[4]T. Taniuti, Phys. Rev. Lett. 25, 1478 (1970).
[5]D. Dobrott and H. Grad, Bull. Amer. Phys. Soc. 16, 1239 (1971).
[6]T. E. Stringer, Phys. Rev. Lett. 22, 770 (1969).
[7]E. C. Bowers and N. K. Winsor, in *Proceedings of the Fourth Annual Conference on the Numerical Simulation of Plasmas, Naval Research Laboratory, Washington, D. C., 1970* (U.S. GPO, Washington, D. C., 1971), p. 619. This work is an extension of N. K. Winsor, J. L. Johnson, and J. M. Dawson, J. Comput. Phys. 6, 430 (1970).
[8]T. E. Stringer, Phys. Fluids 13, 1586 (1970).
[9]M. N. Rosenbluth and J. B. Taylor, Phys. Rev. Lett. 23, 367 (1969).
[10]N. K. Winsor, E. C. Bowers, J. M. Dawson, and M. A. Hellberg, in Proceedings of the Fourth Conference on Plasma Physics and Controlled Nuclear Fusion Research, Madison, Wisconsin, 1971 (to be published), paper CN-28/F-4.
[11]S. I. Braginskii, in *Reviews of Plasma Physics*, edited by M. A. Leontovich (Consultants Bureau, New York, 1965), Vol. I, p. 205.
[12]M. A. Hellberg, N. K. Winsor, J. M. Dawson, and J. L. Johnson, to be published.

Effective Dimensionality Change of Fluctuations in Superconductors in a Magnetic Field

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(Received 4 January 1972)

In an external magnetic field and near the transition temperature $T_{c2}(H)$, bulk and thin-film superconductors exhibit an effective change to one- and zero-dimensional behavior in their fluctuation specific heats, which diverge like $(T/T_{c2}-1)^{-3/2}$ and $(T/T_{c2}-1)^{-2}$, respectively. This enhancement effect is accompanied by a field-dependent broadening of the critical region.

The fluctuation specific heat of clean bulk superconductors is not expected[1] to be observable until $(T-T_{c0})/T_{c0}\approx 10^{-11}$. The situation improves with dirty samples and thin films, and fluctuation specific heat in extremely dirty films has recently been observed by Zally and Mochel.[2] In this note we would like to study the effect of a magnetic field on these fluctuation phenomena.

The basic physical idea is the following. In a uniform field the fluctuating Cooper pairs may be thought of as moving in Landau orbits of helical motion characterized by k_z and n. The transition temperature $T_{c2}(H)$ is the temperature at which the $n=0$ Landau orbit becomes stable, giving rise to the vortex state. Slightly above $T_{c2}(H)$ one would expect the lowest orbit $n=0$ to dominate the fluctuation contributions since the $n\neq 0$ states correspond in some sense to more distant transition temperatures. As a result only one degree of freedom remains, namely, that along the z direction; and a bulk superconductor behaves like an array of one-dimensional rods parallel to the field, with the number of rods per unit area given by $2eH/2\pi\hbar c$, the Landau degeneracy factor. The fluctuation specific heat is then proportional to the field and becomes one-dimensional in nature, diverging within the mean field theory like $(T/T_{c2}-1)^{-3/2}$ as compared with a $(T/T_{c0}-1)^{-1/2}$ divergence in the absence of a field. This results in a substantial enhancement of the specific heat close to the transition temperature.

With this physical picture in mind we next outline a calculation of the fluctuation specific heat in the Ginzburg-Landau (GL) approximation. We will begin with the assumption that the free energy for creating a particular fluctuation of the order parameter $\Delta(\vec{r})=\lambda\langle\psi_\uparrow(\vec{r})\psi_\downarrow(\vec{r})\rangle$, where λ is the BCS coupling constant times volume, is given by

$$f(\{\Delta\})=\int d^3r N(0)[\epsilon_0|\Delta|^2+\xi^2(0)|(\nabla/i+2e\vec{A}/\hbar c)\Delta|^2+a|\Delta|^4], \quad (1)$$

where $\xi(0)$ is the usual GL coherence length at zero temperature, $\epsilon_0=\ln(T/T_{c0})\approx(T-T_{c0})/T_{c0}$, and $a=7\zeta(3)/(4\pi kT)^2$. Outside of the critical region we can neglect the $a|\Delta|^4$ term in Eq. (1). Following Schmidt[3] and Schmid,[4] we obtain the fluctuation contribution to the partition function Z' by doing a functional integration over all possible fluctuations in the order parameter,

$$Z'=\int D\{\Delta(\vec{r})\}\exp[-f(\{\Delta\})/kT]. \quad (2)$$

In the absence of a magnetic field $\Delta(\vec{r})$ can be expanded in terms of plane waves and the functional in-

tegral in Eq. (2) readily performed. We obtain the fluctuation contribution to the free energy,

$$F' = kT \sum_{\vec{k}} \ln\{N(0)\lambda[\epsilon_0 + \xi^2(0)\vec{k}^2]\}. \quad (3)$$

This expression can also be obtained microscopically.[5] In the presence of a field H, the electron pairs can be thought of as falling into Landau orbits and $\Delta(\vec{r})$ should be expanded in terms of Landau states $\langle \vec{r}|n, k_z, q\rangle$, where

$$(\nabla/i + 2e\vec{A}/\hbar c)^2\langle r|n, k_z, q\rangle = [k_z^2 + (4eH/\hbar c)(n+\tfrac{1}{2})]\langle r|n, k_z, q\rangle . \quad (4)$$

It has been shown that this procedure is valid even in the presence of a strong field, when Eq. (1) no longer holds.[6] Within the GL approximation the functional integral in Eq. (2) can again be done and we obtain

$$F_H' = \frac{2AeHkT}{2\pi\hbar c} \sum_{k_z\, n} \ln\{N(0)\lambda[\epsilon_0 + \xi^2(0)k_z^2 + 2h(n+\tfrac{1}{2})]\}, \quad (5)$$

where $2AeH/2\pi\hbar c$ is the Landau degeneracy factor coming from the sum over q, with A being the area of the sample perpendicular to the field, and $h = \xi^2(0)(2eH/\hbar c)$. The field at which a divergence first occurs in Eq. (5), i.e., for $n = k_z = 0$, defines $H_{c2}(T)$ and the parameter h has a simple physical meaning:

$$h = H[T_{c0}(\partial H_{c2}/\partial T)_{T_{c0}}]^{-1}. \quad (6)$$

Introducing $\epsilon_H \equiv \ln[T/T_{c2}(H)]$ and using the fact that at the transition $\ln[T_{c2}(H)/T_{c0}] = -h$, we rewrite Eq. (5) as

$$F_H' = \frac{2AeHkT}{2\pi\hbar c} \sum_{k_z\, n} \ln\{N(0)\lambda[\epsilon_H + \xi^2(0)k_z^2 + 2hn]\}. \quad (7)$$

The fluctuation specific heat per unit volume is given by $C_H(T) = -(T/V)\partial^2 F'/\partial T^2$. Keeping only the part that is most rapidly diverging as $\epsilon_H \to 0$, we obtain for a three-dimensional (3D) sample, after performing the k_z sum,

$$C_H(T) = (k/8\pi)\xi(0)^{-3}h \sum_{n=0}^{\infty} (\epsilon_H + 2hn)^{-3/2}. \quad (8)$$

Within the GL approximation we see that $\xi^3(0)C_H$ is a universal function of the dimensionless variables h and ϵ_H for arbitrarily dirty samples. A more careful treatment, taking higher orders in the field into account, gives universality only in the clean and dirty limits. For a given ϵ_H and a sufficiently weak field such that $2h \ll \epsilon_H$, the sum over n can be converted to an integral and we recover the result of Thouless[1] and Aslamazov and Larkin,[7]

$$C_{H=0}(3D) = (k/8\pi)\xi(0)^{-3}\epsilon_0^{-1/2}. \quad (9)$$

However, for a fixed h and a temperature close to T_{c2} such that $2h \gg \epsilon_H$, the $n=0$ term in Eq. (8) dominates as anticipated in the physical argument earlier and

$$C_H(3D) = (k/8\pi)\xi^{-3}(0)h\epsilon_H^{-3/2}. \quad (10)$$

On comparing Eqs. (9) and (10) we see that as long as $2h \gg \epsilon_H$ the specific heat for a given distance from $T_{c2}(H)$ is enhanced in the presence of a field by the factor h/ϵ_H. For $h = 0.28$ a rough estimate indicates that for clean niobium,[8] the fluctuation and normal electronic heat capacities are comparable for $\epsilon_H = 10^{-4}$, in contrast to $\epsilon_0 \approx 10^{-11}$ in the absence of a field.[1] In two dimensions with field perpendicular to the film, the same argument again shows an h/ϵ_H enhancement. The fluctuation is now zero-dimensional in nature, the k_z degree of freedom being suppressed. We obtain for a film of thickness d

$$C_H(2D) = \frac{\xi^{-2}(0)k}{2\pi d} h\epsilon_H^{-2} = \frac{k}{2\pi d}\left(\frac{2eH}{\hbar c}\right)\epsilon_H^{-2}. \quad (11)$$

In view of the fact that the zero-field specific heat for a dirty film has been observed experimentally,[2] this enhancement and effective change in dimensionality should be easily observable if the experiment of Zally and Mochel is repeated with a magnetic field perpendicular to the film.

The above analysis has been based on the GL approximation which is valid only for weak fields $h \ll 1$. To make sure that our conclusion remains valid for moderate fields, we have calculated the specific heat for clean bulk samples in a strong field, using the formalism developed in Ref. 6 for the fluctuation magnetization, which enables us to keep all higher order terms in $\nabla/i + 2e\vec{A}/\hbar c$

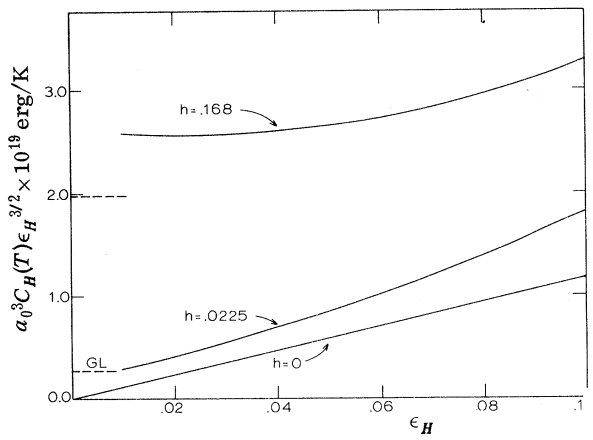

FIG. 1. Heat capacity per unit volume, $C_H(T)$, of clean bulk superconductors, multiplied by $\alpha_0^3\epsilon_H^{3/2}$, versus $\epsilon_H = \ln[T/T_{c2}(H)]$ for different values of magnetic field. The parameter h is defined in Eq. (6), and $a_0 = \hbar v_F/4\pi kT = 0.44\xi_0 T_{c0}/T$. (For strong fields, T is sufficiently different from T_{c0} that the introduction of a temperature-dependent a_0 is necessary.) The dashed line is the Ginsburg-Landau prediction for the small-ϵ_H limit for the respective field strengths.

that have been dropped in Eq. (1). In Fig. 1 we show the specific heat multiplied by $\epsilon_H^{3/2}$ for various magnetic field strengths. [The numerical calculation has been terminated at $\epsilon_H = 0.01$ because for smaller ϵ_H the graph becomes extremely sensitive to the value of $T_{c2}(H)$ which has to be obtained numerically. There is no doubt, however, that the level trend will continue until we reach the critical region.] The GL results are also shown for comparison. For a moderate field one can clearly see the change from an $\epsilon_H^{-3/2}$ behavior (flat region) to an $\epsilon_H^{-1/2}$ behavior (linear region) for $\epsilon_H \gtrsim 0.08$. Comparison with the straight line labeled $h = 0$, which is the zero-field GL result given by Eq. (9), clearly shows a substantial enhancement of the specific heat close to the transition. We also find that the effect of nonlocal electrodynamics,[9] which gives rise to a large suppression of the magnetization in moderate fields for clean superconductors, plays no important role for the specific heat. Details of this calculation will be presented elsewhere.

From the physical picture it is clear that this change in dimensionality will occur for other physical effects, like the electric conductivity in bulk samples parallel to a magnetic field. This latter problem has been discussed by Maki,[10] Mikeska and Schmidt,[11] and Usadel[12] in connection with the anisotropy of the fluctuation conductivity parallel and perpendicular to a magnetic field.[13]

Since the nature of the fluctuation is changed rather drastically when a field is applied, one might expect the width of the critical region to be affected also. We expect that the critical region will be broadened and we have to make sure the broadening is not so large as to invalidate the above discussion in the temperature region in which we hope to obtain large enhancement of the specific heat. The critical region is the temperature interval $\epsilon < \epsilon_c$ close to the transition temperature where the interaction between fluctuations may no longer be neglected. Since the $a|\Delta|^4$ term in Eq. (1) may be interpreted as the free energy contribution due to such fluctuation interactions, we can calculate following Ferrell[14] the parameter ϵ_c by equating the first two terms in Eq. (1) with $a|\Delta|^4$ calculated in a Hartree-type approximation, i.e., with $a|\Delta|^4 \approx a\langle|\Delta|^2\rangle|\Delta|^2$, where the angular brackets denote an average in the sense of Eq. (2). After some straightforward calculations we obtain in the dirty limit the following estimates for ϵ_c in two and three dimensions in the presence of a field:

$$\epsilon_c(3D) \approx h^{2/3}(k_F\xi_0)^{-1/3}(k_F l)^{-1}, \tag{12a}$$

$$\epsilon_c(2D) \approx h^{1/2}(k_F^2 ld)^{-1/2}, \tag{12b}$$

where l is the mean free path and d is the film thickness. This is to be compared with the expression obtained by Ferrell in the absence of a field

$$\epsilon_c(3D) \approx (k_F\xi_0)^{-1}(k_F l)^{-3}, \tag{13a}$$

$$\epsilon_c(2D) \approx (k_F^2 ld)^{-1}. \tag{13b}$$

It is interesting to note that ϵ_c both with and without a field can also be identified as the ϵ at which the fluctuation-induced specific heat is of the order of the jump in specific heat at the second-order phase transition.

For the experimental situation of Ref. 2, ϵ_c is estimated from Eq. (12b) to be 10^{-2} with the application of a moderate field $h = 0.1$. With this magnetic field and for $\epsilon_H > 10^{-2}$ we expect our previous analysis to apply, and one should observe a ϵ_H^{-2} behavior. For $\epsilon_H > 0.1$ the ϵ_H^{-1} behavior should be recovered. On the other hand, comparing Eqs. (12) and (13) indicates that the application of a magnetic field has the effect of broadening the critical region. Furthermore, the width of the critical region can be controlled by varying the field. Application of a magnetic field may then prove to be a useful way to probe and study the critical region in greater detail.

[1]D. J. Thouless, Ann. Phys. (New York) 10, 554

(1960).

[2]G. Zally and J. Mochel, Phys. Rev. Lett. 27, 1710 (1971).

[3]H. Schmidt, Z. Phys. 215, 210 (1968).

[4]A. Schmid, Phys. Rev. 180, 527 (1969).

[5]Microscopic calculation actually results in a sum over "excited pair" energies. We have retained only the zero-energy term in Eq. (3) because it is expected to dominate near the transition. See P. A. Lee and M. G. Payne, Phys. Rev. Lett. 26, 1537 (1971), and 27, 170(E) (1971), and Phys. Rev. B 5, 923 (1972), for details.

[6]Lee and Payne, Ref. 5.

[7]L. G. Aslamazov and A. I. Larkin, Fiz. Tverd. Tela 10, 1104 (1968) [Sov. Phys. Solid State 10, 875 (1968)].

[8]For type-I materials the first-order phase transition intervenes and one has to use supercooling techniques to get close to T_{c2}.

[9]By nonlocal electrodynamics we refer to the complications that arise when higher-order terms in $\nabla/i + 2e\vec{A}/\hbar c$ are kept in Eq. (1), because different components of this operator do not commute. As a result the usual replacement of k^2 by $k_z^2 + (4eH/\hbar c)(n + \frac{1}{2})$ is not valid. See Ref. 6 for details.

[10]K. Maki, J. Low Temp. Phys. 1, 513 (1969).

[11]H. J. Mikeska and H. Schmidt, Z. Phys. 230, 239 (1970).

[12]K.-G. Usadel, Z. Phys. 227, 260 (1970).

[13]We should point out that for physical effects that do not arise *directly* from fluctuating pairs treated in the GL approximation, the kind of dimensionality change we discussed may not occur. Examples are the contribution to the conductivity from the Maki diagram [see K. Maki, Progr. Theor. Phys. 39, 897 (1968)] and fluctuation electronic density of states [E. Abrahams, M. Redi, and J. W. F. Woo, Phys. Rev. B 1, 208 (1970)].

[14]R. A. Ferrell, J. Low Temp. Phys. 1, 241 (1969).

X-Ray Photoemission Band Structure of Some Transition-Metal Oxides

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The valence-band structures of MnO, CoO, NiO, Cu_2O, CuO, and ReO_3 have been obtained by x-ray photoemission spectroscopy. It is found that in every case a narrow metal *d* band lies above the center of the oxygen 2*p* valence band.

The transition-metal oxides exhibit a wide variety of electric and magnetic properties[1]: There are magnetic insulators (e.g., NiO), compounds with a metal-to-insulator transition (e.g., V_2O_3), and metals (e.g., ReO_3), This wide variety makes these compounds an attractive subject for a systematic study of magnetic and electric properties. The most basic information required for an understanding of these properties is their band structure. Adler,[1] in a recent review of the properties of the transition-metal oxides, has shown that this knowledge is still incomplete, even in the most thoroughly investigated case, that of NiO. In fact, two different theoretical approaches[1,2] yield quite different band structures, clearly indicating the need for reliable experimental information. In this note we provide data which, for the first time, locate the O(2*s*), O(2*p*), and *d* bands of a number of transition-metal oxides quite accurately. We also show that x-ray photoemission spectroscopy (XPS) must be used with care even in the valence-band region because of the occurrence of multielectron excitations.

The XPS spectra were recorded with a Varian IEE 15 spectrometer, operated with Mg $K\alpha$ radiation at a linewidth of 1.2 eV. Samples consisting of thin layers of MnO, CoO, NiO, and Cu_2O were produced directly on the corresponding metals by exposing them to air under conditions such as to assure the formation of the desired oxide.[3] As a cross check we ran a sample made up from freshly crushed green NiO crystal mounted on double-sided Scotch tape. It gave results identical to those of NiO grown on Ni except for a charging shift of about 3 eV. The spectra of CuO and ReO_3 were obtained only from Scotch-tape-mounted samples. Figure 1 shows the typical valence-band spectra of the rock-salt-structure oxides MnO, CoO, and NiO; Fig. 2 shows the spectra of CuO, Cu_2O, and ReO_3. To facilitate comparison, the energy scales have been normalized to the O(2*s*) lines in each case.

The position of the Fermi energy shown in the figures has to be viewed with some caution. The Fermi energy of the instrument was determined from Ag and Au valence-band spectra. For the oxides produced directly on the metals there should be negligible charging effects; nevertheless, it is not certain that the concept of Fermi energy applies to a thin film of insulator or semiconductor under x-ray bombardment. The Fermi energy for CuO has been tentatively assigned the