Pressure Effect and Thermal Expansion for Superconducting Tin*

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The superconducting critical field curve of white tin has been measured between 1.15° and 3.7°K at pressures up to 2800 bars using solid helium as the pressure transmitter. The results at T_c agree with previous work at this Laboratory. An analysis of the data indicates a relatively small pressure dependence of the electronic specific heat coefficient γ, and, consequently, a small electronic contribution to the thermal expansion in the normal state. The thermal expansion in the superconducting state is predicted to be large and negative, and extremely anisotropic. The deviation of the superconducting properties of tin from "simple similarity" is discussed.

THE critical field curve for a superconductor gives a direct representation of the differences between the thermodynamic properties of the normal and the superconducting states.[1] White (or beta) tin is perhaps the most convenient substance for superconducting studies, since it has a conveniently accessible transition temperature (3.72°K) and can be obtained easily in high-purity single-crystal form. It is gratifying that substantial agreement (of the order of a few tenths of a percent) exists among various recent measurements of the critical field curve for tin at zero pressure.[2,3] Extensive specific heat data for both the normal and superconducting states exist for tin, and the zero pressure critical field curve which can be calculated from these measurements agrees well with the direct H_c vs T measurements.[4]

The application of the pressure variable to critical field measurements presents appreciable technical difficulties.[5] The variation of the critical field of a metal with applied hydrostatic pressure is of interest since the magnitude of this effect can be related directly to the small differences between the molar volumes and volume thermal expansions of the normal and superconducting states.[1] Considerable direct and related work of this type has been done with various superconductors in recent years.[5,6] In addition, a measurement of the dependence of the critical field curve on uniaxial stress can be related directly to the differences in the linear thermal expansions of the crystal along these directions, and stress data of this type were first obtained by Grenier for tin.[7]

Although data do exist for the effects of pressure on the critical field curve for tin, a comparison of these data shows disagreements which are apparently outside the indicated experimental error.[8] The work which is reported in this paper was initiated to fill a gap which it was felt existed in the reported thermodynamic properties of tin at low temperatures, and to investigate in some detail the reality of the discrepancies in the literature. This investigation is important from a technical standpoint also, since the superconducting pressure effect in tin has been used by us as a means for determining the magnitudes of the pressures which were attained at low temperatures in experiments with other superconductors.[9,10]

Earlier experiments in this Laboratory were concerned with the effect of pressures up to 10 000 bars (1 bar$=10^6$ dyn/cm$^2=0.987$ atm) on the zero-pressure transition temperature T_c of polycrystalline samples of various superconductors, including white tin.[11] Some sample deformation resulted from the use of solid hydrogen as the pressure transmitter in these experiments so that the origin of deviations from previous results could not be ascertained. Following this work of Jennings and Swenson (JS), additional experiments were undertaken which showed that the shape of the critical field curve of tin above 3°K was independent of sample geometry, was the same for both single and polycrystalline samples, and also was unaffected (except for a broadening of the transitions) by deformations at liquid helium temperatures of up to three percent.[12] Hence, it was felt that the earlier work (reference 11) was not subject to error due to these effects.

A far more satisfactory technique than that of JS involves the use of solid helium to produce pressures at low temperatures which are very close to hydrostatic in nature. This technique has been used to study the effects of pressure on the critical field curves of tantalum[9]

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† Present address: H. H. Wills Physical Laboratory, University of Bristol, England.
[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), 2nd ed., Chap. 3.
[2] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).
[3] J. E. Schirber, unpublished results, Ames Laboratory, Iowa State University.
[4] D. K. Finnemore and D. E. Mapother (to be published). We are indebted to Dr. Finnemore and Dr. Mapother for communicating their results to us prior to publication.
[5] C. A. Swenson, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 41.
[6] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **33**, 872 (1960).
[7] C. Grenier, Compt. rend. **238**, 2300 (1954); **240**, 2302 (1955); **241**, 1275 (1955).
[8] Reference 5, p. 116.
[9] C. H. Hinrichs and C. A. Swenson, Phys. Rev. **123**, 1106 (1961).
[10] J. E. Schirber and C. A. Swenson, Phys. Rev. **123**, 1115 (1961).
[11] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).
[12] V. W. Hestermann, M. S. thesis, Iowa State College, 1958 issued as an Ames Laboratory Atomic Energy Commission Report, ISC-1159 (unpublished).

and the mercuries.[10] These papers (references 9 and 10) give details of the experimental methods, sample sizes, and type of analysis which are applicable also to the present work on tin. A preliminary discussion of these results has been given.[13]

The pressures which were used were of the order of 1800 bars. The data of JS suggested that the H_c vs P relationship should be linear to within 1% over this pressure range, and our experience with the use of tin as a pressure gauge in the mercury experiments over a range of pressures confirmed this hypothesis.[10] No irreversible effects or transition broadenings were observed which could be attributed to deformation of the single-crystal samples. The tin was from the same stock as that used in the experiments of JS and had a residual resistivity ratio of roughly 17 000. Unpublished results from this Laboratory showed that critical-field data for our tin at zero pressure were in excellent agreement with the results published by Mapother and his co-workers, and the zero-field thermodynamic properties given in Table I are due to their work.[2,4]

In principle, the method which is described in detail in reference 9 is as follows. Two identical samples are used, one at zero pressure and the other surrounded by solid helium in a nonmagnetic high-pressure bomb. These are placed in close proximity in a highly homogeneous magnetic field and are maintained at the same temperature to within 10^{-4}°K. The field is increased at constant temperature, and the critical fields of first the high-pressure (H_P) and then the zero-pressure (H_L) sample are noted; $(\partial H/\partial P)_T$ is then given by $(H_P-H_L)/P$. The precise temperature need not be known to better than 0.5%, since this derivative is a slowly varying function of temperature.

The helium was solidified initially at constant pressure and then cooled to T_c at constant volume.

TABLE I. Various thermodynamic properties of tin.

The source of the zero-pressure superconducting transition properties is reference 4, while the effects of pressure were determined in this paper. The molar volume and compressibility at absolute zero were taken from Rayne and Chandrasekhar.[14]

$T_c=3.722$°K
$H_0=305.5$ G
$(\partial H/\partial T)_{T_c}=-150.5$ G/deg
$\gamma=1.74\times10^{-3}$ joules/mole-deg
$V_0=16.1$ cm³/mole
$k_T=1.73\times10^{-6}$ bar^{-1}
$dT_c/dP=-4.90(\pm0.15)\times10^{-5}$ deg/bar
$dH_0/dP=-4.40(\pm0.13)\times10^{-3}$ G/bar
$(\partial H/\partial P)_T=-7.27(\pm0.2)\times10^{-3}$ G/bar
$d\ln T_c/d\ln V=7.51(\pm0.25)$
$d\ln H_0/d\ln V=8.30(\pm0.25)$
$d\ln\gamma/d\ln V=1.2(\pm0.4)$
$\beta_n^{el}=2(\pm1)\times10^{-9}T(deg)^{-1}$
At T_c, $\beta_n-\beta_s=87(\pm3)\times10^{-9}(deg)^{-1}$

[13] C. A. Swenson, Proceedings of the IBM Conference on Superconductivity, 1961 [IBM J. Research Develop. **6**, 82 (1962)].
[14] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **120**, 1658 (1960).

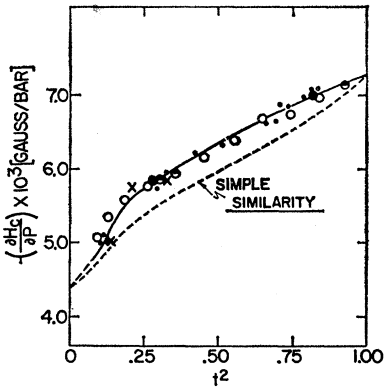

FIG. 1. Superconducting pressure effect for tin. The experimental data were obtained in six runs with different tin samples. Data from only two of the runs are indicated individually (by × and ○) to show typical scatter.

The final pressure in the bomb could be calculated from the initial pressure of the solid at the melting line and the equation of state data due to Dugdale and Simon.[15] This procedure gives the major uncertainty (about 2%) in the data at high temperatures. The pressures during any one run could be expected to remain constant to better than 1%, and it was hoped that the relative values of the pressure effect during a run would be more accurate than this.

A plot of our experimental data is given in Fig. 1. The sharp break in the $(\partial H/\partial P)_T$ curve near $t^2=0.2$ is real and was verified in the course of several experiments which involved different pairs of samples (of differing crystallographic orientation), different pressures, etc. The reasoning which leads to the extrapolation of these data to absolute zero follows from the relationship,

$$H^2=H_0^2-(4\pi\gamma/V)T^2, \quad (1)$$

which is valid at low temperatures if there is no change in the lattice properties at the transition.[9,10] This expression can be differentiated with respect to pressure at constant temperature to give

$$(\partial H^2/\partial P)_T=dH_0^2/dP-4\pi[d(\gamma/V)/dP]T^2. \quad (2)$$

Thus, a plot of $2H(\partial H/\partial P)_T$ vs T^2 should give a straight line at low temperatures, with the limiting slope at absolute zero being directly related to the volume dependence of γ. Figure 2 shows a reduced plot of this type $[2h(\partial H/\partial P)_T$ vs t^2, where $h=(H/H_0)$ and $t=(T/T_c)]$ for our data. The extrapolation now is fairly obvious. The value of h which was chosen for each point on this plot was, whenever possible, the direct experimental value which was observed for the zero-pressure sample. In other cases, it was taken from the data of reference 2. The agreement between the various runs near T_c was within the estimated uncertainty in the pressure determination, with an internal consistency

[15] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

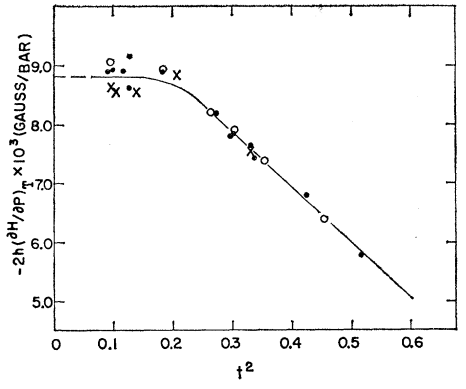

FIG. 2. A plot of $(1/H_0)(\partial H_c^2/\partial P)_T$ vs t^2 for the low-temperature portion of the data shown in Fig. 1.

for any given run which was appreciably better than this. Thus, the data for the various runs (six in all) were normalized so as to agree from $t^2=0.3$ to T_c. Data for only two of the runs are shown explicitly in Figs. 1 and 2, with the data for the other four runs being lumped together under a common symbol. An additional scatter can be observed in Fig. 2 at low temperatures, and the reason for this is not known. There is some possibility that it may be associated with the different crystallographic orientations of the samples, since the runs indicated by the open circles and the crosses, respectively, were obtained with samples whose orientations differed by 90°.

The rapid change in the slopes of the curves of Figs. 1 and 2 at $t^2=0.2$ is very puzzling, and is quite different from the behavior which was found for the mercuries using the same equipment.[10] Unpublished data on the effect of pressure on the residual electrical resistivity of single crystals of white tin show an unexpected anisotropy which must be confirmed by further experiment.[16] The behavior of the critical field curve for tin upon the application of uniaxial stress also is extremely anisotropic.[17] Both of these phenomena substantiate our conclusion that the electronic properties of tin are very sensitive to external influences and make it difficult to draw definite conclusions from any experiment such as ours which determines only a bulk, average, effect.

These data can be compared directly with the results of the previous measurements of the variation of T_c with pressure which are given by JS for polycrystalline tin.[11] The present measurements involved the determination of an average value of $(\partial H/\partial P)_T$ in, roughly, 2000 bars, so the value of the pressure effect which is found at $T_c(-7.27\times10^{-3}$ G/bar) must be compared with an average value calculated over this same pressure range in the previous experiments. The resulting JS value for $(\partial H/\partial P)_T=-(\partial H/\partial T)_P(dT_c/dP)=-7.34\times10^{-3}$ G/bar is in excellent agreement with the present work. Certainly, there is no indication of a basic difference between the superconducting properties of single and polycrystalline samples of tin as was suggested earlier.[11]

The disagreement with the work that was done prior to that of JS still exists. Recently, Kan *et al.*[18] redetermined the value of dT_c/dP using liquid helium as the pressure transmitter to 100 atm and found a value for $dT_c/dP=(-4.4\pm0.2)\times10^{-5}$ °K/atm which is in excellent agreement with the earlier low-pressure determinations.[19–21] They also redetermined the pressure effect for high pressures, using the ice bomb technique and mixtures of alcohol and water. The pressure effect in a separate sample of indium was used as an indication of the pressure in the bomb. The indium data which they obtained in a separate set of experiments, using the same techniques, agree well with the work of JS.

The data of Kan *et al.* indicate a discontinuity in the T_c vs P curve between 100- and 800-atm pressure. Unfortunately, the total change in T_c which they observe in 2000 atm (0.110 ± 0.004°K) is considerably larger than that which we observe (0.098 ± 0.002°K). The consistency which we find between the completely independent measurements of JS and the present data indicates perhaps an unexpected source of difficulty which arises when tin is studied using the ice bomb technique. We have an additional, secondary indication of this consistency through the mercury experiments, where data on tin were obtained near T_c for a wider range of pressures.[10] Tin differs from indium mostly in that it is relatively hard and has a very small thermal expansion.[12,14] Both of these factors could combine with its anisotropy to produce difficulties. Nevertheless, it is not inconceivable that T_c does behave anomalously for tin at low pressures, as Kan *et al.* suggest.

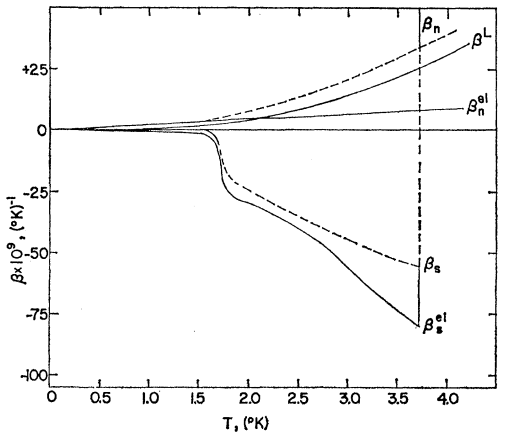

FIG. 3. Estimated volume thermal expansion contributions for tin.

[16] J. E. Schirber (unpublished data, 1961).
[17] D. P. Seraphim and P. M. Marcus, Phys. Rev. Letters **6**, 680 (1961); a more detailed paper will be published.
[18] L. S. Kan, B. G. Lazarev, and V. I. Makarov, Soviet Phys.—JETP **13**, 317 (1961); J. Expt'l. Theoret. Phys. (USSR) **40**, 457 (1961).
[19] M. Garber and D. E. Mapother, Phys. Rev. **94**, 1065 (1954).
[20] N. L. Muench, Phys. Rev. **99**, 1814 (1955).
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Zero-pressure critical field data and the data given in Figs. 1 and 2 can be used together with the physical data in Table I to calculate the difference between the volume expansions in the normal and superconducting states.[1]

$$\Delta\beta=\beta_n-\beta_s=(T/4\pi)\{\partial/\partial(T^2)[\partial(H^2)/\partial P]_T - k[\partial(H^2)/\partial(T^2)]_P\}. \quad (3)$$

This expression takes on a particularly simple form at T_c (where $H=0$),

$$\Delta\beta=(1/4\pi)(\partial H/\partial T)_{T_c}(\partial H/\partial P)_{T_c} = 87(\pm 3)\times 10^{-9}(^\circ\mathrm{K})^{-1}. \quad (3a)$$

If it is assumed that only the electronic properties change at the superconducting transition, Eq. (2) can be used to calculate $d\ln\gamma/d\ln V=1.2(\pm 0.4)$ from Fig. 2, and the volume thermal expansion contribution due to the electrons in the normal state can be written as,[9,10]

$$\beta_n^{\mathrm{el}}=(k\gamma/V)(d\ln\gamma/d\ln V)T=2(\pm 1)\times 10^{-9}(^\circ\mathrm{K})^{-1}. \quad (4)$$

One can conclude from Eqs. (3a) and (4) that β_s^{el} would be negative at T_c. The calculated values of β_n^{el} and β_s^{el} are given in Fig. 3 as a function of temperature.

The Mie-Grueneisen equation of state can be used to estimate the lattice contribution to the thermal expansion at T_c to be of the order of $25\times 10^{-9}(^\circ\mathrm{K})^{-1}$, using $\Gamma^L=1.8$ and $\theta_D=197^\circ\mathrm{K}$.[14] This contribution should vary as T^3. The magnitude of this contribution to the total thermal expansion is shown also in Fig. 3, together with the estimated total thermal expansions for both the superconducting state in zero magnetic field and the normal state.

The predicted behavior of β_s^{el} which is shown in Fig. 3 is indeed unusual and is a direct reflection of the data shown in Fig. 2. The precise details of the curves for the normal-state electronic and lattice contributions to the thermal expansion depend on the assumptions that have been made, although if the pressure-effect data are correct, the value of $\Delta\beta=\beta_n-\beta_s$ at high temperatures should be correct to within roughly 5%. Thus, the qualitative features of Fig. 3 must be retained, and the total thermal expansion should be large and negative in the superconducting state near T_c and should drop very abruptly to a small value at about 1.7°K. The residual thermal expansion contribution to β_s^{el} below this temperature is due to the existence of the second term in Eq. (3). This equation applies to both β_n and β_s in zero field, and the second term arises because of an appreciable magnetostriction effect which occurs in the superconducting state, but not in the normal state. The magnitudes of the predicted thermal expansions are such that they should be easily observable with present experimental methods.[22,23]

[22] G. K. White, Cryogenics **1**, 151 (1961).
[23] K. Andres and H. Rohrer, Helv. Phys. Acta **34**, 398 (1961).

The previous discussion applies only to the total volume thermal expansion. In practice, tin has a tetragonal crystal structure, and meaningful direct measurements of the linear thermal expansion α can be carried out only by using single crystals which are oriented along or at right angles to the four-fold axis. The uniaxial stress experiments of Seraphim and Marcus[17] which are related to $\Delta\alpha$ indicate a maximum effect on H_c for stress along the fourfold axis. Hence, one would expect that the difference in the linear thermal expansion $\Delta\alpha$ at the superconducting transition to be a maximum (roughly equal to $\Delta\beta$) in this direction and to be very small at right angles to it. No information exists as to the anisotropy of α in the normal state.

Recently, Mapother and his co-workers[24] and Marcus and Seraphim[17] have discussed again the concepts of "similarity" as they are applied to critical field measurements. Two types of similarity are possible. The first, which is called "simple" or geometrical similarity, requires that the shape of the critical field curve be an invariant with respect to, for instance, external stress, when the variables are expressed in reduced units. This concept has been used by Olsen and his coworkers[6] in the analysis of their measurements of the changes in sample length at the superconducting transition. This type of similarity also follows from the microscopic theory of superconductivity as given by Bardeen, Cooper, and Schrieffer.[25] The second, more rigorous type of similarity requires in addition that the ratio of H_0/T_c remains unchanged (as in the isotope effect). Obviously, tin does not obey this latter requirement, since from Table I,

$$(d\ln T_c/d\ln V)/(d\ln H_0/d\ln V)=R_1=0.905. \quad (5)$$

It is of interest, however, to ascertain whether or not tin satisfies the first condition for similarity.

The condition for simple similarity can be expressed as

$$h=f(t^2), \quad \text{or} \quad H=H_0 f(t^2). \quad (6)$$

Here $f(t^2)=1-t^2+D(t^2)$, where $D(t^2)$ is a small quantity (called the deviation function) which measures the departure of the critical-field curve from parabolic shape. Equation (6) can be differentiated to give,

$$(\partial H/\partial P)_T=(dH_0/dP)[1-t^2(1-2R_1)+D(t^2) - 2R_1t^2D'(t^2)]. \quad (7)$$

$D'(t^2)$ is the slope of the $D(t^2)$ vs t^2 plot. This expression [Eq. (7)] is rather complex, but the contribution of the last two terms in the brackets is small. Equation (7) has been evaluated for tin, using the experimental values for the pressure derivatives from Table I and the deviation plot of reference 4, and is plotted in Fig. 1.

[24] M. Garfinkel and D. E. Mapother, Phys. Rev. **121**, 459 (1961).
[25] J. Bardeen, L. W. Cooper, and J. R. Schrieffer, Phys. Rev. **103**, 1175 (1957).

The disagreement appears to be greater than our experimental error.

A direct comparison can be made of the values of $d\ln\gamma/d\ln V$ which are obtained, first, by direct calculation, and second, by the use of this requirement. Equation (1) can be rewritten in reduced form as

$$h^2=1-4\pi(\gamma T_c^2/VH_0^2)t^2+\cdots. \quad (8)$$

The requirements of simple similarity imply that the dimensionless quantity in the brackets must remain unchanged by variations in the pressure (or volume). This can be expressed as,

$$d\ln\gamma/d\ln V=1+2d\ln H_0/d\ln V-2d\ln T_c/d\ln V. \quad (9)$$

The value of $d\ln\gamma/d\ln V$ which can be calculated from Eq. (9) and our experimental data [2.4($\pm$0.7)] is significantly higher than the directly calculated [Eq. (2)] value of 1.2($\pm$0.4). If the data in Fig. 1 are fitted to Eq. (7) from $t^2=1$ to $t^2=0.3$ (where the rapid curvature begins), a value for $d\ln\gamma/d\ln V$ can be calculated from the extrapolation of this function to absolute zero which differs from the directly calculated value by a factor of three.

One can conclude from these experiments that the electronic behavior of tin is complex at low temperatures and is extremely sensitive to pressure effects. This is undoubtedly associated with the shape of the Fermi surface for tin, although direct correlations are not possible at present.[26] Certainly, as Kan *et al.* also suggest, further measurements of the electronic properties of high-purity single crystals of tin should be extremely profitable.

[26] A. V. Gold and M. G. Priestley, Phil. Mag. **5**, 1089 (1960).

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Paramagnetic Resonance Spectrum of Manganese in $CdWO_4$

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The paramagnetic resonance spectrum of Mn^{2+} in $CdWO_4$ was measured at 34 kMc/sec at room temperature. The spectrum can be described by the spin Hamiltonian,

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2+\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)+A\mathbf{I}\cdot\mathbf{S},$$

with $g_z=2.001$, $g_x=2.003$, $g_y=1.997$, $|D|=5.153$ kMc/sec, $|E|=1.395$ kMc/sec, $|A_z|=0.246$ kMc/sec, $|A_x|=0.242$ kMc/sec, $|A_y|=0.259$ kMc/sec, $S=5/2$, and $I=5/2$.

INTRODUCTION

RECENTLY, considerable interest has been shown in the tungstates as host lattices for paramagnetic ions because of their possible application to quantum devices. Some of the paramagnetic resonance spectra that have been studied are Fe^{3+} in the monoclinic tungstates of Cd, Zn, and[1] Mg and Mn^{2+} and Gd^{3+} in the tetragonal $CaWO_4$.[2] In this paper we report our extension of this study to Mn^{2+} ($^6S_{\frac{5}{2}}$) in $CdWO_4$.

APPARATUS

The spectra were obtained with a radiation frequency of 34 kMc/sec. The spectrometer was a conventional bridge design with crystal detection. A VA97B klystron provided the radiation power and was stabilized to the cavity frequency by a circuit similar to that of George and Teaney.[3] The cylindrical (TE_{011}) cavity was made of lavite and silvered by thermal reduction of $AgNO_3$. With this technique it was possible to obtain a high Q ($\sim$3000) with a silvering thin enough to permit field modulation at 5 kc/sec for phase sensitive detection. The microwave frequency was measured with a wavemeter.

Magnetic fields in excess of 20 kOe were obtained with a 12-inch Varian electromagnet having $3\frac{1}{2}$-in. tapered polecaps and $1\frac{1}{4}$-in. air gap. The field was calibrated with an NMR probe[4] whose frequency was counted by a 10-Mc/sec decade counter. Since the narrow gap necessary to obtain the field required for the high field resonances did not permit the use of a Dewar, all measurements were made at room temperature.

OBSERVATIONS

The crystals of $CdWO_4$ were purchased from the Linde Company and had been grown by the Verneuil method. Spectrographic analysis indicated an impurity

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[2] C. F. Hempstead and K. D. Bowers, Phys. Rev. **118**, 131 (1960).

[3] A. J. George and D. T. Teaney, Rev. Sci. Instr. **31**, 997 (1960).

[4] J. R. Singer, Rev. Sci. Instr. **30**, 92 (1959).