## MIXED-STATE SPECIFIC HEAT OF VANADIUM AT VERY LOW TEMPERATURES\*

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We have measured the specific heat of a pure sample of vanadium' (resistivity ratio 150) in the superconductive, normal, and mixed states. The specific heat in the mixed state at very low temperatures can be represented by a sum of two terms, one linear and one cubic in temperature. The results are in quantitative agreement with a proposal of Rosenblum and Cardona.<sup>2</sup> They proposed the existence of normal-like regions in the mixed state which occupy a fraction  $H/H_{c2}(T)$  of the material. This follows from calculations by Caroli, de Gennes, and Matricon,<sup>3</sup> who show that near an Abrikosov vortex line excitations have a very small energy gap. They conclude that each vortex line is equivalent to a normal region of radius  $\xi$ . The results for the three different states are plotted in Fig. 1. The data for normal and superconductive states can be represented by the following formulas:

$$
C_n = \gamma T + \alpha T^3
$$

(measured in a field of 14 kOe),

$$
C_{S} = a\gamma T_{C} \exp(-bT_{C}/T) + \alpha T^{3} \quad (H = 0 \text{ and } T < \frac{1}{2}T_{C}),
$$
  
with

with

 $\gamma = 9.92 \text{ mJ/mole deg}^2$ ,  $\alpha = 0.03 \text{ mJ/mole deg}^4$ ,

which corresponds to  $\theta_0$  = 399°K and is identical with results from the velocity of sound<sup>4</sup>;  $T_c$ 



FIG. 1. Specific heat of vanadium in the normal and superconductive state and (in the top left corner) in the mixed state.

 $=5.37^{\circ}$ K,  $a = 7.0^{\circ}$ K, and  $b = 1.34^{\circ}$ K. The results are consistent with a second-order transition and give for  $H_c$  at 0°K 1427 Oe.

Results in the mixed state were obtained in a field of 2700 Oe, which is about twice  $H_c(0)$ . The transition to the normal state is not sharp, but appears to be second order. If the transition is idealized, entropy considerations give for this transition temperature the value  $T_{\rm s}$ =1.76°K. This leads to  $H_{c2}/H_{c}$  = 2.14. The specific heat in the mixed state below 1.6'K can be given by

$$
C_m = 8.8T + 1.1T^3 \text{ mJ/mole deg.}
$$
 (1)

Rosenblum and Cardona' proposed a formula for the specific heat of the electrons in the mixed state. Neglecting the contribution of the superconductive fraction and assuming the parabolic law for the critical fields, their formula can be reduced to

$$
C_{em} = \gamma T (1 - t_s^2)(1 + 3t^2), \tag{2}
$$

where  $t = T/T_c$  and  $t_s = T_s/T_c$ . To compare with expression (1) the lattice term should be added to (2). The comparison can be improved by including deviations from the parabolic law. Below 2'K, the reduced critical field can be written as  $h = 1-1.1t^2$ . Substituting the experimental numbers given above we get

$$
C_m = 8.8T + 1.04T^3
$$
 mJ/mole deg.

The agreement with Eq. (1) is excellent.

Gorter<sup>5</sup> proposed a formula for the specific heat in the mixed state at very low temperatures which is nearly identical with Eq. (2). However, it includes an additional constant in the term cubic in temperature. The constant is expected to be 1.3, which appears to be in agreement with results on niobium.<sup>4</sup> The data for vanadium require  $\alpha = 1$ .

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<sup>&</sup>lt;sup>2</sup>B. Rosenblum and M. Cardona, Phys. Rev. Letters 12, 657 (1964).

<sup>3</sup>C. Caroli, P. G. deGennes, and J. Matricon, Phys. Letters  $9, 307$  (1964).

G. A. Alers, Phys. Rev. 119, 1532 (1960). <sup>5</sup>J. Ferreira da Silva, J. Scheffer, N. W. J. van Duykeren, and Z. Dokoupil, Phys. Letters 12, 166 (1964).

## TEMPERATURE AND PURITY DEPENDENCE OF THE SUPERCONDUCTING CRITICAL FIELD,  $H_{c2}$

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A solution is given for the temperature and mean-free-path dependence of the upper critical field,  $H_{c2}$ , of a bulk, type-II superconductor. Spin paramagnetic effects are omitted here.

Previously, this calculation has been carried out in several limiting cases. The Ginzburg-Landau-Abrikosov-Gor'kov<sup>1-3</sup> (GLAG) theory although applicable for all mean free paths,  $l$ , is restricted to temperatures,  $T$ , in the immediate vicinity of the zero-field transition temperature,  $T_c$ . Recently, Maki<sup>4</sup> and de Gennes' have independently solved for the full temperature dependence of  $H_{c2}$  in the dirty, or small- $l$ , limit. In addition, Gor'kov<sup>6</sup> has determined the value of  $H_{c2}$  at zero temperature for clean  $(l + \infty)$  samples.

We are concerned exclusively with the critical field at a second-order transition, where the superconductor gap function,  $\nabla(\vec{r})$ , is vanishing. Thus the analysis may be based upon a determination of the largest field for which the linear, homogeneous equation for  $\nabla(r)$ , due to Gor'kov,<sup>3</sup> has a nonzero, bounded solu $\cdot$ tion. This equation may be written in the form

$$
\chi^{\rm OP} \Delta(\vec{r}) = \ln(T_c/T) \Delta(\vec{r}), \qquad (1)
$$

where

$$
\chi^{\text{OP}}\Delta(\vec{r}) = \int d^3r' \, X(\vec{r}, \vec{r}') \Delta(\vec{r}'), \tag{2}
$$

and

$$
X(\vec{r}, \vec{r}') = \sum_{\nu = -\infty}^{\infty} \left[ 2\nu + 1|^{-1} \delta(\vec{r} - \vec{r}')
$$

$$
- \frac{T}{N(0)} \langle G_{\omega H}(\vec{r}, \vec{r}') G_{-\omega H}(\vec{r}, \vec{r}') \rangle \right]. \quad (3)
$$

Here  $\omega = \pi T(2\nu + 1)$ ,  $N(0)$  is the density of states

at the Fermi surface, and we measure temperatures and frequencies in energy units.  $G_{\omega H}$ is the one-electron Green's function in the presence of both a uniform, static magnetic field,  $\dot{H}$ , and a particular fixed configuration of impurities. The angular brackets in Eq. (3) indicate an averaging over a random ensemble of impurity distributions.

In the field-free case, Abrikosov and Gor'kov<sup>7,3</sup> have discussed the impurity-averaging procedure. They show that to lowest order in the impurity concentration, a physically valid limit, one need only take account of unlinked chains and ladders in a diagrammatic development. In the presence of the magnetic field, their procedure need be modified only by allowing the field to affect electron propagation between independent impurity-scattering events, but not during a scattering event, which is of very short range.

For actual experiments, it is almost always true that the spacing of the Landau levels in the field is small compared to their thermal and impurity broadening. In this semiclassical limit, the magnetic field enters the expression for the Green's function merely via a phase factor.

In this manner it is found that the operator of Eq. (2) may be written

$$
\chi^{OP} = \sum_{\nu = -\infty}^{\infty} \chi_{\omega H}^{OP},
$$
 (4)

$$
\chi_{\omega H}^{\text{op}} = |2\nu + 1|^{-1} - \frac{s_{\omega H}^{\text{op}}}{[1 - (s_{\omega H}^{\text{op}}/2\pi T\tau)]},
$$
(5)

where  $\tau = l/v_f$ , and  $s_{\omega H}^{\text{op}}$  is an integral operator with eigenvalue equation

$$
\mathcal{S}_{\omega H}^{\text{op}}(\vec{\mathbf{r}}) \equiv \frac{T}{N(0)} \int d^3 r' \langle G_{\omega H}(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \rangle \langle G_{-\omega H}(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \rangle \varphi(\vec{\mathbf{r}}') \tag{6}
$$

$$
\mathcal{E}_{\omega H}^{\text{op}}(\vec{\mathbf{r}}) = \mathcal{E}_{\omega H}^{\text{op}}(\vec{\mathbf{r}}). \tag{7}
$$