SUPERCONDUCTIVITY IN GRAPHITIC COMPOUNDS

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Superconductivity has been discovered in intercalation compounds[1] of graphite with alkali metals. Typical formulas for these compounds are C_8A ($A = $K, Rb, or Cs). The well-known layer structure of graphite is preserved, the alkali-metal atoms lying in layers alternating with the graphite carbon layers. The transition temperatures observed are from 0.020 to 0.135°K in the Cs-graphite system; from 0.023 to 0.151°K in the Rb-graphite system; and up to 0.55°K in the K-graphite system. While the transition temperatures vary to this extent with the quality of the graphite and the treatment it had experienced, the width for any given transition is relatively small, usually of the order of several millidegrees.

The compounds were prepared in the classical manner[2] by heating highly purified alkali metal with pyrolytic graphite[3] in an evacuated tube. By controlling the ratio of the reactants it was possible to obtain both the gold and the blue compounds corresponding to C_8A and $C_{16}A$. Fredenhagen and Cadenbach[2] have also reported evidence for the formation of a C_4A compound when the alkali metal was in sufficient excess to wet the surface of the graphite, although such a compound does not seem to have been found by later workers. We have observed the highest transition temperatures for the compounds prepared with excess alkali metal present. The alkali metals and the pyrolytic graphite used in these experiments were tested separately down to 0.011°K and found not to be superconducting. Temperatures below 0.32°K were obtained by adiabatic demagnetization of a chromium-potassium alum cooling salt and measured with a cerium-magnesium nitrate thermometer. Superconductivity was detected with a low-frequency (30 cps) phase-sensitive detector. Measurements above 0.32°K were made in the manner described previously.[4]

The structures of these compounds are highly anisotropic; the well-defined hexagonal planes are essentially parallel to each other throughout the sample. The alkali-metal atoms lie in every second layer in the C_8 compound, opposite the centers of alternate carbon hexagons. The C_{16} structure is similar, but with the alkali-metal atoms in every third layer. According to Hennig,[1] the alkali-metal atoms are ionized at all compositions to the extent of one-third to one-fourth. This is confirmed by the atomic spaces reported by Schleede and Wellmann[5] for the hexagonal plane which shows a Cs-Cs spacing less than the interatomic distance of the metal. The anisotropy is reflected also in the electrical properties.[6] Thus the mean free path and the electrical conductivity in the plane of interconnected carbon atoms is much higher than along the c axis. The unusual electrical properties of a two-dimensional carbon network have also been shown in studies of pyrolyzed polymers.[7] A large variation in H_{c2} as a function of field direction is both expected and observed as a result of the anisotropy of mean free path. H_{c2} is taken as the magnetic field at which shielding currents are first observed. At 0.32°K the compound ($T_c = 0.55$°K) made with excess potassium had an H_{c2} of 160 gauss with $H \perp [\mathrm{C}]$ and 730 gauss with $H \parallel [\mathrm{C}]$. A C_8K compound made with stoichiometric amounts of the elements ($T_c = 0.39$°K) had an even higher anisotropy; H_{c2} for $H \perp [\mathrm{C}]$ was 25 gauss and for $H \parallel [\mathrm{C}]$ was 250 gauss.

We did not observe any superconductivity down to 0.011°K for the blue [most like the $C_{16}K$] compound. The significant difference between the C_8 and C_{16} compounds is that the carbon atoms are connected along the c axis only by metal atoms in the former case, but not in the latter. If two-dimensional superconductivity were to occur in the present systems in the hexagonal planes perpendicular to the c axis, one might expect that the interconnection along the c axis would not be crucial, and that the T_c for the C_{16} compound would not be greatly different from that for the C_8 compound. Our preliminary results quoted above show more than an order of magnitude difference in the respective transitions, as any transition for the C_{16} lies below 0.011°K.

The above results suggest, of course, the examining of other lamellar compounds such as those formed by graphite with electron acceptors, and those formed by boron nitride.

The existence of well-ordered higher stage compounds (where the stage is defined as the ratio of the number of layers of carbon to those of the other constituent) opens the way to further studies bearing on the possible existence of two-dimensional superconductivity, which might be expected by analogy with the Ising model if it is applicable in the present case.

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[1] For a review see G. R. Hennig, Progress in Inorganic Chemistry (Interscience Publishers, Inc., New York, 1959), Vol. 1.

[2] K. Fredenhagen and G. Cadenbach. Z. Anorg. Chem. 158, 249 (1926).

[3] The pyrolytic graphite was obtained from High Temperature Materials, Lowell, Massachusetts. The alkali metals were triply distilled in high vacuum from 99.9% purity starting material. All samples were protected during measurement by degassed and prereacted mineral oil.

[4] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. 129, 1025 (1963).

[5] A. Schleede and M. Wellmann, Z. Physik. Chem. (Leipzig) B18, 1 (1932).

[6] See, for example, A. R. Ubbelohde, Proceedings of the Fifth Conference on Carbon (The Macmillan Company, New York, 1962), p. 1.

[7] F. Winslow, W. O. Baker, N. Pape, and W. Matreyek, J. Polymer Sci. 16, 101 (1955).

[8] G. R. Hennig and L. Meyer, Phys. Rev. 87, 439 (1952).

INERTIAL MASS OF A MOVING FLUXOID*

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Recently, Stephen and Suhl[1] have proposed a time-dependent form of the Landau-Ginsburg theory. In this note it is shown that this gives rise to an inertial mass per unit length of flux line. The resulting acceleration term may be compared with the damping term suggested by Strnad, Hempstead, and Kim,[2] and investigated by Bardeen and Stephen[3]; the result indicates that the relaxation time of a fluxoid is less than 10^{-12} seconds. This suggests that collective modes of a fluxoid system will be very difficult to observe.

For an order-of-magnitude estimate we neglect all normal fluid effects, yet assume that the gap is small enough so that the linear form of the theory of reference 1 may be used. In a notation in which the gradient term in the Landau-Ginsburg equation for the order parameter Ψ is written $(1/4m)[\hbar\nabla-(2ie/c)A]^2\Psi$ where Ψ has the dimensions $(\text{volume})^{-1/2}$, the equations of reference 1 may be derived from a Lagrangian $\mathcal{L}=\int L dt dV$, where

$$L=F-\left[\frac{1}{4mv^2}\left|\left(\hbar\frac{\partial}{\partial t}+2ie\varphi\right)\Psi\right|^2+\frac{E^2}{8\pi}\right], \qquad (1)$$

provided electromagnetic propagation effects are ignored. In Eq. (1) F is the usual free-energy expression in equilibrium form, including the magnetic energy density $H^2/8\pi$; v is the Fermi velocity v_F divided by $\sqrt{3}$; and the fields are $H=\nabla\times A$ and $E=-(1/c)(\partial A/\partial t)-\nabla\varphi$.

Since the shielding distance in the metal is small compared with all other lengths in the problem, the charge on the moving line, proportional to $\varphi+(1/c)(\partial W/\partial t)$ to the first order in the potentials, will be nearly zero. Here W is proportional to the phase of the order parameter:

$$2ieW/\hbar c=\arg\Psi.$$

The time-derivative term in Eq. (1) is then simply $(\hbar/4mv^2)(\partial|\Psi|/\partial t)^2$. The variational problem $\delta\mathcal{L}=0$ may now be parametrized as follows: Considering first the motion of a set of parallel or antiparallel fluxoids relative to each other, one substitutes the Abrikosov equilibrium form 4 of the solution for Ψ and A, but allows the centers r_i of the fluxoids to be functions of time. The last two terms in the Lagrangian L then transform into bilinear functions of the velocities r_i. If the fluxoids are well separated, by more than the coherence