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Critical Currents in the Superconducting Surface Sheath*

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Results are presented of magnetization measurements on Pb-Tl cylinders in axial magnetic fields of such magnitude that superconductivity is confined to the superconducting surface sheath. Specimens whose Ginzburg-Landau κ values range from 0.6 to 1.4 have been investigated. For these cylindrical specimens a nonzero magnetization exists beyond the upper critical field H_{c2} up to a field H_{c3} (1.7 to 1.75 H_{c2}) identifiable with the surface nucleation field (1.695 H_{c2}). Evidence is presented that indicates the observed magnetization results from partial shielding of the interior of the cylinders by critical currents induced in the multiply-connected surface sheath. Our experimental results are in quantitative accord with recent theoretical calculations of Fink and Barnes concerning the influence of critical sheath currents on the effective bulk-magnetization characteristics of a cylinder. It is observed that diamagnetic ($M<0$) and paramagnetic ($M>0$) shielding occur in uniformly increasing and decreasing fields, respectively, which is consistent with the existence of a multiconnected superconducting region which can carry a total current. The surface localization of the superconductivity involved is demonstrated by the proximity effects of electroplated normal metals on the specimens. Cu plating reduces both the magnetization and H_{c3} ($\sim$1.4 H_{c2}). Owing, perhaps, to their magnetic properties, electroplated Ni and Cr have a much more drastic effect than electroplated Cu. To the limit of experimental sensitivity, all traces of superconductivity above H_{c2} are removed by Ni and Cr platings.

I. INTRODUCTION

It has been observed that on the surface of a superconductor with a Ginzburg-Landau $\kappa>0.417$ a "layer" of material remains superconducting in magnetic fields larger than the maximum bulk critical field H_c or H_{c2} for type-I or -II superconductors, respectively. When the magnetic field is parallel to the surface, the superconducting sheath exists up to $H_{c3}=1.695H_{c2}$.[1] It is reasonable to expect that a multiply-connected surface sheath can support a lossless current generated by induction in analogy with a superconducting ring. In particular, one would expect that current values up to some critical value can be supported by a multiconnected sheath. In this respect its behavior would be similar to that of a superconducting thin-film hollow cylinder.[2] The dependence of the critical sheath current upon sample volume, applied magnetic field, etc., would not, however, be expected to be the same as in the case of thin films since the sheath and films differ in some important respects (e.g., boundary conditions; the thickness of surface sheath is larger than the coherence length and it varies with applied magnetic field; the order parameter is not a constant over the width of the sheath).

The ability of a multiply-connected sheath to support an induced lossless current would lead to partial or total shielding of the interior of the superconductor depending upon the manner in which the currents are induced. Direct-current magnetization measurements would show only partial shielding, if the concept of the critical sheath state discussed above is correct. Once the critical sheath current has been established, for example by uniformly increasing the external magnetic field, the total shielding capacity of the sheath will have been exhausted and any further field increase will result in flux penetration into the bulk of the metal which is normal conducting. Thus, if the field is consistently increased or decreased, the observed magnetization will be due to magnetic shielding of the critical sheath current. Livingston and Schadler[3] suggested that the hysteretic dc magnetization tail observed above H_c on an In-3.6% Pb alloy (type I) by Chiou *et al.*[4] might be due to shielding afforded by the surface sheath. The authors[5–7] and Park[8] have discussed the possibliity that induced currents in a multiply-connected surface sheath can influence the effective bulk-magnetization properties. Recent qualitative dc magnetization[9,10] and torque[11] measurements made on specimens in the sheath state have been interpreted on this basis.

Measurements of the properties of the surface sheath using ac magnetic fields yield more complicated results than in the case of dc fields. Depending upon the amplitude of the ac field, either total or partial magnetic

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shielding can be observed.[12–16] The experimental results obtained using ac fields can also be explained by the critical-state concept.[7,17,18] If the amplitude of the applied ac magnetic field is not large enough to induce the critical current in the sheath then its perfect shielding capacity will not be exceeded and the specimen will exhibit perfect diamagnetic behavior[19,20] due to fluxoid conservation. If the ac field amplitude is large enough, the shielding capacity of the sheath can be exceeded over part of each field cycle and flux penetration in the bulk of the samples does occur and losses appear.[12–16] The physical mechanisms giving rise to these phenomena have been discussed elsewhere in more detail.[18] Because the behavior of the surface sheath subjected to ac magnetic fields is complex and not as straightforward to interpret as in the case of applied dc fields we have concentrated in the present investigation on the dc magnetic behavior of the surface sheath.

We report dc magnetization measurements made on dilute type-I and -II Pb-Tl alloy cylinders ($0.6 \leq \kappa \leq 1.4$) in axial magnetic fields of such magnitude that superconductivity is confined to the surface sheath. The magnetization of these specimens does not become zero at H_{c2} (or H_c if alloy exhibits type-I behavior) but remains finite and extremely hysteretic up to the sheath nucleation field H_{c3}. Measurements of both the dc magnetization M in static fields and also dM/dH in fields varying at a constant rate were made. The results indicate that the magnetization we observe results from partial shielding of the interior of the cylindrical specimens by critical currents induced in the superconducting surface sheath. Further, our results are in *quantiative* accord with recently reported theoretical calculations[7] concerning the influence of critical-sheath currents on the bulk magnetization characteristics of a cylinder.

II. COMPARISON WITH THEORY

On the basis of the critical-state concept discussed in the previous section the experimental magnetization values can be compared with various theoretical calculations of the sheath critical current. Abrikosov[21] and more recently Park[8] have calculated the critical sheath transport current for a semi-infinite half-space. Their results, however, do not bear directly upon the present experiment since they are calculated strictly for $\kappa \gg 1$ whereas in our case $\kappa \sim 1$, and further, they do not take into account the magnetic field energy which is proportional to the volume shielded by the surface currents. More pertinent are calculations we have recently reported[7] which involve no adjustable parameters, are valid for all κ, and do take into account the magnetic field energy due to partial shielding of the volume of the cylinder.

For the theoretical calculations of Ref. 7, it was assumed that critical currents could be induced in the superconducting surface sheath of a cylinder in an axial magnetic field. It was also assumed that this critical state if it is achieved, for example, by increasing the magnetic field will persist as the field is further increased and likewise for decreasing fields. If the above assumptions are valid the currents in the multiply connected surface sheath will result in magnetic shielding that is diamagnetic in increasing fields and paramagnetic in decreasing fields. It follows that a macroscopic specimen can be taken from the diamagnetic to the paramagnetic critical-state magnetization curve or vice versa along a line whose slope $4\pi(dM/dH) = -1$ (perfect shielding) by reversing the direction of magnetic field change. With the above and other simplifying assumptions an expression for the effective bulk magnetization per unit volume of a macroscopic cylinder, resulting from the shielding of critical sheath currents, was obtained.[7]

$$4\pi M = \pm \eta \frac{H_c}{\kappa} \left(\frac{2\lambda}{R} \right)^{1/2} \frac{\Delta}{\xi} F^2(R) . \qquad (1)$$

In this expression η is a parameter of order unity ($\eta = 1$ was used in our calculations), H_c the thermodynamic critical field, λ the low-field penetration depth, R the radius of the cylinder, Δ the thickness of the sheath, and ξ the coherence length. The values of Δ/ξ and $F(R)$ as functions of H/H_{c2} may be obtained from Ref. 6 or $(\Delta/\xi)[F^2(R)]/\kappa$ may be obtained directly from Ref. 7. It should be noted that the explicit $1/\kappa$ dependence shown in Eq. (1) is modified by the implicit κ dependence of the remaining terms. This implicit κ dependence is shown graphically in Fig. 1 where values of $(\Delta/\xi)F^2(R)$ are plotted as functions of κ and H/H_{c2} for $R \gg \lambda$.

Equation (1) explicitly predicts that the magnetization per unit volume should increase as the cylinder radius decreases. This size dependence is the result of including in the calculations the magnetic field energy which is proportional to the volume of the sample. As discussed in Sec. IV, we were unable to verify the explicit $R^{-1/2}$ dependence; however, we did observe on all specimens the magnetization to increase consistently with a small reduction in radius.

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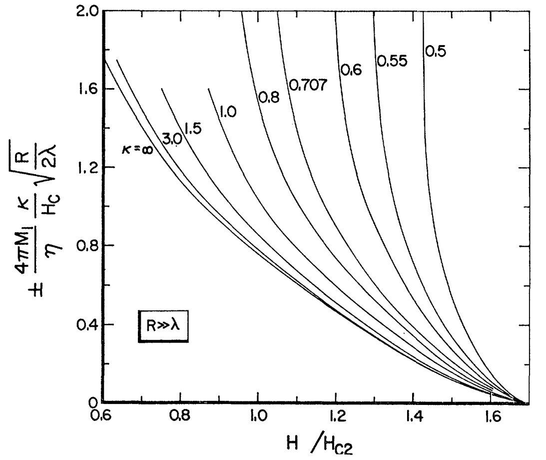

FIG. 1. The reduced axial magnetization per unit volume of a cylinder in the superconducting sheath state as a function of the parameter κ and the reduced external field H/H_{c2}. See text for details.

III. EXPERIMENTAL

Cylindrical specimens were used in order that the entire surface area of the superconducting sheath could experience a parallel external magnetic field. Maximum critical sheath currents could be induced in this case. The specimen axis was oriented parallel to the external field to better than 1°. Each specimen was initially 18 mm long and 2 mm in diameter. They were machined from vacuum-cast ingots, and then annealed at 320°C for 1 to 2 weeks in a vacuum of about 2×10^{-6} Torr.

The magnetization measurements were performed using two axially aligned, oppositely wound, and series-connected detection coils. The detection coils were situated in the homogeneous field region (better than 0.2% over an axial distance of 3.9 cm) of a superconducting Nb-Zr Helmholtz pair with the two coil pairs having a common axis. The liquid-He-bath temperature was 4.2°K for all measurements. Measurements were performed with the external field H constant and also with the external field changing at a constant rate. With $H=\text{const}$, ballistic magnetization measurements were obtained in a standard manner by moving the specimen from the middle of one detection coil to the middle of the other and observing the deflection of a flux meter placed across the two coils. In the swept field case ($\dot{H}=\text{const}$) measurements of dM/dH were made. In the latter case, the specimen was held stationary in one of the detection coils, and the dc voltage generated across both coils was amplified and recorded on an X-Y recorder. This voltage, which is proportional to dM/dH of the specimen, was recorded on the Y axis, and the X axis was driven by a Hall probe which monitored the magnetic field. Using the difference between signals associated with the Meissner state and the normal state ($H>H_{c3}$) as a calibration, values of $M(H)$ were obtained by integration of the recorder traces. Although this method is indirect, it has the advantage of being more sensitive than the ballistic technique. Typical recorder traces for $H>H_{c2}$ with H increasing and decreasing are shown in Fig. 2. In the increasing and decreasing field cases the signals have the same polarity but $\dot{H}$ differs in sign, and thus dM/dH must have opposite signs in the two cases. A small and unavoidable drift in $\dot{H}$ is also evident from Fig. 2.

Initially, measurements were taken on all specimens with their surfaces untouched after annealing. The surfaces were then chemically polished, which resulted in removal of a surface layer about 10^{-2} cm deep, and measurements were repeated. In all cases chemical polishing increased the observed magnetization. Extreme care was taken in handling of the cylinders. The magnetization of each specimen was measured repeatedly, each time with a fresh chemical polish. The uncertainties associated with the physical state of the surface along with the strong dependence of the critical current on the angle of the surface with the external field[22] lead one to expect differences between such sets of data. Differences were observed, but, even in extreme cases, they amounted to less than a factor of 2. In the sets of data there were several cases that exhibited relatively larger magnetization values near H_{c3} (with consequent sharper transitions) than the remaining sets. These particular sets of data were consistent with one another and are felt to represent the closest approach to ideal conditions in respect to the specimen surface and specimen orientation in the external field. It is these data that are presented below.

IV. RESULTS AND DISCUSSION

Representative data on magnetization per unit volume [$4\pi M(H)$ in G], which were obtained using the two different measuring techniques (with chemi-

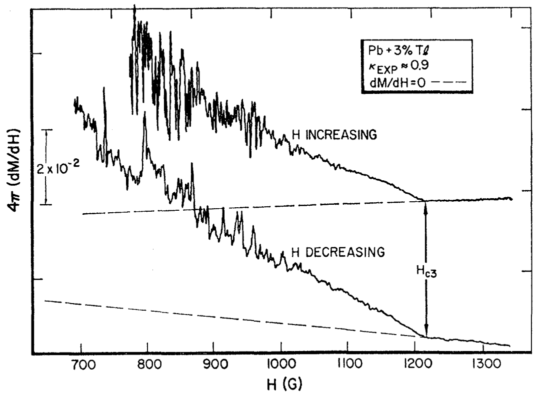

FIG. 2. Recorder traces of voltage, which is proportional to dM/dH of specimen, that is generated across the detection coils by a constant external field sweep (8 G/sec) for $H>H_{c2}$. The dashed lines are extrapolations of the normal-state traces ($H>H_{c3}$ and $dM/dH=0$) and coincide with the traces generated when there is no specimen in the detection coils. $H_{c2}\approx680$ G.

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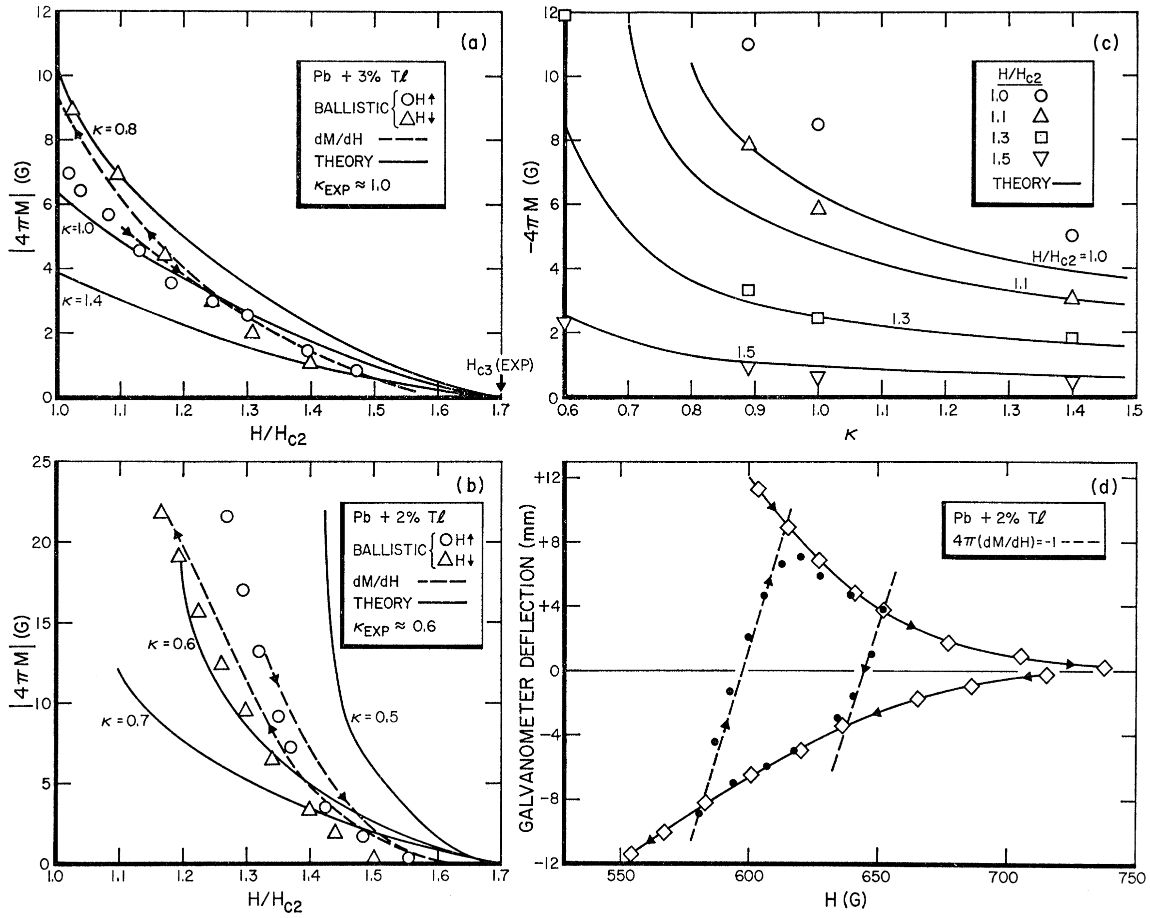

FIG. 3. Sections (a), (b), and (c) are graphical comparisons of experimental magnetization data with Eq. (1). Section (d) shows a minor hysteresis loop (●) in the magnetization characteristics (◇) of a cylinder in the superconducting sheath state.

cally polished surfaces), are shown in Figs. 3(a) and 3(b) where they are compared with the theoretical curves [Eq. (1)] for various κ values. Only the absolute magnitude of $M(H)$ is plotted in the two figures; however, the data indicate that diamagnetic ($M<0$) and paramagnetic ($M>0$) shielding occur in increasing and decreasing fields, respectively [see Fig. 3(d)]. In Fig. 3(c) the theoretical and experimental κ dependences of $M(H)$ are compared explicitly for various values of the reduced field H/H_{c2}. It is seen that the magnitude of the observed $M(H)$ and its κ and field (H/H_{c2}) dependences are in quantitative agreement with the theoretical predictions. The κ values of the type-II alloy specimens were determined from the expression[23] $\kappa=H_{c2}/\sqrt{2}H_c$ using experimentally determined H_{c2} and H_c values. H_c values were obtained from the magnetization characteristics of ellipsoidal specimens and agreed with published values on the Pb-Tl alloy system.[23a] It was assumed that $H_{c2}=H_{c3}/1.7$ for the type-I specimen ($\kappa\approx0.6$). Values of λ were obtained from the Ginzburg-Landau expression[6] $\lambda=\kappa^{1/2}(\hbar c/\sqrt{2}H_c 2e)^{1/2}$ using experimental κ and H_c values.

In the derivation of Eq. (1) the cylinders were assumed to be infinitely long, in which case end- or self-field effects do not arise. The specimens investigated being of finite length are subject to self-field effects. However, since the field produced by the induced current is much smaller than the external magnetic field ($4\pi M/H\sim10^{-2}$ to 10^{-3}), one would expect the self-field effects to be small. Surface conditions lead to the major concern in the experimental data.

Magnetization curves for increasing and decreasing fields and a minor hysteresis loop obtained on a type-I alloy specimen for $H>H_c$ are shown in Fig. 3(d). Almost complete hysteresis is exhibited by this specimen. Further the traverses between the continuously increasing and decreasing field curves follow closely paths characteristic of perfect shielding ($4\pi dM/dH=-1$). This behavior is consistent with the sup-

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position that the magnetization is the result of shielding currents induced in a multiply-connected surface sheath and that the sheath can support a lossless current up to some critical value which depends upon the magnitude of the applied magnetic field and not upon its time derivative as in the case of eddy currents. The dM/dH measurements also tend to confirm the critical-state nature of the observed magnetization. Varying the field sweep rate by an order of magnitude (2 to 20 G/sec) does not effect the magnetization values $4\pi M$ derived from the dM/dH measurements to within experimental accuracy, and these $4\pi M$ values agree with those obtained ballistically [see Figs. 3(a) and 3(b)].

In Fig. 2 it is seen that the magnetic field at which all trace of superconductivity disappears can be determined accurately by using the derivative technique. The experimental critical fields H_{c3} (expt), determined in this way, agree reasonably well with the expected sheath critical fields. It is found that $H_{c3}(\text{expt}) \approx 1.7$ to $1.75\ H_{c2}$, whereas it is predicted theoretically[1] that $H_{c3} = 1.695\ H_{c2}$. This is a further confirmation that the superconductivity involved is associated with the surface sheath and not due to defect-stabilized surface currents.

Measurements taken on specimens with thin (10^{-2} cm) layers of normal metal electroplated on the surface further confirm the surface nature of the superconductivity involved. Electroplating Cu onto the surfaces reduces the magnitude of the magnetization considerably, presumably by the proximity effect.[24–26] In contrast to the latter observation, no trace of superconductivity exists at $H \geq H_{c2}$ when Ni or Cr are electroplated onto the specimen surfaces. The magnetic properties of Ni and Cr[27] might account for their more drastic effect upon the surface sheath; however, more intimate contact of the Ni and Cr layers with the specimens than in the case of the Cu layers might also give the observed effects. The magnetic hysteresis observed in the mixed state ($H \leq H_{c2}$) of these specimens is also considerably reduced by Ni and Cr platings.[28] Near H_{c2} the hysteresis in the mixed state was completely eliminated. In Ref. 28 it is shown that a portion of the mixed-state hysteresis in these well-annealed specimens results from induced surface currents but their nature has not been unambiguously established.

A difference between the observed magnetization for H increasing and decreasing at the same value of the external field, was a consistent feature of our results. This difference or asymmetry appears to be enhanced in the low κ alloy where the largest induced sheath currents occur. In the theoretical calculations[7] it was assumed that the order parameter was not dependent upon the sense of circulation of the induced currents (dia- or paramagnetic shielding), and consequently, no asymmetry, such as that observed, is predicted. In reality, the order parameter is undoubtedly distorted by the induced current, as the internal field the sheath experiences will depend upon the sense of circulation of the currents, and an asymmetry is expected. Park[8] finds in his calculations an asymmetry in the order parameter between the two cases equivalent to dia- and paramagnetic shielding. However, as mentioned previously, no valid comparison of his calculations and our results can be made. Swartz and Hart[22] observed a much larger asymmetry in the critical transport current in the superconducting sheath, which they tentatively ascribe to self-field effects. Because of the asymmetric distortion of the order parameter due to the sense of circulation of the persistent currents in the surface sheath, the magnetization will also become slightly asymmetric. For a higher order correction to the magnetization see Ref. 18.

We were not able to reduce the radius of the specimens by any significant amount by chemically polishing without severely rounding the ends. We observed, however, that the magnetization per unit volume did increase as the radius was reduced but due to the departure of the specimens from their cylindrical shape and loss of sensitivity due to reduced volume we could not verify explicitly the predicted $R^{-1/2}$ dependence of Eq. (1).

V. CONCLUSIONS

We have shown that persistent currents can be induced in a multiply-connected superconducting surface sheath. It is evident that currents up to some critical value, which is dependent upon the parameter κ and the applied magnetic field, can be supported by the surface sheath. The critical state of the surface sheath, which is the situation when a critical or maximum current is flowing, is maintained as the applied field is uniformly increased (or decreased) in either a continuous or discontinuous manner. The induced sheath current magnetically shields the volume enclosed by the sheath and gives rise to nonzero effective-bulk-magnetization values above the upper critical field H_{c2}. This magnetization is found to be in quantitative accord with recent theoretical calculations[7] concerning the shielding capacity of a multiply-connected surface sheath regarding the dependence upon the parameter κ and the applied magnetic field. We did observe the magnetization to be size-dependent but were unable to adequately test the explicit $R^{-1/2}$ prediction.[7]

The magnitude of the critical-sheath current is extremely sensitive to the surface state of the specimen. All our observations are consistent with the supposition that relatively rough physical treatment of the surface

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(introducing strains), an oxid layer, or absorbed gases, increase the κ value of the surface material and lead to a reduced critical current. This is in accord with recent work of LeBlanc.[29]

Note added in proof. Recently, J. G. Park has presented calculations of Eq. (1) [Phys. Rev. Letters **16**, 1196 (1966)] which he claims are more accurate than ours[7] in several respects. He claims to have included the minimization of the free energy with respect to the vector potential in the calculation of Eq. (1); however, he appears to have made the same approximation that we did,[7] namely, he assumes that one can ignore the effect of the total current density J_c upon the order parameter of the sheath. Our values of Δ/ξ and $F^2(R)$ (see text) were taken from Ref. 6 in which the total current was taken to be zero.

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Proton and Chlorine Nuclear Magnetic Resonance in Antiferromagnetic $MnCl_2 \cdot 4H_2O$†

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The magnetic structure of the antiferromagnetic phase of $MnCl_2 \cdot 4H_2O$ has been examined using proton and chlorine NMR. By combining observations on the symmetry and number of proton internal magnetic fields with x-ray and neutron-diffraction data, one is led to three possible magnetic structures. However, only one of these ($P2_1/a'$) predicts fields at the proton sites whose orientation and magnitude is in reasonable agreement with the experimentally observed fields. The chlorine resonance data corroborate the proton-resonance results and provide information on the transferred hyperfine interaction.

I. INTRODUCTION

Although the antiferromagnetic phase of $MnCl_2 \cdot 4H_2O$ has been the subject of a number of experimental investigations, very little appears to be known of the antiferromagnetic spin arrangement. The form of the H-T phase diagram[1] and the temperature dependence of the magnetic susceptibility[2] indicate that $MnCl_2 \cdot 4H_2O$ is probably a simple two-sublattice antiferromagnet with a rather small but quite anisotropic molecular field which results in a low Néel temperature (1.62°K)[3,4] and a sublattice magnetization along the c axis. The work reported here deals with an experimental study of the proton and chlorine nuclear resonance in the antiferromagnetic phase. The main objective is to obtain the spin arrangement which is inferred by combining the nuclear-resonance data with the crystal-structure data considered in the next section.

II. CRYSTAL STRUCTURE

According to Zalkin, Forrester, and Templeton,[5] the structure of the modification of $MnCl_2 \cdot 4H_2O$ which grows at room temperature is as shown in Fig. 1. In discussing the interrelation of the magnetic properties and the crystal structure, two different unit cells are useful. The first outlined by solid lines in Fig. 1 has dimensions $a_1 = 11.186$ Å, $b_1 = 9.513$ Å, $c_1 = 6.186$ Å, and $\beta_1 = 99.74°$. The space group is $P2_1/n$ and there are four formula units in the cell. This cell is that used by Zalkin, Forrester, and Templeton and by Groth[6] in his morphological description of the crystal. The second unit is shown by dashed lines in Fig. 1. Its dimensions are $a_2 = 11.830$ Å, $b_2 = 9.513$ Å, $c_2 = 6.186$ Å, and $\beta_2 = 111.27°$. The space group is $P2_1/a$ and there are again four molecules in the unit cell. The latter cell was used by Delain[7] in earlier x-ray work. It has the advantage that it locates the symmetry elements in conventional places in the unit cell and permits the use of conventional notation when discussing the *magnetic* space group of the crystal.

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† This work supported by the U. S. Air Force Office of Scientific Research.

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