors. The observed departure from such a simple law of corresponding states, with $E_g(0)/kT_c$ increasing slowly as $T_c/\theta_D$ increases, is of the sort pointed out by Goodman[6] on the basis of nonspectroscopic data.

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* This research was supported in part by the Office of Naval Research and the National Science Foundation.

† National Science Foundation Predoctoral Fellow.

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## FERROELECTRICITY IN $NaNO_2$

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It is well known that sodium nitrite ($NaNO_2$) has the orthorhombic structure ($C_{2v}^{20}$) at room temperature[1] and this structure changes to the more highly symmetric one ($D_{2h}^{25}$) at about 160°C.[2,3] The piezoelectric effect observed in the low-temperature form disappears at this temperature.[2] Although the structural investigations of $NaNO_2$ crystal have been carried out well by several researchers,[4,5] other properties, in particular the dielectric properties, have scarcely been noticed.

We have studied the dielectric properties of this crystal and found that it is ferroelectric along the $b$ axis below the 160°C transition point. Crystals were prepared by the fusion method, where $NaNO_2$ powder had been dried in advance in $10^{-3}$ mm Hg vacuum at about 120°C during 48 hr, since this substance is considerably deliquescent. Crystals were transparent, slightly yellowish, and easily cleaved along the (101) plane. Figure 1 shows the dielectric constant vs temperature relation measured at the frequency of 100 kc/sec, using air-drying silver paste electrodes. The dielectric constant in the direction of $b$ axis, $\epsilon_{010}$ (dimension of specimen: thickness 0.0835 cm, area 0.537 cm$^2$), is 7.4 at room temperature and reaches 780 at 164°C on heating and 1100 at 162°C on cooling, respectively, where the rate of temperature change was about 0.5°C/min. Above this transition temperature, the Curie-Weiss law holds with the Curie-Weiss temperature of 433°K and the Curie constant of $5.0 \times 10^3$°K. The dielectric constant perpendicular to the $b$ axis, $\epsilon_{101}$ (dimension of specimen: thickness 0.114 cm, area 1.032 cm$^2$), is 6.4 at

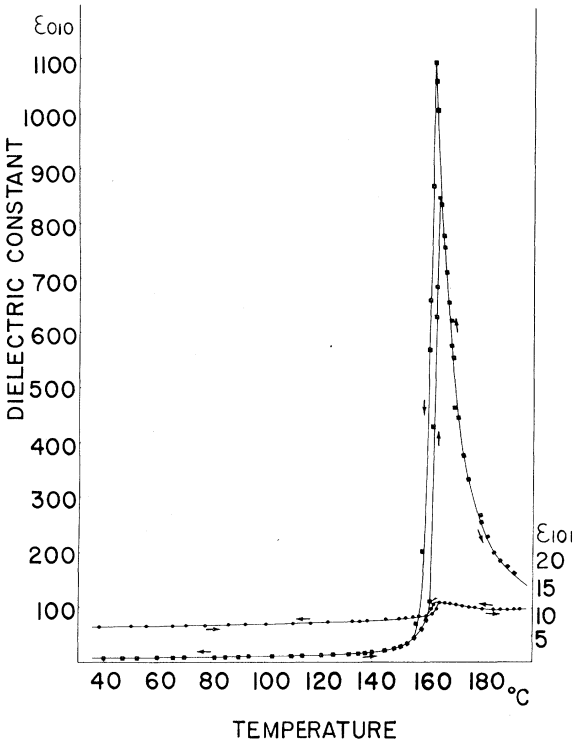


FIG. 1. Dielectric constant $\epsilon_{010}$ and $\epsilon_{101}$ (100 kc/sec) vs temperature. Squares: $\epsilon_{010}$; circles: $\epsilon_{101}$.

room temperature and remains low at high temperatures, though a small anomaly was observed at the transition.

The pyroelectricity was clearly observed along the $b$ axis below the transition temperature and furthermore its polarity could be easily reversed by applying a dc field to the crystal. We obtained about 7 $\mu$coul/cm$^2$ as the value of spontaneous polarization at room temperature from the pyroelectric measurement, using a sample which had been cooled to room temperature from 180°C applying the dc field of 1.4 kv/cm. The typical $D$~$E$ hysteresis loop was observed below the transition temperature in the direction of $b$ axis at 50 cps. An example is shown in Fig. 2, where the coercive field and the spontaneous polarization are seen to be 2.3 kv/cm and 6.4 $\mu$coul/cm$^2$ at 143°C, respectively. This value of spontaneous polarization nearly coincides with that obtained from the measurement of pyroelectricity. The coercive field derived from the hysteresis loop varied with temperature and strongly depended on the applied field strength. At room temperature, the loop did not open out even for the field of 25 kv/cm, because of its large coercive field. A double hysteresis loop could be observed just above the transition tem-