HYPERFINE ENHANCED NUCLEAR
MAGNETIC COOLING IN PrCu_6

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**Solid State and Low Temperature
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SCHOOL OF PHYSICS AND ASTRONOMY

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MAGNETIC COOLING IN PrCu_6 *

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MASTER

ABSTRACT

An experimental investigation has been carried out on the physical properties of PrCu_6 relevant to its use, when adiabatically demagnetized, as a coolant for ultralow temperature solid state and nuclear physics research. The crystal structure of PrCu_6 results in a singlet ground state for the praseodymium electron system and an externally applied magnetic field polarizes the two 4f praseodymium electrons to give an effective enhancement, via the hyperfine interaction, to the magnetic field seen by the praseodymium nuclear magnetic moment. As determined from magnetic susceptibility measurements, this enhancement factor was found to be 15.0 ± 1.0 in a 0.55 kG applied magnetic field. Starting conditions of 20 kG and approximately 22 mK yielded 3.0 mK for a final field of 0.55 kG. The specific heat of PrCu_6 was found to obey an a/T^2 law over the approximate range 6 to 30 mK with $a = 4 \times 10^{-5}$ J-deg/mole in a 0.55 kG field. At higher and lower temperatures an excess specific heat appears; around 4.5 mK there appears to be a large, very sharp specific heat anomaly. The nuclear magnetic susceptibility shows Curie law behavior down to 10 mK where the susceptibility begins increasing more rapidly until apparently resuming its higher temperature behavior below 4 mK. The bulk electronic thermal relaxation

time of PrCu_6 would seem to go through a peak value of approximately one hour just above 3 mK and decrease to much less than a minute by 8 mK. The above results point to a possible nuclear ordering in the praseodymium nuclear spin system at approximately 4.5 mK.

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I. INTRODUCTION

Forty years have past since the first successful electronic demagnetization produced a cooling effect. Within the past five years hyperfine enhanced nuclear magnetic cooling has emerged as a method to obtain lower ultimate temperatures in the electronic system which is necessary to cool other materials for low temperature experiments.

This investigation concerns the usefulness of the rare earth intermetallic compound PrCu_6 as a coolant in ultralow temperature solid state and nuclear physics research. A stable temperature around three millikelvin would provide the opportunity to perhaps resolve a number of questions in the area of local moments in metals and the Kondo effect. For example, Mn in Cu is a Kondo system with a characteristic temperature T_{Kondo} of about $0.06 \text{ K}^{1,2}$ and therefore a study of its magnetization in the $T \rightarrow 0$ limit requires cooling to somewhat below six millikelvin. Such low temperatures, or even lower, would be useful in a study of the Au-Cu alloy system with Mn to try to extrapolate a value for the Kondo temperature of Mn in Au which must be very low as free spin behavior is seen down to 0.02 K^3 .

Due to the orthorhombic crystal structure of PrCu_6 and the even number of 4f electrons in the praseodymium

atom, its electronic system has a singlet ground state. At temperatures low enough that Van Vleck paramagnetism is observed, the application of an external magnetic field results in a net polarization of the two 4f electrons in this rare earth ion. The net polarization of the electrons has the effect of multiplying the magnetic field seen by the praseodymium nuclei due to the hyperfine interaction between electron and nuclear spins. For an external applied field H_{app} there is a local field $H_{loc} = (1+K)H_{app}$ seen by the praseodymium nuclear moment where K is the Knight shift. The hyperfine enhancement of the applied field and the small interaction energies associated with the nuclear moments, as compared to the electronic moments, provide an opportunity to achieve extremely low temperatures by adiabatic demagnetization, providing sufficiently low initial temperatures can be obtained to realize a finite nuclear spin system entropy reduction. The hyperfine interaction along with the exchange interaction between 4f electrons and conduction electrons results in very rapid nuclear spin-lattice relaxation for such rare earth compounds and so these materials are useful in cooling other systems in contact with them. The temperatures reached are lattice-conduction electron temperatures--not just nuclear spin system temperatures.

The compound $PrCu_6$ was chosen as a good candidate

for a nuclear coolant because of several desirable traits beyond the basic requirements for obtaining hyperfine enhanced cooling: (1) praseodymium nuclei possess a large magnetic moment which means lots of cooling power; (2) the nuclei have a large spin so the spin system entropy is large; (3) the electronic spin angular momentum of praseodymium is small so that exchange interaction induced ordering effects are minimized; (4) its electronic orbital angular momentum is relatively large so that crystal field effects will play a significant part in inhibiting any electronic ordering; (5) the Van Vleck paramagnetic susceptibility is large so the enhancement factor $(1+K)$ was expected to be reasonably high; (6) PrCu_6 is metallic which means its thermal conductivity should be very good and good thermal contact to it by soldering should be possible; and (7) PrCu_6 was metallurgically realizable with available preparation equipment.

Measurements will be presented on physical quantities relevant to the use of PrCu_6 as a nuclear coolant. High and low temperature susceptibility in low applied magnetic fields and low temperature specific heat measurements have been made. Bulk sample electronic thermal relaxation times have been determined from a number of sources in the lowest temperature region. Calculations of thermodynamic consistency for the demagnetiza-

tions are made. End temperatures achieved are compared to the case of an ideal paramagnetic system and the magnitude of nuclear spin interactions is estimated.

II. THEORY

A History of Magnetic Cooling

In 1933 Giauque and MacDougall⁴ performed the first successful electronic demagnetization using 61 grams of gadolinium sulphate to reach temperatures of 0.53 K from an initial temperature of 3.4 K and a 3.4 kG initial magnetic field. Two weeks later De Haas, Wiersma and Kramers,^{5,6} working independently, obtained 0.27 K by demagnetization of 50 mg of cerous fluoride from 27.6 kG and 1.26 K to 4.5 kG. In addition to reporting their own electronic demagnetization results, Kurti and Simon,⁷ in 1935, suggested the possibility of obtaining much lower temperatures by demagnetizing a nuclear paramagnetic system because of the factor of 10^3 reduction in moment size; they envisioned a multiple stage apparatus using an electronic demagnetization stage as the platform for nuclear cooling experiments. Gorter⁸ had also recognized the potential of using the smaller nuclear magnetic moments to reach very low temperatures.

By removing approximately one per cent of the nuclear entropy with a 28 kG field at 0.01 K using an electronic demagnetization stage, Kurti et al.⁹ demagnetized the nuclear spins of a bundle of copper wires to 20×10^{-6} K as determined from a ballistic measure-

ment of nuclear susceptibility and assuming Curie law behavior. Hobden and Kurti¹⁰ improved the experiment and produced a nuclear spin temperature of 1.2×10^{-6} K in 1959.

The first successful cooling of another system using demagnetized nuclei occurred in 1966 when Osgood and Goodkind¹¹ produced an equilibrium temperature of 0.003 K in copper wires and in addition managed to cool He^3 to 0.006 K. They started from an electronic demagnetization stage temperature of 0.013 K and applied magnetic field of 57 kG. Nuclear magnetic resonance measurements of magnetization in copper and platinum nuclei were used for thermometry. The nuclear stage suffered from a 4 erg/min heat leak. Further progress was made by Symko¹² in 1967 by using indium, which has a spin-lattice relaxation time an order of magnitude less than that of copper, to reach 1.7 mK. By 1972 Berglund et al.¹³ were obtaining conduction electron temperatures of 0.37 mK using twelve moles of copper wire and staying below 2 mK for twelve hours.

Experiments mentioned so far have employed "brute force" alignment of nuclear spins at a low temperature by relying on strong external magnetic fields. In 1966 S. A. Al'tshuler¹⁴ suggested the use of rare earth ions with an even number of electrons, that is non-Kramers degenerate ions, for nuclear magnetic cooling because

the hyperfine interaction is large in these ions; application of a modest external magnetic field results in a large local field at the nucleus. Andreas and Bucher¹⁵ utilized this hyperfine enhancement of an external magnetic field to cool with PrBi from 0.026 K to 0.010 K, as measured by a germanium resistance thermometer, in 1968. Since that time they have reached 1.5 mK using PrTl₃ starting from 0.060 K in a 20 kG magnetic field.¹⁶

Singlet Ground State Rare Earth Ions:

Hyperfine Enhancement

The sixteen rare earth elements--or lanthanide group--have an incomplete 4f electron shell with complete 5s and 5p subshells which screen the 4f electrons from crystal field effects. Those rare earths which have an even number of 4f electrons are candidates for hyperfine enhanced nuclear cooling because they possess a singlet electronic ground state. Even if some levels remain degenerate because of symmetries in the crystal field, the ground state of these "non-Kramers degenerate" rare earths is usually a singlet. The electronic energy level splittings caused by the internal electric (or crystal) field are not necessarily evenly spaced and possess no regular level assignment of the $2J+1 m_J$ values for an ion of total electronic angular momentum J ; these details are very

dependent on the crystal field. For rare earths the total splitting is in the range of 10 to 100 K.

By deriving an expression for the susceptibility of a singlet ground state system, it will become clear why a large Van Vleck paramagnetism is desirable. Neglecting the diamagnetic term, the magnetic energy of an ion in state j subjected to a magnetic field in the z direction, while free or in a crystal, can be written¹⁷

$$E_H = -\mu_{jj}H - \sum_n \frac{2|\mu_{nj}|^2}{E_n - E_j} H^2 + \dots \quad (1)$$

The matrix element μ_{nj} of the permanent dipole moment operator $\mu_z^p = (L_z + 2S_z)\mu_B/\hbar$ is a measure of the admixing of state n into j by the applied magnetic field. The dipole moment in this state j consists of a permanent moment term and induced moment part:

$$\langle \mu_{zj}^p \rangle = - \frac{\partial E_H}{\partial H} = \mu_{jj} + \sum_n \frac{4|\mu_{nj}|^2 H}{E_n - E_j} + \dots \quad (2)$$

For a crystal in thermal equilibrium there will be N_j ions in each ionic state j where the relative population of the states is governed by the Boltzmann factor $\exp(-E_j/kT)$. The magnetization M becomes a thermal average:

$$M = \sum_j N_j \langle \mu_{zj}^p \rangle = \frac{\sum_j \left(\mu_{jj} + \sum_n \frac{4|\mu_{nj}|^2 H}{E_n - E_j} \right) \exp(-E_j/kT)}{\sum_j \exp(-E_j/kT)} \quad (3)$$

assuming no ion energy dependence on the excitations of others. By expanding the exponentials in a series and saving the first few terms, a relatively simple expression is obtained for the case where a subset of states lie closely spaced within kT of the ground state and the rest are widely separated from this subset.

The resulting expression for volume susceptibility is

$$\chi_v = \frac{M}{H} = \frac{N}{n} \sum_j \frac{\mu_{1j}}{3kT} + \frac{N}{n} \sum_{\substack{i,j \\ i \neq j}} \frac{|\mu_{1j}|^2}{3kT} + \frac{N}{n} \sum_{i,k} \frac{2|\mu_{ik}|^2}{E_k - E_1} \quad (4)$$

where n equals the number of nondegenerate states within kT of the ground state and the sum in the second term is over n . The last term is summed over the states i within kT of the ground state and states k which are widely separated. The first term of Eq. (4) is due to the permanent electronic moment, the second is the part of the induced moment contributed by the states within kT of the ground state and the final term is the induced moment part due to admixing one of the levels near the ground state with one widely separated compared to kT . This final term is usually referred to as Van Vleck paramagnetism and is temperature independent as shown by Eq. (4). For the purposes of this work we will consider the case of no electronic levels within kT of the ground state--all are widely separated. Eq. (4) then becomes

$$\chi_V = N \sum_j \frac{\mu_j^2}{3kT} + N \sum_k \frac{2|\mu_{\text{ground}-k}|^2}{E_k - E_{\text{ground}}} \quad (5)$$

For low enough T , where the expansion and approximation for M does not hold and the permanent moments are reaching saturation, the Van Vleck contribution χ_{VV} can be large compared to the temperature dependent term. An alternative way to write the volume susceptibility is the modified Curie law form

$$\chi_V = \frac{C'}{T + \Delta} \quad (6)$$

where Δ is the characteristic temperature calculated to give $\chi_V = \chi_{VV}$ as $T \rightarrow 0$. So for a singlet ground state the susceptibility begins to level out around the characteristic temperature Δ whereas a degenerate ground state system will continue to show temperature dependent paramagnetism until $g\mu_B H$ is much greater than kT .

At temperatures much lower than 1 K the net polarization in an applied magnetic field of the 4f electrons of a singlet ground state rare earth ion (as manifested in the Van Vleck paramagnetic susceptibility) causes an enhancement of the applied field seen by the nucleus because of the hyperfine interaction between the spins. This local magnetic field at the nucleus can be expressed as

$$H_{\text{loc}} = H_{\text{app}}(1 + h\chi_{VV}) = H_{\text{app}}(1 + K) \quad (7)$$

where h is the coupling constant of order 10^6 kG/ μ_B

due to the hyperfine interaction and K is the Knight shift. Contributions to the enhancement from other electron shells are at least an order of magnitude lower than the $4f$ and are not considered. Praseodymium compounds possess a Van Vleck susceptibility of order 10^{-2} to 10^{-1} cm³/mole and a resultant Knight shift from two to twenty. Figure 1 shows the resultant nuclear Zeeman energy splittings as a function of applied field for PrCu_6 which has an enhancement factor $(1+K)$ equal to 15.0 as determined from susceptibility measurements below 0.040 K made during this investigation.

Thermodynamics

There are two essential requirements for obtaining a significant temperature reduction by adiabatic demagnetization. Figure 2 shows an entropy versus temperature plot for two values of magnetic field. The spin system is first cooled by contact with another stage in a large field H_i until an initial temperature T_i is obtained. The system is then isolated and the magnetic field reduced to a low field H_f adiabatically (constant entropy) as shown by the dashed line so that a final temperature T_f is reached. The two necessary conditions for successful demagnetization become clear; The entropy at the initial conditions must be finite with the possibility of reduction and the process of

SPLITTING IN PrCu_6 IN EXTERNAL FIELD

Figure 1. Splitting in PrCu_6 in an external field.

decreasing the magnetic field at constant entropy must be reversible. The figure also reveals that it is very difficult to obtain temperatures much lower than that point at which the curve starts to drop sharply due to the onset of ordering by interactions within the spin system.

Fig. 2. Entropy vs temperature and magnetic field showing adiabatic process.

The nuclear cooling entropy for a singlet ground state system has the maximum of $R \ln(2I+1)/\text{mole}$ where R is the ideal gas constant and I is the nuclear spin. For an applied magnetic field H and temperature T the actual entropy reduction is given by¹⁸

$$\frac{\Delta S}{R} = \ln(2I+1) - \frac{x}{2} \coth \frac{x}{2} + (2I+1) \frac{x}{2} \coth(2I+1) \frac{x}{2} - \ln \left[\frac{\sinh(2I+1) \frac{x}{2}}{\sinh \frac{x}{2}} \right] \quad (8)$$

where x is the ratio of adjacent nuclear energy level spacings to thermal energy:

$$x = \frac{g_n \mu_n (1+K) H}{kT}. \quad (9)$$

g_n is the nuclear splitting factor and μ_n is the nuclear magneton. This expression for x is valid only when the external applied field is such that $\mu_J H$ is less than the crystal field splitting where μ_J is the electronic magnetic moment. For higher fields the elect-

ronic moment and therefore the hyperfine interaction saturates. When x is less than about 0.2, Eq. (8) can be approximated

$$\frac{\Delta S}{R} \approx \frac{x^2}{6} I(I+1). \quad (10)$$

The above is true only if other interactions are negligible compared to the hyperfine interaction strength. Because the entropy reduction, Eq. (8), depends only on H/T , a constant entropy demagnetization requires a constant H/T giving the condition

$$T_F = T_I \frac{H_F}{H_I} \quad (11)$$

for the ideal paramagnetic case. Other interactions can be accounted for by introducing an effective interaction field h so that

$$T_F = T_I \frac{\sqrt{H_F^2 + h^2}}{H_I} \quad (12)$$

when H_I is much greater than either H_F or h . So h is a measure of the dipolar and exchange fields acting on the hyperfine enhanced nuclear moments.

Due to the hyperfine enhancement the magnetization becomes

$$M = Ng_N \mu_N (1+K) I \left[\frac{2I+1}{2I} \coth\left((2I+1)\frac{x}{2}\right) - \frac{1}{2I} \coth\frac{x}{2} \right] \quad (13)$$

where the induced electronic moment contributes the factor of K to the bare nuclear magnetization. The quantity inside the brackets is the Brillouin function and $Ng_N \mu_N (1+K)I$ is the saturation value of magnetiza-

tion. The measured susceptibility is obtained by dividing the magnetization by the applied magnetic field; making an expansion for x less than about 0.2 gives

$$\chi = \frac{g_N^2 \mu_N^2 I(I+1)(1+K)^2}{3kT} \quad (14)$$

The heat capacity due to the hyperfine enhanced nuclear Zeeman splitting should appear as

$$\frac{C}{R} = \frac{x^2}{3} I(I+1) = \frac{g_N^2 \mu_N^2 (1+K)^2 I(I+1) H^2}{3k^2 T^2} \quad (15)$$

from Eqs. (9) and (10). The heat capacity due to any cooperative phenomena would be expected to sit on top of a background given by Eq. (15).

Interactions at Low Temperatures

Deviations from the case of an ideal nuclear paramagnet will appear when temperatures become low enough so that the various interactions become energetically significant. One possibility for representing these interactions has been shown in Eq. (12) where they appear as an effective residual magnetic field h .

The nuclear electric quadrupole moment due to non-spherical nuclear charge distribution interacts with the gradient of the internal electric field it sees. Contributions to the electric field gradient come from the incomplete 4f electron shell, the crystalline field of surrounding ions in the solid, and the so-called "pseudoquadrupole" term. For rhombic symmetry of the crystal field the nuclear Hamiltonian

may be given by¹⁹

$$K = P \left[\left\{ I_z^2 - \frac{1}{3} I(I+1) \right\} + \frac{1}{3} \eta (I_x^2 - I_y^2) \right] \quad (16)$$

with

$$\eta = \frac{3 \langle |J_z^2| \rangle}{\langle |3J_z^2 - J(J+1)| \rangle}. \quad (17)$$

Here $\langle |---| \rangle$ is the matrix element of the enclosed expression between the appropriate electronic states. P contains the dependence on different electric field contributions:

$$P = P_{4f} + P_{\text{crystal}} + P_{\text{pseudo}}. \quad (18)$$

The 4f electron cloud contribution can be written

$$P_{4f} = - \frac{3e^2 Q \langle r_Q^{-3} \rangle}{4I(2I-1)} \langle J || \alpha || J \rangle \langle |3J_z^2 - J(J+1)| \rangle \quad (19)$$

while

$$P_{\text{crystal}} = - \frac{3QA_2^0}{I(2I-1)} (1-\gamma_m) \quad (20)$$

is the term due to neighboring ionic electric fields. α is a normalizing coefficient between terms in different representations of the crystal field potential; $\langle J || \alpha || J \rangle$ is -0.021 for Pr^{3+} in the 3H_4 state.²⁰ Q is the electric quadrupole moment of the nucleus. The mean value of the inverse cube of radial distance between the nucleus and electronic 4f orbitals, modified by a factor to account for the polarization of closed electron shells by the unfilled 4f shell and the consequent extra field gradient generated, is given by $\langle r_Q^{-3} \rangle$. ($\langle r_Q^{-3} \rangle \approx 0.8-0.9 \langle r^{-3} \rangle$.) The Sternheimer

antishielding factor which accounts for polarization of closed shells by external charges is represented by $(1-\gamma_m)$ and $A_2^0 = (1/2)\sum_i Z e_1(3z_i^2 - r_i^2)$ where the sum is over the nucleons. The pseudoquadrupole term is actually a second order hyperfine interaction. The magnetic moment of the nucleus produces a field at the electrons which induces an electronic magnetic moment. The induced electronic moment's field causes a nuclear moment interaction, that is a nuclear energy level shift, which is now proportional to the square of the nuclear moment.²¹ This pseudoquadrupole term can be represented as an addition to equation (18)

$$\rho_{\text{pseudo}} = - \frac{2A_J^2}{\Delta E} \quad (21)$$

where $A_J = Z g_n \mu_n \mu_B \langle r^{-3} \rangle \langle J \| N \| J \rangle$ is the hyperfine constant in $\mathcal{H} = A_J(\vec{J} \cdot \vec{I})$ and ΔE is the energy level difference between differing electronic levels. The factor $\langle J \| N \| J \rangle = (\vec{N} \cdot \vec{J})/J(J+1)$ where $\vec{N}$ is the sum over electrons of the hyperfine interaction for individual electrons. For Pr^{3+} in the 3H_4 state, $\langle J \| N \| J \rangle = 1.32$.²⁰

Besides revealing information on the nature of internuclear forces, the observation of cooperative phenomena leading to some sort of nuclear ordering sets a lower limit to the temperatures attainable with the material under study. Possible interactions to be considered include: the magnetic dipole-dipole (bare and

enhanced) interaction; electric quadrupole-quadrupole interaction; and the indirect interaction of nuclear magnetic moments through the hyperfine interaction with 4f electrons and subsequent exchange interaction between 4f electrons of neighboring praseodymium atoms via the conduction electrons in the metallic compound. Presumably the possibility for direct nuclear exchange is quite small and so is not to be considered.

The nuclear magnetic dipole interaction will have a characteristic energy of

$$E_{\text{dip}} \approx \frac{\mu_i \mu_j}{r_{ij}^3} \quad (22)$$

between atoms of moment μ_i and μ_j separated by a distance r_{ij} . This can of course be represented as a characteristic temperature $T_{\text{dip}} = E_{\text{dip}}/k_B$. The CeCu_6 structure that PrCu_6 possesses is orthorhombic with four formula units per cell. A praseodymium atom is surrounded by nineteen copper atoms at an average spacing of $3.1 \text{ \AA}$ and by six nearest Pr atoms at approximately $5.0 \text{ \AA}$ with six next nearest neighbors at about $5.7 \text{ \AA}$. Using $4.3\mu_N$ for Pr and $2.3\mu_N$ for Cu nuclear moments yields characteristic temperatures of

$$T_{\text{dip}}^{\text{Pr-Pr}} \approx \frac{(1+k)^2(4.3\mu_N)^2}{k_B} \left[\frac{z_1}{(5.0 \text{ \AA})^3} + \frac{z_2}{(5.7 \text{ \AA})^3} \right] \\ \approx 6.3 \times 10^{-5} \text{ K} \quad (23a)$$

$$T_{\text{dip}}^{\text{Pr-Cu}} = \frac{(1+K)(4.3\mu_n)(2.3\mu_n)}{k_B} \left[\frac{z_1}{(3.1 \text{ \AA})^3} \right] \approx 1.6 \times 10^{-5} \text{ K} \quad (23b)$$

where z_1 and z_2 are the number of nearest and next nearest atoms per type, respectively, and $(1+K) = 15.0$ is the hyperfine enhancement.

The electric quadrupole moment interaction between praseodymium atoms can be estimated by¹⁸

$$T_Q^{4f} = \sum_{i,j} C_{ij} \langle J_{4f,i}^e \rangle \langle J_{4f,j}^e \rangle \quad (24)$$

for the polarized 4f electron moment with $g_J \mu_B \langle J_{4f} \rangle = K g_n \mu_n I$, yielding

$$T_Q^{4f} \approx C_0 K^4 \left(\frac{g_n \mu_n}{g_J \mu_B} \right)^4 I^2 (I+1)^2 = 5 \times 10^{-5} \text{ K} \quad (25)$$

for $C_0 \approx 10 \text{ K}$.

The exchange part of the cooperative interactions, written as¹⁸

$$T_{\text{ex}}^{4f} = \sum_{i,j} J_{ij} \langle J_{4f,i} \rangle \langle J_{4f,j} \rangle, \quad (26)$$

becomes

$$T_{\text{ex}}^{4f} \approx J_0 K^2 \left(\frac{g_n \mu_n}{g_J \mu_B} \right)^2 I(I+1) \approx 2 \times 10^{-3} \text{ K} \quad (27)$$

for $J_0 \approx 1 \text{ K}$ and so it is the exchange contribution which dominates the internuclear forces.

It has been shown^{22,23} that magnetic ordering can occur in singlet electronic ground state systems with weaker exchange compared to crystal field interaction due to hyperfine effects although it is possible to

obtain ordering in such systems without consideration of hyperfine effects if the exchange interaction exceeds a critical value. For a system where crystal field effects prevent exchange interactions from producing magnetic ordering, hyperfine effects can provide the balance necessary for ordering to occur. The Hamiltonian per ion is²³

$$R = V_C - 2J_0 \langle J \rangle J + AJI \quad (28)$$

where V_C is the local crystal field and $J_0 = \sum_i J_{ij}$ is the exchange coupling. $\langle J \rangle$ is the average angular momentum of all ions. The eigenstates of V_C are assumed to be singlets separated by the energy Δ . The resulting ground state moment at $T=0$ K has the self consistent form

$$\langle J_1^+ \rangle = \frac{\eta \langle J_1^+ \rangle - ac}{\sqrt{1 + \left(\frac{\eta \langle J_1^+ \rangle - a}{c} \right)^2}} \quad (29)$$

where $a = 2AJI^+/\Delta$, $\eta = 4J_0 c^2/\Delta$, $c = \langle 1|J|-1 \rangle$, $|1\rangle$ and $|-1\rangle$ are the singlet eigenstates of V_C , and I^+ is the nuclear spin $+1/2$. The 1 and + are used, respectively, to designate the electronic and nuclear spin states for which the moment is calculated. Alternatively it can be written

$$\langle J_1^+ \rangle = \frac{c \sqrt{\eta^{*2} - 1}}{\eta^*} \quad (30)$$

with

$$\eta^* = \eta - \frac{ac}{\langle J_1^+ \rangle} \quad (31)$$

This can be compared to the same result without including hyperfine effects in which case

$$\langle J_1 \rangle = \frac{c/\eta^2 - 1}{\eta} \quad (32)$$

so there is an effective shift of η by $ac/\langle J_1^2 \rangle$ downward when including the hyperfine interaction. The result then is that the singlet state is stable until η (or η^2) equals one or greater for positive η or η^2 at which time a self induced moment appears and hyperfine effects serve to decrease the exchange strength necessary to break up the singlet state. A transition temperature T_c can be calculated for the point at which the breakup occurs by looking for the temperature at which the sum of $\langle J \rangle_T$ for all states is zero; as a result T_c is given by

$$kT_c = \frac{2g_0 a^2 c^2}{1-\eta} \quad (33)$$

For temperatures much higher than T_c , molecular field theory allows another method to produce an estimate of this characteristic temperature. If the field on each ion is

$$\vec{H} = \vec{H}_{app} + \gamma \vec{M} \quad (34)$$

where $\vec{H}_{app}$ is the externally applied magnetic field and $\gamma \vec{M}$ is the molecular field due to exchange forces with γ as the molecular field constant, then for

$$m = n_m \frac{I+1}{3I} \cdot \frac{\mu_m H}{kT} \quad (35)$$

the susceptibility becomes

$$\chi_V^{\text{molecular}} = \frac{M}{H_{\text{app}}} = \frac{C}{T - T_C} \quad (36)$$

with $C = \frac{M_m \mu_m}{3k} \cdot \frac{I+1}{I}$ and $T_C = \gamma C$. M_m is the saturation value of magnetization $N g \mu_N I$ and $\mu_m = g \mu_N I$. The Curie law result

$$\chi_V^{\text{Curie}} = \frac{N \mu_N^2 g_N^2 I(I+1)}{3kT} \quad (37)$$

combined with rewriting

$$C = \frac{N \mu_N^2 g_N^2 I^2(I+1)}{3kI} \quad (38)$$

allows the molecular field susceptibility to be written

$$\chi_V^{\text{molecular}} = \frac{\chi_V^{\text{Curie}}}{1 - \gamma \chi_V^{\text{Curie}}} \quad (39)$$

Consequently an ordering temperature can be determined from the condition

$$\gamma \chi_V^{\text{Curie}} = 1 \quad (40)$$

or

$$T_C = \frac{\gamma N \mu_N^2 g_N^2 I(I+1)}{3k} \quad (41)$$

Low Temperature Nuclear Spin-lattice

Relaxation in Metals

Achieving thermal equilibrium within a system at millidegree temperatures is a universal problem in low temperature research. For nuclear cooling experiments the relaxation time between nuclear spins and lattice structure of the coolant material is an important consideration. Achieving low nuclear spin temperatures

and high nuclear specific heats without cooling the lattice system can not be considered a practical success in the sense that such a material will be of no use in cooling other systems of low temperature interest.

The Korringa relation, which can be written as

$$T_1 T = \text{constant}, \quad (42)$$

says that the product of spin-lattice relaxation time T_1 and conduction electron temperature T is a constant for a given metal. At very high ratios of magnetic field to temperature this relation has been shown not to hold. A saturation effect sets in around the characteristic temperature equivalent to the nuclear energy level separations; for the Co^{60} in Fe system studied by Brewer *et al.*,²⁴ a saturation value of approximately one minute was reached at around 14 mK. The explanation of this effect rests on the Fermi statistics which the conduction electrons obey. At high temperatures the transition probabilities for an electron giving up or absorbing an energy quantum from a relaxing nucleus are both proportional to temperature, but as temperature decreases sufficiently the probability for a nucleus acquiring a quantum from an electron goes to zero as $\exp(-g_n \mu_n H / kT)$ while the opposite transition probability approaches a constant as kT becomes much less than $g_n \mu_n H$. Consequently, for a given system

there will be a point past which further increases in equilibrium times in a macroscopic sample can not be accounted for by increasing nuclear spin-lattice relaxation times.

In explaining the results of nuclear magnetic cooling of copper, Kittel²⁵ points out that with a finite conduction electron-lattice system it becomes necessary to consider the heat capacities of the nuclear and conduction electron spin systems in calculating an effective relaxation time. Because of the low entropy associated with the conduction electrons, only a few nuclear spins need relax to obtain equilibrium. Although $\tau_1 T = 1$ sec-K for copper, the relaxation time at $T = 0.01$ K is 1 sec for an initial nuclear spin temperature of 10^{-5} K. Kittel also estimates a maximum conduction electron-phonon equilibrium time from

$$\tau_{ep} \approx 234 \tau_0 T_F / T \approx 0.1 \text{ sec} \quad (43)$$

where τ_0 is the thermal conduction relaxation time at the Debye temperature (approximately 3×10^{-4} sec for copper) and T_F is the Fermi temperature.

For the singlet ground state magnetic system PrCu_6 , the nuclear spin-lattice relaxation time is expected to be short as the nuclear spins are strongly coupled via the hyperfine interaction to the 4f electrons and the 4f electrons are exchange coupled to the conduction electrons.²⁶ Long relaxation times to equi-

librium in the bulk sample would be explained for this case by a long electron-electron relaxation time t given by

$$t = c_{\text{nuc}} L / \lambda A \quad (44)$$

where c_{nuc} is the nuclear specific heat per volume, L and A are the length and cross section of the sample, and λ is the thermal conductivity of the electron system. Only the nuclear specific heat need be considered here as the lattice and electron contributions are negligible at millidegree temperatures.

PrCu₆

The rare earth intermetallic compound PrCu₆ was chosen as a likely candidate for hyperfine enhanced nuclear cooling based on known physical properties. Also PrCu₆ proved to be metallurgically possible to obtain with facilities available as opposed to an initial investigation with PrIn₃ where the compound was not successfully produced.

One of the light rare earths, Pr³⁺ has two 4f electrons which are responsible for its useful properties in this work. This ion possesses a ³H₄ electronic ground state with $g_J = 4/5$; the nuclear magnetic moment is $4.3\mu_N$ and the nuclear spin is $5/2$. Pr³⁺ should be an effective nuclear coolant to low temperatures since $S=1$ and $L=5$. The exchange interaction depends on the spin angular momentum and will tend to cause

ordering while the crystal field effects depend on the orbital angular momentum and will inhibit any cooperative effects. The rather large nuclear moment insures that large cooling power will be available for a praseodymium system.

The Pr-Cu phase diagram shown in fig. 3 reveals that PrCu_6 is thought to be a stable compound which could be produced by reacting the constituents in the correct stoichiometric ratio above the melting point. The compound has an orthorhombic crystal structure of the CeCu_6 type²⁷ with lattice constants $a=8.101$, $b=5.081$, $c=10.140$ Å.²⁸ Using these constants and four formula units per cell, a theoretical molar volume of 62.9 cm^3/mole and density of 8.3 g/cm^3 can be calculated. A Van Vleck paramagnet, PrCu_6 has a measured susceptibility of 0.076 $\text{cm}^3/\text{mole Pr}^{3+}$ at 1.0 K.¹⁸

Nuclear Orientation Thermometry

For the purposes of this work only thermal equilibrium nuclear orientation will be reviewed; complete discussions of nuclear orientation can be found elsewhere.^{29,30}

The temperature dependence of the hyperfine nuclear energy levels' populations is the basis for low temperature thermal equilibrium nuclear orientation thermometry. A nucleus of spin I and magnetic moment μ has the degeneracy of its $2I+1$ hyperfine energy levels re-

PR-CU

Figure 3. Pr-Cu phase diagram. From K. A. Gschneidner, Jr., Rare Earth Alloys (D. Van Nostrand Co., Inc., Princeton, N.J., 1961), p. 159.

moved by the application of a magnetic field B_{eff} . The effective magnetic field acting on the nuclei is the sum of external applied field and hyperfine magnetic field which is a result of the electronic system's response to the external field; this can be written as

$$\vec{B}_{\text{eff}} = \vec{B}_{\text{app}} + \vec{B}_{\text{hf}} . \quad (45)$$

The energy separation between levels is

$$\Delta E = \mu B_{\text{eff}} / I \quad (46)$$

as each level's spin has a distinct orientation with respect to the direction of applied magnetic field. In thermal equilibrium the populations of these levels are determined by the Boltzmann distribution. The fractional population of level m is

$$W(m) = \exp(-m\beta) / \sum_m \exp(-m\beta) \quad (47)$$

where $m = I, I-1, \dots, -I+1, -I$ is the quantum number denoting the projection of nuclear spin on the applied field axis and β is equal to $\mu B_{\text{eff}} / k_B T$. For a given nucleus, as the ratio of applied field to temperature increases, the lower levels will become increasingly populated at the expense of the higher levels thereby achieving nuclear polarization.

By defining an axis of rotational symmetry the applied magnetic field allows the radiation pattern of a decaying nucleus to be described by a series of Legendre polynomials. This angular distribution of

the radiation with respect to the field axis can be written as

$$W(\theta) = \sum_{k=0}^{\infty} Q_k B_k U_k F_k P_k(\cos \theta) \quad (48)$$

where $W(\theta)$ is the rate of radiation detection at angle θ from the oriented nuclei compared to the rate detected when the nuclei have essentially no orientation due to a sufficiently low ratio of applied field to temperature. The factors in the above expression will be considered below for a nucleus of initial angular momentum I_a which decays to a state of angular momentum I_b in an unobserved transition carrying away angular momentum L_{un} and then undergoes the observed transition which carries away angular momentum L to a state with angular momentum I_c .

The Q_k are geometrical correction factors for the finite solid angle which any real detector occupies. In this work, correction factors for the Ge(Li) detectors were taken from the tabulations of Camp and Van Lehn.³¹

The only factor depending on temperature and magnetic field is B_k , the orientation factor, which describes the degree of orientation of the nucleus in its initial state with spin I_a . B_k is given by

$$B_k = (2k+1)^{\frac{1}{2}} \sum_m C(I_a k 0 | I_a m) W(m) \quad (49)$$

where C is a Clebsch-Gordon coefficient and $W(m)$ is as

given in Eq. (47). $B_k=0$ for $k > 2I_a$.

Unobserved decays taking place before the one which is observed reduce the degree of orientation obtained in the initial state; the deorientation factor U_k accounts for this effect. For the unobserved transition carrying away spin L_{un} and leaving a state with spin I_b , U_k is given by

$$U_k = (-1)^{I_a+I_b-L_{un}} (2I_a+1)^{\frac{1}{2}} (2I_b+1)^{\frac{1}{2}} \times \\ \times W(I_a I_a I_b I_b; k L_{un}) \quad (50)$$

where W is a Racah angular momentum coupling coefficient. For more than one unobserved transition the final U_k is the product of the individual contributions. It is assumed here that the intermediate state lifetimes are sufficiently short--generally taken to be less than 0.1 nsec³²--that no external effects cause reorientation to occur.

The F_k are angular distribution factors which describe the radiation pattern of the observed decay and hence depend on the multipolarity of the decay and the initial and final angular momenta of the nucleus. F_k is given by

$$F_k = (-1)^{I_c-I_b-1} (2I_b+1)^{\frac{1}{2}} (2L+1) C(LL1-1; k0) \times \\ \times W(I_b I_b LL; k I_c). \quad (51)$$

$F_k=0$ for $k > 2L$ and, for a gamma ray transition, parity is conserved so that $F_k=0$ for k odd.

$P_k(\cos \theta)$ are the Legendre polynomials and contain the only dependence on the detector angle with respect to the magnetic field axis. From the above paragraphs it can be seen that the sum in Eq. (49) goes from 0 to λ where $\lambda = 2l_a$ or $2L$ whichever is smaller. The various factors are defined such that $Q_0 = B_0 = U_0 = F_0 = P_0 = 1$.

Mn^{54} with a 0.835 MeV gamma ray emitted after electron capture and Co^{60} with a cascade of a 1.173 MeV followed by a 1.332 MeV gamma ray after a beta decay were used for nuclear orientation thermometry. For all three gamma decays $L=2$ and so $k=0,2,4$ are the only terms. The Mn^{54} gamma ray has $U_2F_2 = -2\sqrt{3/7}$ and $U_4F_4 = -2\sqrt{22/21}$. Both Co^{60} gamma rays have $U_2F_2 = -\sqrt{78/21}$ and $U_4F_4 = -\sqrt{26/21}$. For purposes of this work, the saturation values of the hyperfine fields at the nuclei are -226.5 kG for Mn^{54} in Fe^{33} and -120.7 kG for Co^{60} in Ni ; ³⁴ the minus signs indicate that the hyperfine fields are opposite to the direction of external field and so it is the difference between the two which represents the effective magnetic field.

III. APPARATUS

The cryostat used in these experiments was the result of extensive modifications to an adiabatic demagnetization cryostat³⁵ previously in use in this laboratory. The dewar set, superstructure, pumping tubes and even the vacuum can remain basically intact. The He³ evaporation refrigerator and paramagnetic salt demagnetization stage were replaced by a dilution refrigerator and nuclear demagnetization stage, respectively.

The superstructure for support of the cryostat provides access for raising and lowering the dewar set from underneath. It consists of two parts: the bottom section, standing 1.8 meters high, is made from aluminum tubing filled with sand and rests on waffle-like vibration isolating pads and the top section, adding an additional 1.4 meters in height, is also made from aluminum tubing filled with sand and vibrationally isolated from the bottom section with additional stacks of waffle pads. The result is a massive, sturdy assembly which is well isolated from vibrations transmitted through the floor. As an additional note, this cryostat is located in a very vibrationally and electrically quiet room on the lowest below grade level of the building.

The glass dewar set consists of a liquid nitrogen dewar and a four inch i.d. liquid helium dewar. They are raised and lowered with a system of ropes and pulleys to the aluminum block through which the cryostat projects. A brass vacuum can isolates the experimental region of the cryostat from the 4.2 K bath; the can is mounted to the pumping tube assembly by an indium O-ring sealed flange.

Electrical Leads

Electrical connections to the inside of the vacuum can are made through room temperature feedthroughs. Two thirty-two pin hermetically sealed connectors each have their own 3/8 inch stainless steel tube running from the top flange of the cryostat to the vacuum can; one is used solely for power leads and the other for signal leads. Each connector pin has a 47 μ H Lenox-Fugle subminiature shielded inductor and a 5000 pF Allen-Bradley capacitor filter inserted in the line for rf filtering as shown in Fig. 4. The bodies of the capacitor filters were passed through a ground plane to which they were attached with conductive, silver-loaded epoxy. The bodies of the connector-filter assemblies were filled with Stycast 2850 FT epoxy to ensure a vacuum tight seal. The power leads include six #32, two #30, and twenty-two #36 manganin wires, a pair of NbZr leads of 0.010 inch diameter with a

Fig. 4. Electrical lead rf filtering.

0.001 inch copper coat, and four twisted #40 copper wires for ground. The signal leads are made up of twenty-eight #36 manganin wires, two sets of three twisted #40 copper wires for grounds, and two 0.003 inch chromel leads for a thermocouple in the dilution refrigerator still. All these leads are heatsunk using Stycast 2850 FT epoxy to fill offset copper fittings through which the leads run just above the vacuum can as shown in Fig. 5. An additional epoxy filled heat-

Fig. 5. Electrical lead heatsinking.

sink is made at the top baffle in the pumping tube assembly for the power leads. An empty piece of teflon tubing through each heatsink ensured that the feed-through and associated tubes were open to the vacuum can and hence no undetected leaks could result in pressure buildups in these volumes upon warming the cryostat.

Inside the vacuum can, all leads are tied to the He⁴ pot in such a way as to make this area a junction box where connections are made or broken for internal electrical changes to the cryostat. From the He⁴ pot down, leads are superconducting except for balanced lengths of manganin wire to the 0.1 K plate for the resistance thermometry network. The superconducting leads are 0.003 inch NbTi with the copper jacket etched away except for the ends where it is needed for soldering. For the most part these superconducting leads are made up into "harnesses" of several leads attached to a lens paper substrate with GE 7031 varnish used as cement and insulation. These assemblies are heatsunk, as are all other wires, to each component of the dilution refrigerator using Apiezon N grease and cotton thread tied around the components to keep the wires tightly in place.

There are leads for a liquid helium boiloff heater, superconducting magnet persistent current heat switches,

a magnetometer, and power for the magnets running into the liquid helium bath. The magnet power leads are four 0.020 inch diameter wires consisting of a 0.010 inch diameter NbTi core with copper jacket. From the room temperature feedthrough on the cryostat flange to the first baffle on the pumping tube assembly there are #23 copper wires in parallel with the superconductors. These magnet leads are heatsunk at each baffle using copper cylinders threaded on one end. The cylinders are mechanically held on the baffles with a nut and thermal contact is made with an interface of gallium. The wires were run through the cylinders and then Stycast 2850 FT epoxy was used to fill the cylinders.

Demagnetization Magnet

The demagnetization magnet is a twenty kilogauss straight superconducting solenoid suspended in the helium dewar at the level of the nuclear stage sample inside the vacuum can. Designed and built in-house, the solenoid has a 3.50 inch (8.90 cm) long winding with a 2.86 inch (7.28 cm) i.d. and a 3.32 inch (8.44 cm) o.d. and utilizes 0.005 inch diameter NbTi wire that has 0.001 inch each of copper and Formvar insulation over it. Twenty-six layers of winding totaled 10 920 turns. The magnet form was made of OFHC copper with a 2.6 inch i.d. A 1/4 inch thick epoxy glass spacer was used at one end of the winding to allow the

power leads to be brought out on a radius. After every two layers of winding were put down, a wrap of mylar tape was used to hold the wire firmly in place and to eliminate the propagation of winding errors. The persistent current heat switch was constructed above the winding by putting eight turns of one of the power leads with the copper removed around a threaded 3/8 inch o.d. epoxy glass cylinder. The room temperature resistance of this stripped section was $11\frac{1}{2}$ ohms. A single layer of $31\frac{1}{2}$ ohm/ft Evanohm wire $3\frac{1}{2}$ ft long was wound over the superconductor and epoxied to the cylinder. Four layers of masking tape and a layer of thread provided thermal isolation from the helium bath. The superconducting joint between the magnet power leads was made with a plasma torch after passing copper coated sections of both wires side-by-side through a 0.018 inch hole in a length of copper tube and filling the tube with indium solder. The inductance of the magnet is about 5.3 H and the midpoint-on axis field was measured at 1.11 ± 0.04 kG/A. Twenty-four milliamperes in the heater wire is sufficient to drive the heat switch normal. The heat switch resistance is much greater than that of the two ohm shunt across the power leads outside the cryostat so that a field quench will dissipate most of the stored energy in the shunt and not ruin the switch. In spite of careful attention

to prevent sharp bends or kinks in the wire and to make sure the wire was held firmly in place at all points, as well as employing the copper form with its high conductivity to smooth out any sharp field changes, the magnet consistently quenches at about 22 kG (19.8 A); this is well below the short sample test results for the wire used.

He⁴ Pot

The He⁴ pot is a brass annulus of inside volume 125 cc--the hole through the center is for the dilution refrigerator pumping line. This chamber is filled with liquid helium from the 4.2 K bath through a length of 0.024 inch i.d. stainless steel capillary coming from a valve on top of the vacuum can. This valve has a brass seat with a stainless steel valve stem from a Hoke 1325M48 valve (56 turns/inch and a 3° taper); the stem is attached to an 1/8 inch o.d. stainless steel tube running up through a Veeco quick connect at the top flange of the cryostat and operated by a knob attached there. The He⁴ pot has a 0.1 cm diameter by 0.5 cm long pumping orifice located just above it in the pumping line to minimize filmflow heat loading. On the top surface of the He⁴ pot there is a boiloff heater and a 470 ohm Speer resistor for monitoring the temperature; both are mounted on copper blocks and contact is made to the He⁴ pot with Apiezon N grease. The pumping line

consists of 3/4 inch to 1-1/2 inch diameter thinwall stainless steel tubing running up to room temperature with two sets of radiation baffles along the way. From the top flange there is a length of 2 inch i.d. line to a 2 inch Consolidated Vacuum Corporation gate valve, oil baffle and 2 inch CVC oil diffusion pump. The backing side of the diffusion pump is 1-1/32 inch i.d. line to a 2-1/2 liter/sec model D-150 Precision Scientific mechanical pump with the exhaust running through a gasmeter to monitor liquid helium level in the evaporator. There is a Pirani vacuum gauge in the line just above the top flange of the cryostat and two thermocouple gauges, one located on the backing side of the diffusion pump and one just ahead of the mechanical pump at the gas handling system board for the dilution refrigerator.

Dilution Refrigerator

Referring to Fig. 6, the dilution refrigerator is made up of a still, a coaxial heat exchanger, three discrete heat exchangers, and the mixing chamber. This refrigerator was designed and built in-house using published design criteria.^{36,37} Returning He³ gas is under sufficient pressure to condense it at the primary impedance which is loosely kept at He⁴ pot temperatures. This impedance was made by stretching a 94 cm length of 0.010 inch manganin wire to 102 cm; 56 cm of this

SCHEMATIC OF DILUTION REFRIGERATOR

Figure 6. Schematic of dilution refrigerator.

stretched wire was inserted in a 0.020 inch o.d. by 0.005 inch wall stainless steel tube to give an impedance³⁶ of $21\,000 \times 10^8 \text{ cm}^{-2}$. The liquid He^3 then passes into the coaxial heat exchanger which consists of 100 cm of 0.020 inch o.d. by 0.005 inch wall stainless tubing inserted inside a 0.050 inch o.d. by 0.006 inch wall length. A secondary impedance of $1030 \times 10^8 \text{ cm}^{-2}$, made by inserting 40 cm of 0.008 inch manganin wire into the high temperature side of the inner coaxial exchanger tube, ensures having liquid in the primary impedance at all times. The cold end of the coaxial exchanger is tied to the 0.1 K plate where posts are provided to thermally ground all electrical leads; this plate is suspended from the bottom of the still on a nylon post around which the coaxial exchanger spirals. Further cooling of incoming liquid He^3 is obtained in a series of three discrete heat exchangers. Each of these exchangers has sintered copper bonded under pressure and heat to the copper body. The returning, concentrated He^3 chamber has a $3/4$ cc volume compared to 1.4 cc on the dilute side. Each level below the 0.1 K plate is suspended by three graphite rods from the component above it. Finally the He^3 enters the 1.8 cc sintered copper mixing chamber where it passes across the phase boundary between concentrated He^3 and dilute $\text{He}^3\text{-He}^4$ thereby providing the cooling power of the

refrigerator.

The diluted He^3 passes back through the heat exchangers and is preferentially evaporated at 0.8 K in the still. At its maximum operable level the still contains 4 cc of liquid. He^3 has approximately a factor of seventy higher vapor pressure than He^4 at 0.8 K; this advantage is cancelled if superfluid He^4 is allowed to filmflow up the pumping tube and evaporate at a higher temperature. The heat input to the still is by means of a heater coil wrapped around the end of an extension of the pumping tube down into the still. This feature, in addition to a chimney structure inside the still, stops the filmflow by boiling off the superfluid at the heater coil and encouraging its recondensation inside the still. The heater consists of slightly less than two feet of 0.0025 inch manganin wire--89.7 ohms at room temperature. At 1.2 mW power input, the He^3 : He^4 gas ratio is 16:1.

Temperatures on the dilution refrigerator are monitored with Speer resistors. On the still there is a 470 ohm resistor in addition to a Cryogenic Linear Temperature Sensor (CLTS)³⁸ resistor which goes from 290 ohms at room temperature to 221 ohms at liquid helium temperatures and is used to monitor cooling progress inside the vacuum can during initial helium transfer in the dewar. The 0.1 K plate has a 220 ohm

resistor and the heat exchangers and mixing chamber have 0.012 inch slabs cut from 50 ohm, grade 1002, 5% Speer resistors. These slabs were sanded to produce a 230 ohm room temperature resistance and mounted in a lens paper sandwich with Apiezon N grease used for thermal contact to copper clips which hold the slabs under spring tension.³⁹ All Speer resistors in the cryostat use 390 pF Elmenco DM5FY-391J capacitors in parallel for shunting any rf pickup still present on the lines.

The gas handling system for the dilution refrigerator, as pictured in Fig. 7, was designed to allow for ease of repair and minimal possibility of He³ loss as well as the obvious functions required. The pumping tube on the still is 3/4 inch diameter which becomes 1-1/2 inch diameter stainless steel outside the vacuum can and extends to the room temperature flange of the cryostat with radiation baffles along the way. From the top of the cryostat the line becomes 2-1/8 inch diameter with a Pirani vacuum gauge and crossover to the returning He³ line inserted at this point. After a two inch CVC gate valve and an oil trap filter, a length of 2-1/2 inch i.d. tube extends to a two inch CVC throttle valve at the gas handling board pictured. The pump used to circulate the He³ is an eleven liter/sec sealed model 660 Edwards High Vacuum Ltd. mechanical

Figure 7. Gas handling system for refrigerator.

pump whose backing side is connected to an oil trap. The He^3 passes through a liquid nitrogen cold trap before entering the 3/8 inch return line to the cryostat. The board includes vacuum gauges and crossover lines to evacuate various parts of the system with the mechanical pump as indicated in the figure. There is a fifteen liter tank for storage of the helium between runs and retaining He^3 drawn out, during operation, to adjust the phase boundary in the mixing chamber. A five liter tank is also included which holds pure He^3 in reserve to make up for losses or changes in the system volume. The cold trap section includes two relief valves; one valve to the fifteen liter storage tank in case of an overpressure during a run; and the other to the outside world which is connected before the cold trap is warmed up to prevent overpressure from trapped gas. The whole dilution refrigerator system runs below atmospheric pressure so that any leaks result in air getting in and being trapped rather than producing He^3 losses. The system runs as shown with 1.6 STP liters He^3 and 7.5 STP liters He^4 in the large storage tank and 1.75 STP liters He^3 in the small storage tank.

The cryostat is electrically and mechanically isolated from the mechanical pumps. All vacuum lines have a nylon spacer installed to electrically isolate the cryostat. Further, the lines have sections of bel-

lows at both ends of a 3-1/2 meter run along a solid concrete wall to which they are firmly attached. From the gas handling board to the Edwards pump there is an additional length of bellows. The He⁴ pot mechanical pump as well as the Edwards pump is firmly bolted to a concrete slab which rests on vibration isolation pads. No perceptible vibration reaches the gas handling board, much less the cryostat.

Nuclear Demagnetization Stage

Referring to Fig. 8, the nuclear demagnetization stage hangs from the mixing chamber in the middle of the 20 kG superconducting solenoid located in the helium dewar. This stage is surrounded by a heat shield from the still and one from the mixing chamber. In addition, there is a spacer between the two shields which is thermally tied to the first discrete heat exchanger. Mechanical rigidity and thermal isolation between all layers and the outer vacuum can is achieved with appropriate thicknesses of cotton or nylon string windings. The still shield consists of many fine copper wires, embedded in epoxy, and screws onto the still flange. The mixing chamber is actually an annulus with threads on the inside to receive the heat shield which hangs from it. This shield is made of textolite fiberglass tubing and has adhesive backed copper foil strips running vertically on the shield. These strips are Cd81

DEMAGNETIZATION CHAMBER

Figure 8. Nuclear demagnetization stage.

soldered to a top copper piece which has its threads gold plated where they screw into the mixing chamber. There is a lead heat switch CdBi soldered to this copper piece and to a set of silver strips which run to the nuclear stage; the heat switch operates in the fringing field of the demagnetizing magnet and switches at the sixteen kilogauss central field level. Sets of eight 0.010 inch by 1/8 inch silver strips, with lens paper and GE 7031 varnish insulation between strips, run from the heat switch to the nuclear demagnetization sample and from there to the nuclear orientation thermometers. This layered structure is used to minimize eddy current heating. The silver strips are silver soldered at the heat switch end and indium soldered at the other points. Silver was used in the nuclear stage because its low nuclear magnetic moment helps minimize the specific heat developed in parts of the nuclear stage other than the PrCu_6 coolant. The nuclear stage sample is typically 5/8 inch in diameter by 3/4 inch long and its preparation for mounting in the cryostat is described fully under the sample preparation section. There is a slab resistor mounted, like those on the dilution refrigerator, on the silver strips just above the nuclear sample. A CLTS resistor is mounted in a copper clip with Apiezon N grease and indium soldered on the silver strips just below the

nuclear demagnetization sample for use as a heater; it works well for this purpose because its resistance does not change below 4.2 K and hence an accurately measured heat input is possible.

Approximately 27-1/2 cm below the center of the nuclear demagnetization sample is the center of a 4.1 kG split solenoid superconducting magnet which polarizes the nuclear orientation thermometers used for absolute thermometry on the nuclear stage. Preparation of these thermometers will be described later. These nuclear orientation thermometers are in the form of 0.005 inch to 0.010 inch thick metal foils which are indium soldered to a copper fin projecting from the nuclear stage silver strips. Another Speer resistor slab is mounted here as well as a glass-ceramic capacitor, fully described in Appendix A, which possesses temperature sensitivity down to the lowest temperatures obtained and is very magnetic field insensitive. Electrical leads for these two secondary thermometers are NbTi wires of 0.003 inch diameter as found throughout the cryostat; they are heatsunk and electrically insulated using lens paper and GE 7031 varnish to cement them to the silver strips running from the nuclear stage. These leads as well as the ones to the nuclear stage are made and disconnected at the mixing chamber for each run so that the whole mixing chamber heat shield

with nuclear stage inside can be unscrewed and removed. This enables changes to be made much more conveniently.

Measurements on the capacitor and the resistors will be covered in Appendices A and B respectively. Magnetization measurements are made on the nuclear stage sample using a Hewlett-Packard fluxgate magnetometer probe model 3529A with model 428B clip-on DC milliammeter electronics package. Two superconducting flux transformers are used to achieve flux coupling through the vacuum can without introducing power into the sample from the magnetometer's driving coil. These flux transformers are 0.005 in. diameter NbTi wire with sections wound and epoxied around Speer resistors to provide a means of quenching the current in either loop. The loop inside the vacuum can takes one turn about the sample and proceeds up the dilution refrigerator as a twisted pair to an eleven turn coil on a form which is inserted in the vacuum can pumping tube. The outer loop has one turn around the outside of the pumping tube and four turns around the fluxgate magnetometer probe mounted on top of the vacuum can. A lead sheet forms a magnetic shield around the tubes and magnetometer probe to eliminate the offset caused by the earth's magnetic field and the fringing field of the superconducting solenoids. All these instruments as well as power supplies to the cryostat are mounted in racks

which possess an isolation transformer in the line.

Gamma-ray Detection and Analysis System

While the glass-ceramic capacitor and Speer resistor slab are used as secondary thermometers, the primary and absolute thermometry is done by observation of gamma rays emitted in the decay of oriented nuclei. The theory of this technique has been covered earlier and preparation of the metallurgical samples used is covered in the Experimental Procedure chapter.

The gamma rays are detected along the axis of the 4.1 kG polarizing magnet with a lithium drifted germanium--Ge(Li)--detector. Two detectors were used in the course of this investigation. The first was a Canberra Industries five sided detector in a straight mount. Its weight was 203 grams with 9.8 cm² active area facing the window. For the 1.33 MeV Co⁶⁰ gamma ray it has: 3.0 keV FWHM; 6.0 keV FWTM; Peak/Compton of 16:1; and 4.3% efficiency. The high voltage supply was a 1300 volt battery pack and the energy pulse was amplified at the detector output with a Canberra model 140BC spectroscopy preamplifier. The second Ge(Li) detector was also from Canberra Industries; the right circular cylinder of 41 mm diameter was drifted coaxially with one open end. Weight was 261 grams with 12.4 cm² active area facing the window. For the 1.33 MeV Co⁶⁰ gamma ray it has: 2.40 keV FWHM; 4.74 keV FWTM;

Figure 9. Gamma-ray detection and analysis system.

Peak/Compton of 27:1; and 8.2% efficiency. The 1700 volts high voltage was supplied by a Fluke model 415B high voltage power supply and the energy pulse was amplified at the detector output with a Canberra model 970 spectroscopy preamplifier.

As shown in Fig. 9, the preamplified energy pulse was fed through a Canberra model 1416 amplifier and then a model 1414 DC restorer before entering a Victoreen SCIPP 400 multichannel pulse height analyzer. Collected spectra were read out on a teletype at the end of a counting period in addition to being displayed on the analyzer screen.

IV. EXPERIMENTAL PROCEDURE

Sample preparation: PrCu₆

The praseodymium was supplied⁴⁰ in 1/4 inch rod form of 99.9% purity and was kept under mineral oil in the laboratory so as to minimize oxidation. In preparation for melting, a length of the rod was cut off so that it would be an eighth of an inch or so shorter than the two inch crucible used for melting. This piece was scraped to remove most of the oxidation on the surface and then immersed in a nitric acid-water solution to finish the oxidation removal. Any surface imperfections on the rod were scraped out until bright metal was seen, then the praseodymium was lightly etched in a 6% nitric acid-methanol solution and rinsed in ethanol; the result was a uniformly bright surface which was fairly resistant to oxidation even when left exposed to the atmosphere. The rod was stored in ethanol at this point until placed in a 1.4% perchloric acid-methanol electropolishing solution⁴¹ maintained at -76 °C by a dry ice-acetone bath. The cathode was stainless steel sheet bent to conform to the inside of the glass beaker holding the electropolishing solution. The rod was suspended by a tweezers with tips bent in to hold firmly yet cover up minimal surface area. Optimum results were obtained by using 100 ma/in.² for ten to fifteen minutes, then flipping the rod over in

the tweezers and repeating. This electropolishing process produces a surface which is not as susceptible to oxidation as a surface freshly exposed due to mechanical means; when left exposed to atmosphere for hours at a time there was no noticeable deterioration of the bright, electropolished surface. To minimize oxidation the electropolished rod was left in ethanol until placed in the crucible for melting--except for a short time when a final weight determination was made. The copper⁴² was supplied in 7 mm diameter rod form at 99.999% purity. A weak nitric acid-water etch was used to remove surface oxidation shortly before melting. After etching, the copper pieces were washed in water and then acetone was used to remove any traces of water. The copper rod was cut in two lengths, shorter than the crucible and of proper size to be approximately the weight required by stoichiometry. After the final praseodymium weight had been determined, the copper weight was trimmed up with small pieces.

The cylindrical tantalum crucibles⁴³ used for melting were two inches long by 5/8 inch i.d. with a 0.015 inch wall. These crucibles underwent a nitric acid-water etch and a rinse in acetone to remove traces of any residue that might be present.

The praseodymium and copper rods were placed side

by side in the crucible and quickly placed in a graphite susceptor on a graphite pedestal which held the crucible in the center of the coil of a 5 kW, 450 kHz Westinghouse industrial radio frequency generator. This generator is part of a vacuum melting system which uses a two inch oil diffusion pump with thermoelectrically cooled baffle to pump on a bell jar and flange enclosure. The graphite susceptor was prebaked with the rf generator in vacuum to eliminate any absorbed gases; after cooling, the bell jar was backfilled with pure argon gas. The bell jar could be quickly removed, the crucible placed in the rf coil and the bell jar replaced immediately. Within 45 minutes a vacuum near 1×10^{-5} Torr was obtained. The rf generator was energized at this point and slowly the power level was increased to maintain the vacuum at this level until a visual determination was made that the constituents had melted. On melting the pressure rose slightly. It was possible to nicely melt the materials in the bottom of the crucible because most of the susceptor's mass was near the bottom, causing this region to be hotter than the top; the rods just slowly sunk into the already molten metal. The rf power level was increased slightly after melting and maintained for about fifteen minutes during which mixing should have been promoted by rf stirring due to the asymmetrical susceptor employed. The sus-

ceptor was a cylindrical graphite crucible which was concentric with the tantalum melting crucible; a wedge cut out on the axis and a cut diagonally from the top almost to the base made it asymmetrical. Vapor deposition of copper during the highest power levels used was easily visible on the inside of the bell jar. Experience dictated the addition of about 0.3% excess copper to compensate for this evaporation and still leave about half of the excess to insure that the composition of the whole metallic system remained on the copper rich side of the desired alloy. Staying on the copper rich side of PrCu_6 was deemed desirable because there is apparently no other stable phase on this side as opposed to the praseodymium rich side where other phases exist which probably order magnetically.

The last two in a long line of ingots produced the lowest temperatures upon demagnetization and were similar in all characteristics. Sample I was melted with the rf coil centered on the bottom of the crucible and the rf power level was decreased from its peak value to zero over an interval of half an hour. This produced a melt with a hole down the center of the crucible that could be due partially to the rf stirring currents and/or material being drawn away from the center as it solidified from the outside. Sample II was prepared on the following day with the rf coil

centered somewhat above the crucible's center. This time an hour was used to reduce the rf power to zero and the resulting ingot was solid for the most part. Both pieces suffered from a dull gray film on the surface inside the crucible.

Both samples were vacuum annealed at 910 °C for two days inside an alumina tube inserted in a resistance furnace. Vacuum was maintained at around 2×10^{-4} Torr with a one inch air cooled oil diffusion pump. The ingots were still inside their crucibles in a vertical position with titanium foil baffles on either side. Coils of copper foil were placed on either side of the titanium and finally stainless steel baffles were located just inside both ends of the alumina tube. The exposed surfaces of the samples in their crucibles came out darker gray than before annealing.

The crucibles were etched away using a hydrofluoric acid-nitric acid solution until only a thin sheet of tantalum remained which was easily peeled off with a pliers. The resulting ingots were lightly etched in a nitric acid solution. Both samples looked very similar with many fine fissures running along the surfaces of the samples. The nitric acid etch served to reveal information on the homogeneity achieved. Earlier attempts had some blackened areas and some copper colored areas in a blotchy pattern; some cases

of very poor mixing were revealed by the etchant when the top half came out black with the bottom copper colored and a crack separating the halves.

The top surface of the samples was ground off with #60 grit sandpaper so that any possible slag or oxidation was clearly removed and a flat surface was prepared for mounting. Both ends of the cylindrical ingots were polished down with #4/0 grit paper and etched in nitric acid and water; this procedure gave uniformly dark surfaces on both ends of both samples. The samples were electropolished in the same manner that the praseodymium was initially except that current levels were around 500 ma/in.². Sample I solidified with a hole down the middle and consequently this surface had to be electropolished with a stainless steel wire inserted down the center. Finally the polished surfaces were coated with GE 7031 varnish to prevent any deterioration. Later the varnish was removed from the ends and a 0.0001 inch coating of gold was electroplated for ease of soldering into the nuclear stage. OFHC copper sheet of 0.010 inch thickness was cut and shaped to allow indium soldering to the entire area of the ends of the samples with a tab projecting 1/4 inch from the center of both ends to which the silver strips in the nuclear stage were also indium soldered. Salmat noncorrosive flux was used for all indium and CdBi

soldering in the cryostat.

Nuclear Orientation Thermometers

Two types of nuclear orientation thermometer were used extensively in these experiments-- Co^{60} in Ni and Mn^{54} in Fe. Their preparation was essentially identical. The nickel⁴⁴ was cut into 0.010 inch discs from a 3/16 inch diameter rod of 99.999% purity. Discs of 0.010 inch thickness were cut from a 1/4 inch diameter, 99.999% iron rod.⁴² The nickel discs underwent the further step of being rolled to a 0.005 inch thickness between stainless steel sheets in a rolling mill. Five to ten minutes of etching was the next step: nitric acid-water solution for the nickel and hydrochloric acid-water for the iron. The radioactivity was purchased⁴⁵ dissolved in a weak hydrochloric acid solution and so could be evaporated a drop at a time on the surface of the foil being prepared. When proper activity levels were deposited, as determined with a geiger counter, the foil was placed in an alumina boat and centered in a quartz tube which held the foil centered inside a resistive box furnace. To impede evaporation of the Mn^{54} activity, due to its high vapor pressure at relatively low temperature, an iron foil was slightly bent and placed over the disc with activity evaporated on it. Glass wool was stuffed in the ends to eliminate radiative heating of the rubber stoppers inserted at

each end of the quartz tube. A glass tube in each stoppered end provided a gas flow path for a 10% hydrogen-90% pure argon atmosphere to bathe the foil during heating. The furnace was heated to 1200 °C and held there for about 24 hours whereupon the foils were allowed to cool slowly inside the furnace with the power off. The nickel foil came out with shiny surfaces and was etched for ten minutes as opposed to the iron foil which came out with dark blueish surfaces and was subsequently etched from 0.0095 inch to 0.0085 inch thickness. This etching of the iron left a shiny surface but microscopic examination revealed small pits in the surface upon which the activity had been evaporated. Absolute activity levels, as compared with the geiger counter to calibrated sources, were 2-3 μCi for the Co^{60} and 6-7 μCi for the Mn^{54} .

Cryostat Operation

After indium soldering the PrCu_6 ingot with its copper mounting clips to the silver strips of the nuclear stage, a turn of NbTi wire of sufficient length to reach the top of the vacuum can was varnished to the sample. After mounting the slab resistor and heater, the bottom half of the mixing chamber heat shield was brought up over the nuclear stage and fastened to the upper half with three brass screws. The copper strips running down the outside of the shield were CdBi sol-

dered together at this joint between halves. Indium soldering of the nuclear orientation thermometers and mounting of the slab resistor and glass-ceramic capacitor at the thermometry end of the nuclear stage were the next steps. The mixing chamber shield with nuclear stage inside was next screwed into the center of the mixing chamber and firmly tightened with a rod inserted through a hole in the threaded copper piece at the top of the shield. Leads to the nuclear stage were then connected to their extensions at the mixing chamber and the twisted NbTi pair for the magnetometer was strung up the dilution refrigerator and alongside the He^4 pot where the pair was plasma spot welded to the leads from the coupling coil and heater inside the vacuum can. The copper wire from the first sintered copper heat exchanger was CdBi soldered to the spacer between the mixing chamber shield and the still shield. After aligning the orientation thermometry foils in the vertical plane, to coincide with the axis of the superconducting solenoids, and drawing up the still shield, a 1/32 inch diameter indium wire O-ring was placed on the vacuum can flange and the can was drawn up tightly to its mating flange surface above the He^4 pot. The can was evacuated and approximately one Torr of hydrogen gas was allowed in to serve as the exchange gas during the initial liquid helium transfer. Next the super-

conducting solenoids were bolted to their support rods around the vacuum can. For purposes of detector alignment a plumb bob was used to put a mark on the floor coinciding with the center of the vacuum can and hence the nuclear orientation foils. The dewar set was raised making sure to insert a liquid nitrogen level sensor into the styrofoam spacer between the top of the two dewars; this sensor controlled a solenoid valve and maintained liquid level automatically. After ensuring that the dilution refrigerator and He^4 pot remained under adequate vacuum, the liquid helium dewar was evacuated and backfilled with nitrogen from a tube immersed in liquid nitrogen. Finally the plumb bob was used once again to mark on the bottom of the liquid nitrogen dewar the correct position for the center of the gamma ray detector as recorded earlier. The detector was positioned properly just below the liquid nitrogen dewar and connected to the associated electronics which were turned on to ensure temperature stabilization in the air conditioned cryostat room by the time data collection began.

After waiting at least six hours the initial liquid helium transfer was made by first adding sufficient hydrogen gas to the exchange gas can to produce a one Torr pressure and flushing the helium dewar with helium gas. The transfer tube from the liquid

helium storage dewar was inserted through a quick connect in the top of the cryostat from an access door in the building hallway which was half a floor up from the cryostat room floor. Connection was made to the building helium recovery system and transfer began using a pressure of about twelve inches water which was maintained until the vacuum can pressure was observed to fall into the 100 micron range. Switching to a transfer pressure of four inches water slowly froze out the hydrogen exchange gas with maximum cooling of the interior cryostat parts. In addition to slowly decreasing the vacuum can pressure to zero, the CLTS resistor on the still was monitored to ensure that maximum cooling was being obtained; transfer pressure was held in the range of four inches water to meet these objectives. After liquid helium had submerged the lead sheet shield around the top of the vacuum can the magnets were run up to the desired levels and put into the persistent mode. "Warm" counts for the nuclear orientation thermometry were started at this point. The He^4 pot was filled from the main bath while maintaining its temperature below the lambda point; the valve from the main bath was adjusted to give a constant temperature filling rate which changed to a rising temperature mode when the level rose into the pumping tube.

The dilution refrigerator could now be put into operation. The He^3 - He^4 gas mixture was condensed down the pumping tube into the still after having been cleaned up through a liquid nitrogen cold trap at the gas handling board. The gas storage tank was completely evacuated using a crossover to the mechanical pump in the refrigerator system and the relief valve to the storage tank was opened to the system as the bypass valve around the storage tank was also opened. Now the gas mixture was circulated around by pumping on the still and condensing the returning gas at the He^4 pot until the flowmeter in the return line indicated little further cooling was occurring as confirmed by monitoring slab resistors throughout the refrigerator. The still heater was turned on with an initial power level that was very high to ensure that any filmflow up the pumping tube was stopped. Then a steady state power level of 1.2 mW was maintained. Knowing the relative volumes of the various parts of the refrigerator system, He^3 was allowed to bleed off into the storage tank to compensate for return line pressure fluctuations until it was determined that the liquid phase boundary was in the mixing chamber. The return line pressure and flow rate seemed to show a variation in the primary impedance by a factor of two over the first couple of days; the reason has not been ascertained. Warm

counts were not collected once the nuclear stage temperature dropped below about 0.2 K.

Eight to ten hours after turning on the still heater the nuclear stage had reached the low twenty millidegree region and a demagnetization was performed. The twenty kilogauss magnet was put into the regulated mode and the magnet controller smoothly ran the field down at $1\frac{1}{4}$ kG/min until the lead heat switch went superconducting in the fringing field at 16. kG central field. The remaining demagnetization was at $5/8$ kG/min to the final field value. During this time the heater on the internal magnetometer flux transformer loop was energized to quench any superconducting current which could lead to flux jumping and consequent excessive irreversible heating in the nuclear stage. After putting the demagnetizing magnet in the persistent mode the external magnetometer loop heater was energized to zero the magnetometer meter reading; a strip chart recorder was used to obtain a continuous record of PrCu_6 magnetization from the electronics package output signal. Heat capacity, magnetization, irreversible heating, and other measurements now could be performed.

The He^4 pot had a holding time of about sixteen hours which was the main limitation on measurement time as it could not be completely refilled without irrecoverably upsetting the dilution refrigerator due to lack

of recondensing He^3 . However it was possible to partially refill the pot until the phase boundary was about to leave the mixing chamber. This technique afforded an additional four hours operating time and could be repeated indefinitely as the refrigerator returned to its steady state configuration within an hour. The only other constraint on experimental time was the required refilling of the main helium bath about every ten hours if the level was not to fall below the magnetometer on top of the vacuum can. Liquid nitrogen should be added to the outer dewar before a helium transfer since the automatic fill was turned off before demagnetization to eliminate vibration. All these refilling operations introduce eddy current heating to the nuclear stage because of vibration in a magnetic field and inability to account for this heating in heat capacity measurements made the operations undesirable.

After completion of measurements the 20 kG magnet was run up again and refilling operations were undertaken. A complete He^4 pot refill required restarting the dilution refrigerator from a recirculating gas with no still power condition.

V. RESULTS

High Temperature Susceptibility

In addition to metallographic examination and powder x-ray diffraction studies, the susceptibility of PrCu_6 samples was measured in the range 2 to 300 K using an applied magnetic field in the neighborhood of 500 gauss. These measurements were performed in a separate cryostat designed for such work although the same sort of superconducting flux transformer and Hewlett-Packard flux gate magnetometer probe inside a lead shield was used as was described earlier in the Apparatus chapter.

Both samples of PrCu_6 showed identical behavior. Their inverse susceptibilities were linear with respect to temperature from room temperature down to about 8 K where the slope tapered off to essentially a constant value to the lowest measured point at 2 K. Such behavior contrasts with that of pure Pr and PrO_2 which were both checked over the same temperature range. The pure praseodymium inverse susceptibility showed a break from Curie's law already at 70 K and continued to about 10 K in a linear fashion as if determined by an altered Curie constant. Below 10 K the susceptibility of the pure Pr looked essentially constant. Curie law behavior was seen in the praseodymium oxide data down to about 70 K where the inverse suscepti-

bility versus temperature curve showed a continuously increasing slope at lower temperatures until the curve appeared to be asymptotically approaching the vertical axis at 2 K. The PrCu_6 data shows the desired characteristics for hyperfine enhanced nuclear cooling. It shows no sign of possessing significant amounts of oxide or praseodymium rich aggregations, both of which might cause irreversible heating on demagnetization as well as lost cooling power, and the onset of Van Vleck paramagnetism at lower temperatures was clearly seen.

Low Temperature Susceptibility

After demagnetization to a final applied magnetic field level the strip chart recorder output of nuclear stage magnetization as a function of time allowed much data to be obtained. Figure 10a shows plots of susceptibility versus inverse temperature as calculated from the strip chart recordings and calibration sweeps of the applied field at about 0.8 K where the nuclear contribution should be insignificant. Hence, assuming χ goes through the origin, the plot is made using

$$\Delta\chi = \frac{SV_m}{4\pi H_{app}} \cdot \Delta\theta \quad (52)$$

where $\Delta\theta$ is the observed magnetometer output change, S is the experimentally determined sensitivity from the calibrated field sweeps to give the true field change at the sample, H_{app} is the externally applied

Figure 10a. X_{nuc} vs $1/T$ for PrCu_6 Sample I.

Figure 10b. X_{nuc} vs $1/T$ for PrCu_6 Sample II.

magnetic field, and V_m is the molar volume of PrCu_6 .

For an applied field of 0.55 kG the plot reveals ideal paramagnetic behavior above 0.010 K with significant deviations below this temperature. Using Eq. (14) for the high temperature susceptibility approximation, as shown by the line drawn through the higher temperature points, an experimentally determined value of 15.0 ± 1.0 can be found for the enhancement factor $(1+K)$ using the slope of the line. For $1/T$ greater than 100 the deviation from an ideal paramagnet becomes clear; in the $1/T$ range 160 to 240 it appears that a consistent value is hard to obtain. Above $1/T$ equal to 240 a well defined value for the nuclear susceptibility again becomes clear and gives the suggestion (dotted line) of following the original slope of the lowest $1/T$ points. Plotting $1/\chi$ versus temperature for 0.55 kG data allows a determination of the molecular field critical temperature T_c as defined in Eq. (36). Extrapolation of the linear higher temperature points yields a critical temperature of $+1.15$ mK.

A straight line has been drawn through points below $1/T$ equal to 100 for the data taken in an applied field of 1.17 kG and deviations are apparent again at lower temperatures. Here the curve appears to dip slightly before finally following the behavior of the lower field data but with a reduced magnitude of shift.

An enhancement factor of 13.6 ± 1.0 can be calculated from the high temperature points. In seeming contradiction, some data taken at a later date with a piece of the PrCu_6 sample II yielded the plot shown in Fig. 10b where a straight line can be easily drawn through all the points taken in a 0.55 kG field. An enhancement factor of 13.5 ± 1.0 results from the slope shown. A similar calculation by Andres and Bucher¹⁸ yields an enhancement factor of 16.7 for two and three kilogauss fields. Their susceptibility data for a 0.55 kG field shows only a gradual decrease from ideal paramagnetic behavior for decreasing temperature.

After each demagnetization the magnetometer revealed a continuing increase in magnetization for periods up to fifty minutes after reaching final applied field. This same effect could be seen with the nuclear stage at high temperatures and so the change probably is magnet drift of maximum magnitude one gauss. Measurements were not begun after demagnetization until this drift had leveled out.

Sample Relaxation Time and Thermal Equilibrium

Several measures of the bulk sample relaxation time were made after the application of a heat pulse to one end of the sample or the other. There appears to be some correlation between them but the roughness of the measurement is apparent. Least precise, although

still significant, was the observation of temperature change with a carbon resistor slab thermometer at one end of the sample after application of a heat pulse at the other end. Because the resistance thermometer loses thermal contact to the sample somewhere below 10 mK and relaxation times are very fast already at 10 mK, there is a very limited region over which the relaxation effect can be seen in this way. Times of about two minutes have been observed between heat pulse and the first thermometer response on the other side at 5.3 mK.

Without question, the most precise relaxation time measurement came from observation of the nuclear stage magnetization on the strip chart recorder. At the lowest and also at the higher temperatures a heat pulse caused a sharp decrease in magnetization for the duration of the pulse and then a relaxation to some still lower value which stayed essentially constant. If the magnetometer was set to highest sensitivity and/or the sample had a sufficiently low heat capacity, the residual heat leak and orientation thermometer radioactive heating were enough to show up as a linear decrease in magnetization as the sample continued to warm up after a heat pulse. For intermediate temperatures, say 3.5 to less than 10 mK, another feature appeared for heat pulses with sufficient intensity--

more than 600 to 700 ergs per minute for the approximately 0.05 mole samples. Several minutes after completion of the heat pulse, under the above conditions, the magnetization reached a minimum and proceeded to increase again, gradually reaching a constant value or being replaced with the gradual warming trend as described above. Magnetization relaxation times were measured from the end of a heat pulse to that point at which the constant or gradual warming behavior became dominant. These measurements revealed a very rapidly increasing relaxation time as a function of decreasing temperature in the range of eight to three millikelvin. Above 8 mK the relaxation time was too small to measure. Well measured times ranged from one minute at 6 mK to about forty minutes at 3.5 mK. Special features were seen at 4.5 mK where anomalously long times were measured for the demagnetization where the largest specific heat "spike" appeared and at lowest temperatures where relaxation times seemed to be decreasing from a maximum around 3.5 mK.

The final measure of bulk relaxation time was made by watching consecutive ten minute counts with the nuclear orientation thermometers until a constant temperature or, in the case of relatively low heat capacities, gradual warming trend set in after application of a heat pulse. Obviously, because of the times

involved to obtain a nuclear orientation temperature, only a long lived effect could be seen this way. Measurements which seemed conclusive were few; 37 min at 3.25 mK; 27 min at 3.33 mK; 40 min at 3.67 mK; 40 min at 4.00 mK; and 20 min at 4.60 mK. These times show some agreement to those obtained by magnetization measurements but could not be considered confirming data. The times above were measured using data obtained while heating the sample from the same side as the orientation thermometers. The long relaxation times were also noticeable when heating the sample from the side opposite the orientation thermometers. In this case there would not be an overshoot and return to equilibrium after applying a heat pulse but a lack of orientation thermometer response at first and then a gradual temperature increase. Such was the case but the equilibrium point was not easily determined for these measurements. Surprisingly, magnetization relaxation never showed any overshoot when heating occurred from the side of the sample opposite the orientation thermometers. Compared to the trend of magnetization relaxation times the direct observation of about two minutes at 5.3 mK fits in well. A measurement by Andres and Bucher¹⁰ of five minutes at 4.0 mK is also consistent with this data.

Associated with the long observed relaxation times

is the question of thermal equilibrium between the PrCu_5 sample and the nuclear orientation thermometers which are separated by a length of silver strip. One of the orientation thermometers is Co^{60} in Ni with an activity level of about three microcuries; the heating due to beta particles from the Co^{60} decay should be about $1\frac{1}{2}$ erg/min while perhaps another $\frac{1}{2}$ erg/min comes from a six microcurie Mn^{54} in Fe thermometer.⁴⁶ As a test of the effect that a constant heat input from the orientation thermometers might have on thermal equilibrium, counting periods were initiated while continuously applying 3 erg/min and also 10 erg/min with a heater located on the orientation thermometer end of the sample. At 3 erg/min there was no apparent increase in orientation thermometer temperature as compared to the no external heating case. Ten ergs per minute increased the measured temperature by about 0.1 mK at 3.5 mK and by 0.25 mK at 4.5 mK.

Temperature and susceptibility measurements were also performed while continuously heating the nuclear stage at a rate of 8 erg/min in addition to the residual heating of 6 erg/min due to heat leak and radioactive heating from the nuclear orientation thermometers. For a heat capacity dependant on $1/T^3$, constant heating should mean $1/T$ will be proportional to time. Consequently the susceptibility becomes proportional to

time for these measurements. Any deviation from the above ideal behavior should be easily observed. Data was collected in a field of 0.55 kG over a period of about eight hours during which time the temperature rose from 3.0 mK to 6.0 mK. On two consecutive demagnetizations, to exactly the same end temperature, the external heating was applied first through a heater on the orientation thermometer side of the nuclear sample and then on the other side during the second trial. For the first case the temperature rose rapidly during the first counting period after heating started; the rise was much too great for the amount of heat added and the known heat capacity at this temperature so the lack of equilibrium within the PrCu_6 was quite clear. As shown in Fig. 11, subsequent counting periods revealed a monotonically decreasing $1/T$ to about 5.3 mK where it joined the linear portion of the second demagnetization's curve. Heating from the opposite side to the orientation thermometers produced a monotonically decreasing $1/T$ from the demagnetization end temperature with no discontinuity at the first count. For the 4 to 6 mK range the $1/T$ curve became linear with time. The data would seem to clearly show the effects of long relaxation time on the bulk sample assuming the heat capacity follows a $1/T^2$ law to lowest temperatures. At lowest temperatures where relaxation

Figure 11. $1/T$ vs time for constant external heating of PrCu_6 at low temperature.

time is longest, the temperature differential across the sample is significant and decreases until by 5.3 mK no difference is seen, using ten minute counting periods, for heating on one side or the other. Extrapolation of the linear portion of the overlapping curves back to time zero reveals an estimate of actual nuclear stage end temperature after demagnetization: 2.4 mK. The susceptibility during these constant heating trials was a linear function of time.

From the knowledge of temperature on one end and heating rates applied on both ends of the nuclear stage it is possible to calculate a thermal conductivity when data is available under two sets of conditions so that simultaneous equations can be solved. A minimum value of 2.8×10^{-2} mW/cm-K at 3.4 mK is obtained and the thermal conductivity seems to increase on either side of this temperature. If a $1/T^2$ heat capacity is assumed for the entire range of temperature, Eq. (44) then yields relaxation times around 3 mK which are about a factor of three higher than the times determined from magnetization data. By 4 mK the times appear an order of magnitude larger than magnetization data values, but there is a peak in this calculated relaxation time around 3.3 mK and a tapering off at higher and lower temperatures. The peak relaxation time is calculated to be about three hours.

Nuclear Specific Heat

Specific heat measurements in the range from 75 to 3 mK show a $1/T^2$ dependence with deviations appearing at the high and low temperature ends. Figures 12 and 13 show all data obtained on the two samples at an applied magnetic field of 0.55 kG. A $1/T^2$ line has been drawn through the midrange points which allows the deviations from ideal paramagnetic behavior to be seen. At higher temperatures there is a gradual excess specific heat buildup which could possibly be an electronic contribution. At very low temperatures--below 5 mK--the average measured value again shows an excess specific heat and a number of points with rather sharp and large differences from $1/T^2$ behavior. Using Eq. (15) for the ideal paramagnet heat capacity and assuming the previously determined enhancement factor $(1+K)$ of 15.0, the applied magnetic field calculates to be 1.33 kG to within ten percent for the line drawn. Measurements by Andrs and Bucher¹⁸ confirm the magnitude and $1/T^2$ dependence of the specific heat but show this behavior continuing to 2.7 mK with no deviations except for what might be interpreted as a small bump above the $1/T^2$ background at about 4.5 mK.

Making specific heat measurements with nuclear orientation thermometry as the only temperature sensor

Figure 12. C vs T. PrCu₆ Sample I in a 0.55 kG applied field.

Figure 13. C vs T. PrCu₆ Sample II in a 0.55 kG applied field.

is not an especially accurate method. The ten minute counting periods used were sufficient to obtain a two percent determination of temperature but this means only a ten percent specific heat measurement when dealing with 0.5 mK or less temperature differentials associated with a heat pulse. After applying a heat pulse, ten minute counts were taken until consecutive temperature determinations revealed no temperature change or at least no greater increase than could be accounted for by residual heating. Sometimes, because of the long relaxation times, this procedure meant obtaining only one point per hour. Radioactive heating and heat leak from higher temperature parts of the cryostat were determined to total six ergs per minute by watching the temperature drift up with time in the known $1/T^2$ specific heat range; this means that over an hour the residual heating is about equal to the heat pulse put in initially. Above 12 mK a carbon resistor slab calibrated against the orientation thermometers could be used for quick determinations of temperature.

The points shown on the specific heat curves of Figs. 12 and 13 which do not come close to the $1/T^2$ behavior are an elusive, yet consistent, part of almost all specific heat measurements made on both PrCu_6 samples. As the representative error bars show, this

phenomena of a specific heat "spike" is well outside the bounds of statistical variation (the temperature is very well determined and no error bars are needed). What is not well understood is the appearance of this spike at various temperatures on different demagnetizations. The large variation in magnitude of the effect can be explained by averaging of this sharp anomaly over two consecutive specific heat determinations. Only when starting from just below the anomaly, and adding the appropriate heat pulse which will prevent further warming on the high temperature side, can the full effect be seen. Failure to allow enough time for relaxation within the bulk sample after adding a heat pulse will also cause a smoothing of specific heat. A typical series of specific heat measurements obtained from a demagnetization will show several points at lower temperatures than the spike which could fit a continuation of the $1/T^2$ behavior seen at temperatures above the anomaly. Figure 14 shows data obtained on three separate runs which points out the degree to which it may be possible to smooth out the "spike" in the specific heat.

Demagnetization Thermodynamics

A typical demagnetization in these experiments began at about 24 mK in a 20 kG field and ended with a 0.55 kG field and final temperatures from 3.0 to 3.5

Figure 14. Possible specific heat anomaly in PrCu_6 at low temperature. Three specific heat vs temperature curves for PrCu_6 show the smoothing of the possible specific heat anomaly. The anomaly is seen clearly on the top curve, less so on the middle, and is almost indistinguishable on the bottom curve.

mK. Figure 15 shows the progress of the demagnetization for successive halving of the magnetic field and compares the PrCu_5 behavior to that of an ideal paramagnet starting from the same initial conditions. The deviation from ideal behavior appears gradual and continuous. The deviation can be accounted for by using an effective magnetic field h as in Eq. (12) to represent the interaction strengths present. An interaction field of 3.5 kG will do a reasonable job of bringing the plotted points back onto the ideal paramagnet line. Figure 16 sheds further light on calculating a possible interaction field strength by plotting CT^2 versus H^2 in the region where specific heat is proportional to $1/T^2$. The straight line obtained allows the solution of

$$C = k(H^2 + h^2)/T^2 \quad (53)$$

with h determined to be 1.32 kG. These field values compare with Andres and Bucher's work¹⁸ where 1.36 and 1.64 kG respectively were found for the two calculations discussed above.

Measurements designed to give an estimate of irreversibilities in the adiabatic demagnetizations were performed and showed this problem to be minimal. By running the applied magnetic field around a loop--from a low value to high and back again--and keeping track of temperatures at the extremes, it was deter-

Figure 15. Results of PrCu_6 demagnetizations as compared to an ideal paramagnet. The numbered curve shows the successive steps in an irreversible heating test.

$$\text{PrCu}_6 : C = K \frac{H^2 + h^2}{T^2}$$

Figure 16. CT^2 vs H^2 . An estimation of the characteristic nuclear interaction field strength can be made from the intercept with the H^2 axis.

mined that heating of the nuclear sample due to possible interactions among the praseodymium nuclear spins, oxides of praseodymium, and impurities, along with eddy current heating, amounted to approximately 1 erg/sec when changing the field at the rate of 1.25 kG/min. This determination was made from the loop shown in Fig. 15 which goes from point 2 to point 4. The same test made on a 0.55 kG to 2.3 kG loop both at the same rate and at half the magnetic field rate of change revealed no temperature increase and consequently the irreversible heating was less than 0.1 erg/sec at most. Eddy current heating is merely the Joule heating I^2R of the metallic nuclear sample of characteristic resistance R by electrical currents I generated as the magnetic field changes; since the current is proportional to the time rate of change in magnetic field, a halving of rate should produce a fourfold heating rate decrease. Total eddy current heat input during a demagnetization is cut in half by halving the rate of demagnetization because the time to demagnetize is doubled while the rate of heating is cut fourfold. Using the 1 erg/sec rate at 1.25 kG/min field rate of change, the average demagnetization produced approximately 0.04 J/mole-deg entropy increase as calculated by

$$\Delta S_{\text{irrev}} = \frac{\dot{Q}}{\Delta T} \log\left(\frac{T_{\text{init}}}{T_{\text{final}}}\right) \quad (54)$$

where $\dot{Q}$ is the heating rate, t is the time for demagnetization, and ΔT is the difference between the initial temperature T_{init} and final temperature T_{final} .

Comparision of actual nuclear entropy reduction for the initial temperature and magnetic field, minus the final field-initial temperature entropy reduction, with known entropy additions provides a measure of the thermodynamic consistency. The actual nuclear entropy reduction was calculated using Eqs. (8) and (9) with an enhancement factor $(1+K)$ of 15.0; for initial conditions of 20 kG and 24 mK and a final field of 0.55 kG, the entropy reduction is 5.27 J/mole-deg or 35.4% of $R \ln(2I+1)$. Known entropy additions included heat pulses added at lowest temperatures divided by the temperature plus the integral of specific heat divided by temperature over the well determined $1/T^2$ region back to the initial demagnetization temperature and the irreversible entropy contribution on demagnetization as specified by Eq. (54). The 6 erg/min residual heating due to orientation thermometry and higher temperature stage leaks was included over the whole cycle. A typical comparision showed known entropy additions of 3.93 J/mole-deg for a calculated actual entropy reduction of 4.68 J/mole-deg. Using an enhancement factor of 16.7, Andres and Bucher¹⁸ find that entropy additions without considering irreversibilities are

slightly in excess of their calculated entropy reductions at starting conditions of 40 mK and 20 kG. The known entropy additions may be low due to the inflated nonequilibrium temperatures recorded below about 5.5 mK as discussed under thermal equilibrium.

If a temperature differential really exists between the nuclear orientation thermometers and the nuclear stage such that the actual demagnetization end temperature for the constant heating runs should be lower, then better thermodynamic agreement can be obtained. For an initial temperature of 22.2 mK and field of 20 kG the measured final temperature after demagnetization to 0.55 kG was 3.05 mK. The entropy difference at 22.2 mK for the two fields is 5.77 J/mole-deg and demagnetization irreversibilities decrease the available cooling entropy by 0.08 J/mole-deg. Assuming that the specific heat behaves like a/T^2 with $a=4.12 \times 10^{-5}$ J-deg/mole, the net entropy reduction of 5.69 J/mole-deg yields a calculated final demagnetization temperature of 1.90 mK. There was an actual addition of 6300 ergs to the 0.047 mole sample to warm from the final demagnetization temperature to 5.84 mK. Calculation with the experimentally determined a/T^2 specific heat reveals that the final demagnetization temperature would have had to be 2.12 mK to account for the known heat input over this temper-

ature interval. The 2.4 mK demagnetization end temperature determined from the Fig. 11 extrapolation would seem to indicate a temperature differential between thermometers and sample; the 2.12 and 1.90 mK temperatures calculated on the basis of a $1/T^2$ specific heat support this conclusion as well as question the accuracy of the thermometers. Of course, the specific heat would be expected to increase substantially above the calculated a/T^2 value at some point if there is magnetic ordering occurring in the nuclear spin system. In this case the end temperatures discussed above would be too low and the actual temperature would lie between these and the measured orientation thermometer value of 3.05 mK.

Orientation Thermometer Comparison

Basically, two nuclear orientation thermometers were employed on the nuclear stage for absolute temperature determination in the millikelvin region. Co^{60} in Ni and Mn^{54} in Fe foils were located in a 4 kG polarizing field and remained temperature sensitive to lowest temperatures. However, all temperatures quoted and used in calculations are Co^{60} in Ni because this combination gave temperatures 0.6 mK lower than the Mn^{54} in Fe around 3.0 mK; this effect faded out so that around 25 mK both thermometers agreed. Use of the Co^{60} in Ni in this case is justified because

errors in thermometer preparation, detector alignment or other problems result in decreased anisotropy of gamma ray distributions and hence lead to higher than actual temperatures. This lack of agreement between the thermometers used is perhaps a result of "cone angle" effects.⁴⁷ An impurity nucleus dissolved in a ferromagnetic host will not necessarily see a hyperfine field in the same direction as an external applied field which saturates the host; the impurity nuclear moments will tend to align with certain crystalline directions due to magnetically induced crystal forces. The angle between the direction of externally applied field and the direction of the hyperfine field seen by the impurity nucleus defines a hyperfine field vector cone--hence the term "cone angle".⁴⁸

Evidence for Ordering

Taken as a whole, the nuclear susceptibility, specific heat, and relaxation time data seem to indicate the presence of some kind of nuclear ordering phenomenon in PrCu₂ around 4.5 mK. The picture is far from clear though. The long bulk sample relaxation time, the possible lack of thermal equilibrium between sample and orientation thermometry at lowest temperatures, the lack of precision in determining temperature differences for specific heat calculations, and to some extent the ability to get only

averaged temperatures instead of instantaneous values are all responsible for the inability to definitely resolve the question. Still, the nuclear susceptibility takes a significant jog within the same temperature range that the specific heat "spike" appears and relaxation times are extremely long. The entropy associated with the specific heat anomaly represents approximately 15% of the calculated entropy reduction while the x-ray diffraction studies show no sign to within 10% of phases other than PrCu_5 in the nuclear stage samples. The relaxation times appear to pass through a maximum and are decreasing again at lowest temperatures as calculated from thermal conductivity and specific heat information.

Susceptibility measurements provide the only data which seems inconsistent with any ordering. As Fig. 10b shows there is a set of warming measurements which do not reveal any variation from Curie law behavior. Likewise the constant external heating data displayed a linear dependence of magnetization on time which means Curie law behavior; no deviations were seen.

VI. CONCLUSION

As a means for obtaining and maintaining temperatures down to at least 3 mK the rare earth inter-metallic compound PrCu_6 can be quite useful. Moderate initial conditions for adiabatic demagnetization produce significant entropy reductions in the PrCu_6 nuclear spin system because of the hyperfine interaction's enhancement of the externally applied magnetic field. (Approximately one-third of the spin entropy is calculated to be removed by the application of 20 kG at 22 mK.) Irreversibilities appear to be small so that little cooling power is lost during demagnetization. Thermal contact can be obtained via conduction electrons in this metallic system as it is possible to solder to PrCu_6 , but the electronic thermal conductivity is fairly low so that heat loads greater than several ergs per minute could be expected to produce a temperature differential between the system under study and the nuclear coolant unless thermal contact area is unusually high. The specific heat of PrCu_6 is large in the 3 mK region for a 0.55 kG applied field; on a volume basis PrCu_6 has at least a two orders of magnitude greater heat capacity than copper alone under the same conditions. For the cryostat described earlier, the warmup rate would be approxi-

mately 4-1/2 hours from 3 to 4 mK for the total heat loading of 6 erg/min.

Ideal paramagnetic behavior was observed in PrCu_6 down to somewhat below 10 mK where the magnetic susceptibility began increasing more rapidly than Curie law behavior. In the 4 to 5 mK region, where the susceptibility is undergoing its largest deviation, a very sharp "spike" seems to be present in the specific heat curve. Thermal relaxation times become very long in this region--values of at least 40 minutes were measured. These measurements taken together seem to point to a nuclear ordering in the praseodymium nuclear spin system. Molecular field theory predicts a critical temperature of ± 1.15 mK using the experimental data. Andres and Bucher¹⁸ find no deviations from a $1/T^2$ specific heat down to 2.7 mK, but their measurements could well have been taken too rapidly for equilibrium values to be obtained. In this case they would see the "spike" averaged out over several points. Because the specific heat anomaly appeared erratically in terms of temperature and since one susceptibility measurement failed to reveal Curie law deviations the evidence for ordering is confused. The lack of precision associated with nuclear orientation thermometry specific heat determinations is the weakness of the study made so far. A magnetic sus-

ceptibility thermometer, utilizing a SQUID magnetometer and calibrated against a nuclear orientation thermometer for accuracy, would give more than enough precision to resolve the question of whether a specific heat anomaly--and therefore nuclear ordering--really exists in PrCu_6 around $4\text{-}1/2$ mK.

APPENDIX A

Capacitance Thermometer

The glass-ceramic capacitance thermometer referred to earlier has been reported¹⁻³ to have several features which make it appealing for use as a secondary thermometer. Perhaps its most interesting property is magnetic field insensitivity equivalent to less than a one millidegree change at 4.2 K for an applied field difference of eighty kilogauss. In addition it has a broad operating range which includes a linear dependence on temperature from 1.1 to 5.2 K. The capacitance thermometer has a fast response time and low self heating above 1 K.

In the course of investigation into hyperfine enhanced nuclear cooling on PrCu_6 several additional features of the capacitance thermometer were revealed. Figure 17 shows how the capacitance, referenced to the minimum at 0.060 K, depends linearly on temperature from 0.025 K down to at least 0.005 K with sensitivity dC/CdT of approximately $-10^{-4}/\text{mK}$.⁵¹ This dependence contrasts with the previously reported inverse temperature dependence in the 0.025 to 0.080 K region. There is apparently a shift from day to day in either the measuring electronics or the capacitance thermometer as the second and third days' data has been shifted on the vertical axis of the figure to give the

Figure 17. Incremental capacitance vs temperature for the capacitance thermometer. ($\Delta C = C(T) - C_{\min}$) The data shown has been plotted on a T scale with 2.8 pF added to the data points of the 2nd day and 1.4 pF to those of the 3rd day. The slope of the C - T data in the apparently linear region is $dC/dT \approx -1.5 \text{ pF/mK}$. $C_{\min} \approx 16,400 \text{ pF}$.

best overlap to the first day's data. No shift was seen in magnetic fields up to 4 kG at 0.007 K. These measurements were performed at 400 Hz and 5.3 mV_{rms}.

Measurements at 400 Hz and voltages of 2.2 and 5.6 mV_{rms} revealed a capacitance shift with varying applied voltage. Figure 18 shows how the minimum capacitance point shifts to lower temperatures and the capacitance value with respect to this minimum at any temperature drops with decreasing applied voltage. More recent measurements than those plotted in the figure confirm the applied voltage dependence shown as well as indicate a similar dependence on the frequency. However, the sensitivity of the capacitance thermometer in these measurements was decreased by a factor of four from that shown earlier with no apparent explanation; the frequency dependence is therefore not well confirmed. The voltage dependence can not be explained by self heating as the sign of the effect is wrong. A carefully regulated applied voltage is clearly needed to obtain accurate measurements with the capacitance thermometer.

The data in Figs. 17 and 18 were obtained with an Electro Scientific Industries model 707A bridge with a modified capacitance standard, a PAR model 112 pre-amplifier, and a PAR model 122 lock-in amplifier-oscillator. Later data was obtained with the substi-

Figure 18. Voltage and temperature dependence of the incremental capacitance. The minima are very broad and therefore not well defined, as shown by the two points for the 5 mV_{rms} curve.

tution of a PAR model 129 lock-in amplifier-oscillator for the model 122 with preamplifier.

APPENDIX 8

Resistance Thermometry

Measurements on the carbon resistance thermometers throughout the cryostat were taken with a 33 Hz resistance bridge described elsewhere³⁵ with the only modification being a conversion to three terminal measurement. The manganin leads which run from the room temperature connector-filter assembly to superconducting leads at the still inside the vacuum can were carefully balanced for all resistors monitored. Of course all lines were also rf filtered as mentioned in the Apparatus chapter. Power dissipation in the resistors was kept at the 10^{-14} watt level except for special operations taking place at relatively high temperatures.

Figure 19 shows the results of measurements on the specially prepared slabs of Speer resistor described in the Apparatus chapter. The graph extending to 4.2 K is based on measurements below 0.050 K against nuclear orientation thermometry and at the high temperature end against other calibrated carbon resistors while pumping on the helium dewar with helium gas in the vacuum can. Results for the slab resistor mounted with the nuclear orientation thermometers is shown in the low temperature detail graph; a pronounced shift occurs between the first day's demagnetization and

Figure 19. R vs T for specially prepared Speer resistors. The very low temperature detail reveals a shift to higher resistance for equivalent temperatures from the first to second and subsequent days of a run. The resistance saturation effect below 10 mK is clear.

subsequent days' data collections. This second day shift to higher resistance within a run is complemented by an observed shift to higher resistance for equivalent temperatures over the space of months in different runs. The long term shift could be a result of the thermal cycling upon soldering and unsoldering the resistor's leads when altering the nuclear stage. The other noticeable effect on the low temperature detail graph is the saturation of the slab's resistance below 0.010 K--presumably because of self heating since the break is rather sharp.

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