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.

The authors would like to acknowledge the expert assistance of G. W. Hull, Jr., in the measurement, and thank K. A. Jackson for discussions of the structure of pyrolytic graphite. In discussion of these results with Dr. G. R. Hennig of the Argonne National Laboratory, it was called to our attention that an unsuccessful attempt to detect superconductivity in graphite compounds of this type was reported by Hennig and Meyer.[8]

*Also at University of California, San Diego, La Jolla, California.

[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*

H. Suhl
Physics Department, University of California, San Diego, La Jolla, California
(Received 28 December 1964)

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 (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 $\dot{r}_i$. If the fluxoids are well separated, by more than the coherence

lengths, the "core" term $(\hbar^2/4mv^2)\int(\partial|\Psi|/\partial t)^2 dV$ transforms into a sum of squares of the velocities. The electromagnetic term $(1/8\pi)\times\int E^2 dV$, on the other hand, gives a complicated bilinear form with position-dependent coefficients unless the fluxoids are separated by more than a penetration length. We will only deal with such well-separated fluxoids, arguing later that inertial effects from overlap are most probably smaller. The problem is now reduced to a calculation of the mass of one single flux line, located at $r_0(t)$.

The core kinetic energy is, per unit length,

$$\frac{\hbar^2\Psi_\infty^2}{4mv^2}\int(r_0\cdot\nabla f)^2 dxdy=\frac{\pi\hbar^2\Psi_\infty^2}{4mv^2}\int\left(\frac{\partial f}{\partial r}\right)^2 r dr\dot{r}_0^2,$$

where $f=|\Psi(r-r_0)|/\Psi_\infty$. Abrikosov[4] has shown that f varies initially linearly, attaining its terminal value unity at a distance of order ξ, the coherence length, from the center of the line. As a crude approximation we write $f=r/\xi$, $r<1$, and $f=1$, $r>1$. Then we find for the mass per unit length

$$\mu_{\text{core}}=\pi\hbar^2\Psi_\infty^2/4mv^2,$$

or, since $\Psi_\infty^2=(m/\pi)(\xi^2H_c^2/\hbar^2)$ where H_c is the bulk critical field,

$$\mu_{\text{core}}=m(\xi^2H_c^2/4mv^2). \tag{2}$$

At low temperatures $H_c^2\sim 4\pi\Delta^2 n_0/\epsilon_f$, where Δ is the energy gap, so that finally

$$\mu_{\text{core}}\sim m\frac{12\pi\xi^2 n_0}{8}(\Delta/\epsilon_f)^2,$$

where n_0 is the electron concentration. With $n_0\sim 10^{23}$ cm^{-3}, $\xi\sim 10^{-6}$ cm, $\Delta/\epsilon_f\sim 10^{-4}$, this gives approximately 4000 electron masses per unit length of line.

To calculate the electromagnetic mass μ_{em}, we note that for zero charge on the line, E may be written

$$E=-\frac{1}{c}\frac{\partial}{\partial t}(A-\nabla W)$$

$$=\frac{1}{c}\frac{\partial}{\partial t}\frac{\sqrt{2}\lambda H_c}{\kappa c}K_1\left(\frac{r-r_0}{\lambda}\right)$$

(see Abrikosov[4]). Here λ is the penetration length. Since $K_1(x)\sim 1/x$ for small x, this would lead to an infinite result for the kinetic energy. Hence a closer examination of the region $<\lambda$ is needed. We do this first for the case of extreme low temperatures, neglecting the Caroli-de Gennes-Matricon excitations[5] (see comments below), when Poisson's equation becomes

$$\nabla^2\varphi=(\varphi+\dot{W}/c)/\lambda_d^2,$$

where λ_d is a shielding length, of order a few times $(k_F)^{-1}$. In polar coordinates, with $W(r')=\hbar c\theta'/2e$, it is readily seen that the solution of this equation is

$$\varphi(r)=-\frac{\hbar}{2e}\lambda_d\left[K_1\left(\frac{\bar{r}}{\lambda_d}\right)\left\{I_0\left(\frac{\bar{r}}{\lambda_d}\right)-1\right\}-I_1\left(\frac{\bar{r}}{\lambda_d}\right)K_0\left(\frac{\bar{r}}{\lambda_d}\right)\right]\dot{r}_0\sin\theta,$$

where θ is the angle between the direction of motion and $\bar{r}=r-r_0$. When $\bar{r}\gg\lambda_d$, this goes over into

$$\varphi=-\frac{\hbar}{2e}\frac{1}{\bar{r}}\dot{r}_0\sin\theta$$

(compare with reference 3, where this result is written $v_s\cdot v_L$). But this is also $-\partial W/\partial t$, as is most easily seen by writing W is the form $\hbar c/2e\tan^{-1}(y-y_0)/(x-x_0)$. Therefore, $(1/c)\times(\partial A/\partial t)+\nabla\varphi$ is the same as $(1/c)(\partial/\partial t)(A-\nabla W)$ (i.e., the London acceleration) down to distances of several λ_d. This sets the lower cutoff for the seemingly divergent integral. At smaller values still, A becomes small and can be neglected by comparison with $\nabla\varphi$, which remains finite. That A becomes small follows from the Abrikosov solution

$$\frac{1}{c}A=\frac{1}{c}(A-\nabla W)+\frac{1}{c}\nabla W=-\frac{2^{1/2}\lambda H_c}{\kappa c}K_1\left(\frac{\bar{r}}{\lambda}\right)+\frac{\hbar}{2e\bar{r}},$$

and since $\sqrt{2}\lambda^2H_c/\kappa=\hbar c/2e$, we obtain

$$A\sim\frac{\hbar c}{4e\lambda}\frac{\bar{r}}{\lambda}\ln\left(\frac{\bar{r}}{\lambda}\right)$$

for small $\bar{r}/\lambda$.

The bulk of the electromagnetic kinetic energy thus comes from the region $>\lambda_d$, and in calculating it, $K_1(\bar{r}/\lambda)$ may be replaced by $\lambda/\bar{r}$.

Thus, per unit length, we have

$$\frac{1}{8\pi}\int E^2 dxdy = \frac{\lambda^4 H_c^{\,2}}{4\pi\kappa^2 c^2}\int\left(\frac{\dot{r}_0\cdot\bar{r}}{|\bar{r}|^3}\right)^2 \bar{r}d\bar{r}d\theta$$

$$= \frac{\lambda^4 H_c^{\,2}}{4\kappa^2 c^2}\dot{r}_0^{\,2}\int_{\lambda_d}^{\infty}\frac{1}{r^3}dr$$

$$= \frac{\xi^2 H_c^{\,2}}{8c^2}\left(\frac{\lambda}{\lambda_d}\right)^2\dot{r}_0^{\,2}.$$

Hence

$$\mu_{\mathrm{em}} = \frac{1}{4}\frac{\xi^2 H_c^{\,2}}{c^2}\left(\frac{\lambda}{\lambda_d}\right)^2,$$

and, from (2),

$$\frac{\mu_{\mathrm{em}}}{\mu_{\mathrm{core}}} = \frac{1}{3}\left(\frac{v_F}{c}\right)^2\left(\frac{\lambda}{\lambda_d}\right)^2 \qquad (3)$$

for $\lambda/\lambda_d \sim 10^3$, $v_F/c \sim 10^{-2}$.

So far, we have written Poisson's equation in the extreme low-temperature limit, in fact so low that $\Delta_\infty\lambda_d/\xi \gg kT$, which allows all of the fluid down to λ_d to be superfluid. More realistically, we would have to solve (see reference 1)

$$\nabla^2\varphi = \left(\varphi + \frac{\rho_s}{\rho_s+\rho_n}\frac{W}{c}\right)\Big/\lambda_d^{\,2},$$

where ρ_s and ρ_n are the superfluid and normal densities. Then μ_{em} would have to be reduced by some average of $\rho_s/(\rho_s+\rho_n)$. ρ_s depends exponentially on $\Delta_{\mathrm{local}}/kT$. Therefore, if, as a crude guess, we assume that all the fluid is normal wherever the local gap is less than kT and superfluid where it is greater, the effect will be to replace the lower limit λ_d by λ_{th}, where

$$\lambda_{\mathrm{th}} = \xi kT/\Delta_\infty,$$

so that, with $\kappa = \lambda/\xi$,

$$\frac{\mu_{\mathrm{em}}}{\mu_{\mathrm{core}}} = \frac{1}{3}\left(\frac{v_F}{c}\right)^2\left(\frac{\lambda}{\xi}\right)^2\left(\frac{\Delta_\infty}{kT}\right)^2$$

$$= \frac{1}{3}\kappa^2\left(\frac{v_F}{c}\right)^2\left(\frac{\Delta_\infty}{kT}\right)^2 \qquad (4)$$

for $kT > \Delta_\infty\lambda_d/\xi$, so that near T_c, the core mass dominates. Finally, if we assume that the localized excitations of reference 5 (whose range is essentially ξ) reduce all of the superfluid component to zero within a radius ξ, then λ_d must be replaced by ξ, and so

$$\frac{\mu_{\mathrm{em}}}{\mu_{\mathrm{core}}} = \frac{1}{3}\kappa^2\left(\frac{v_F}{c}\right)^2, \qquad (5)$$

and for moderate κ, $\mu_{\mathrm{em}} < \mu_{\mathrm{core}}$. Assuming the most favorable case, i.e., extremely low temperatures, and neglect of the excitations of reference 5, we may compute the relaxation time $\tau = \mu_{\mathrm{em}}/\eta$ of a fluxoid, where η is the viscous coefficient of references 2 and 3:

$$\eta \sim \pi\hbar^2\sigma_n/4e^2\xi^2,$$

so that, with $\xi H_c/c = \hbar/2e\lambda$, we get

$$\tau = \frac{\mu_{\mathrm{em}}}{\eta} = \frac{1}{3\pi\kappa^2}\left(\frac{\lambda}{\lambda_d}\right)^2\frac{1}{\sigma_n}$$

in the extreme low-temperature limit. For $\kappa \sim 1$, $\sigma \sim 10^{17}$ sec^{-1}, $\lambda/\lambda_d = 10^3$, this gives about 10^{-12} second and diminishes rapidly with increasing κ, as well as with increasing temperature. (It has been assumed that the Caroli, de Gennes, and Matricon[5] low-lying excitations near the center of a flux line are responsible for essentially normal conductivity of the core. Any reactive effect of these excitations on the mass of the line is neglected in this paper.)

Finally, the forces on the lines are obtained by varying F in Eq. (1) with respect to the flux positions. In the present approximation, no Magnus force appears[3]; however, in the presence of a uniform transport current J, a Lorentz force independent of fluxoid velocity does occur. For in that case, we must write

$$H = H_{\mathrm{fluxoid}} - \frac{2\pi}{c}(r\times J),$$

and so the F in Eq. (1) acquires a cross term

$$-\frac{1}{4\pi}\int dV H_{\mathrm{fluxoid}}(r-r_0)\cdot\frac{2\pi}{c}(r\times J).$$

Varying this with respect to r_0 gives the Lorentz force of reference 3. The current J only adds a time-independent phase to W, and so the rest of the calculation is unchanged.

These results can be used to discuss the oscillations of a fluxoid along its own length. However, in view of the extremely short re-

laxation time, these do not have wavelike character. Finally, we remark that kinetic-energy effects arising from overlap terms in E^2 for several fluxoids are not likely to exceed the ones discussed here, since the coefficients of $\dot{r}_1^2$ will contain rapidly diminishing Bessel functions of the distance between the lines.

The author gratefully acknowledges discussions with M. Stephen and N. R. Werthamer, and wishes to thank the authors of references 2 and 3 for an opportunity to see their manuscripts prior to publication.

*Work supported by U. S. Air Force Contract No. AF-AFOSR-610-64.

[1]M. J. Stephen and H. Suhl, Phys. Rev. Letters 13, 797 (1964).

[2]A. R. Strnad, C. F. Hempstead, and Y. B. Kim, Phys. Rev. Letters 13, 794 (1964).

[3]M. J. Stephen and J. Bardeen, Phys. Rev. Letters 14, 112 (1965).

[4]A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [translation: Soviet Phys.-JETP 5, 1174 (1957)].

[5]C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Letters 9, 307 (1964).

RECOMBINATION RADIATION IN ANTHRACENE CRYSTALS*

W. Helfrich† and W. G. Schneider
Division of Pure Chemistry, National Research Council, Ottawa, Canada
(Received 16 November 1964)

In this note we report the observation of fluorescence due to recombination of electrons and holes in anthracene single crystals. High concentrations of carriers were obtained by using injecting electrodes. The crystals used were 1 to 5 mm in thickness and 1 cm in diameter. They were melt-grown from chromatographed and repeatedly zone-refined material. Glass tubes cemented to the crystal surface contained the liquid electrodes. The contact areas were 0.2 cm^2, and the direction of current was perpendicular to the *ab* plane.

It is known that steady-state space-charge-limited (SCL) hole currents can be injected into anthracene.[1-3] Most of the space charge is trapped, the traps being distributed more or less exponentially in depth. In previous work a concentrated solution of $KI+I_2$ in water[4] was often used for hole injection. We found that this electrode was Ohmic only up to 3×10^{-8} A. We could obtain a saturation current of 3×10^{-6} A and higher by use of a solution of positive anthracene ions (prepared by adding $AlCl_3$ to a solution of anthracene in nitromethane[5]). Aqueous Na_2SO_4 solution served as the opposite noninjecting electrode.

Injection of electrons into anthracene has hitherto not been observed. Using a solution of negative anthracene ions (prepared by interacting metallic sodium with a solution of anthracene in tetrahydrofuran[6]), we could inject steady-state electron currents up to 10^{-5} A without observing saturation effects. The following observations indicated that these currents were SCL: (1) At low voltages the dependence of current on voltage is greater than a second power, as is generally found with SCL hole currents. (2) These low currents can be increased by light, the wavelength dependence of the response being completely analogous to that of SCL hole currents.[7,8] Besides a response in the singlet absorption region, we observed four triplet absorption maxima and two weak maxima in the near infrared. (3) At high voltages the current is proportional to the square of the voltage and much larger than the SCL hole current measured on the same crystal. Apparently the trap-filled limit is reached. Using Child's law, electron mobilities of 0.36 and 0.44 $cm^2\ V^{-1}\ sec^{-1}$ ($\perp ab$ plane, taking $\epsilon = 3.4$) for two different crystals were calculated.[9]

Two-carrier SCL currents were obtained when the electron-injecting electrode was combined with a hole-injecting electrode. At low voltages these currents were considerably larger than those with only one injecting electrode. At high voltages the currents were much larger than the SCL hole currents but only by a factor of three larger than the SCL electron currents. The flow of doubly injected current is accompanied by the emission of blue light, observed from the side of the crystal between the opaque electrodes. No light could be seen with only one injecting contact. The emitted light was analyzed with a monochromator and shown to be the fluorescence spectrum of anthracene modified on the short-wavelength