Superconductivity and charge-density waves in Ta- and Ti-doped $NbSe_3$

W. W. Fuller and P. M. Chaikin
Department of Physics, University of California, Los Angeles, California 90024

N. P. Ong
Department of Physics, University of Southern California, Los Angeles, California 90007
(Received 2 February 1981)

We have measured the resistance and critical fields of a series of alloys of Ti and Ta substituted for Nb in $NbSe_3$. For concentrations of 5 at.% Ta and 0.1 at.% Ti we find that the charge-density-wave transitions are greatly smeared or suppressed and that the alloys become bulk anisotropic superconductors. Our results are discussed in terms of the competition between the charge-density waves and superconductivity for states at the Fermi surface.

Recently the interplay between charge-density waves (CDW's) and superconductivity has been a topic of much interest. This interplay has been studied in several materials. The *A*15 superconductors undergo a structural instability which has been compared to a Peierls distortion. The interplay between this instability and superconductivity has been studied by several authors.[1–4] CDW's and superconductivity compete in the layered compounds $NbSe_2$ and $TaSe_2$.[5] More recently work has been done on the transition metal trichalcogenide[6] $NbSe_3$ and on the organic superconductor $(TMTSF)_2PF_6$.[7]

$NbSe_3$ is a quite novel material with highly anisotropic bands and two incommensurate charge-density-wave transitions which have been observed by transport measurements[8] as well as electron-[9] and x-ray-diffraction[10] studies. Associated with these transitions are spectacular nonohmic conductivities in small electric fields.[11] The purpose of the present study is to see the effect of transition-metal substitutional doping on the CDW transitions and the effect of the CDW's on superconductivity. Previously investigations have studied the effects of these impurities on the nonohmic conductivity.[12]

The question of superconductivity in $NbSe_3$ has been addressed by several authors and conflicting results found. Under ambient pressure Monceau *et al.* do not see any sign of superconductivity in magnetization measurements down to 50 mK.[6] Haen *et al.*[13] reported a current-dependent resistance below 2.2 K. They saw a drop in the resistance of $NbSe_3$ between 2.2 and 1.5 K where a plateau was reached and then a linear drop in the resistance below 0.4 K. Buhrman *et al.*[14] report a diamagnetic susceptibility for $NbSe_3$ which begins to appear where the knee in the resistance occurs ~ 1.5 K. They also see that the knee moves to a lower temperature when a magnetic field is applied.

It has been seen that pressure suppresses the charge-density-wave transition temperature as well as the size of the resistance anomalies.[6] Simultaneously a superconducting transition appears in $NbSe_3$ with applied pressure. A pressure of 6 kbar completely suppresses the CDW and permits a superconducting transition at 2.4 K.

In order to study further the suppression of superconductivity by CDW, we have studied the effect of replacing some of the Nb with either Ta or Ti. The samples were grown at the University of Southern California by first mixing together known amounts of Nb and either Ta or Ti and then forming the trichalcogenide as was done in $NbSe_3$. This resulted in two types of doping: isoelectronic, Ta, and nonisoelectronic, Ti, with Ti having a much larger effect per impurity. Measurements were made on samples with 0.5 at.% Ta, 5.0 at.% Ta, and 0.1 at.% Ti as well as pure $NbSe_3$. Preliminary results for 5 at.% Ta have been reported elsewhere.[15]

The resistivity, as a function of temperature *T* was measured for several samples of each concentration. The samples were ribbonlike with typical dimensions being 5 mm long, a few tens of micrometers wide, and less than 10 μm thick. The resistance was measured along the chain direction using the four-probe method. The electrical leads were made of 1-mil Au wire which were silver painted to the sample. Both dc and low-frequency (<200 Hz) ac measurements were made. A variety of currents (0.01–100 μA) was used to check for nonohmicities in the resistance. The ac measurements were performed with a lock-in voltmeter at low frequency. The low temperature was obtained in either a ^{3}He cryostat or a dilution refrigerator.

Critical-field measurements were made on the superconducting samples by monitoring the resistance while sweeping a magnetic field at constant temperature (± 2 mK). The critical field was defined as the value of the field where the resistance was one-half of its normal value. The angular dependence of the critical field was obtained by using a rotating electromagnet. To account for difficulties in mounting the sample in the correct orientation a field in the perpendicular direction could be applied with a superconducting magnet. This allowed an accuracy of $\pm 1°$ in the parallel orientation of the field.

The low-temperature magnetic susceptibility was measured with a commercial superconducting quantum interference device (SQUID) from S.H.E. Corporation. Several $Nb_{0.95}Ta_{0.05}Se_3$ samples were mounted in one coil of an astatically wound pair. The other coil held a piece of indium which was used to find zero magnetic field. This is important in measurements on fibrous samples where flux trapping becomes a large effect.[16] The samples were cooled through their transition temperature in zero field, a magnetic field was then applied, and the sample was warmed and the change in the SQUID output was recorded.

Figure 1 shows the resistance, normalized to the room-temperature value, as a function of temperature for various amounts of Ta and Ti. In Fig. 1 the pure $NbSe_3$ clearly shows the two CDW anomalies at 145 and 59 K. As the amount of Ta is increased the CDW anomalies at 145 and 59 K decrease and the residual resistance increases. The anomalies are both broadened and reduced in size. As the concentration of impurity is increased, the temperature at which the CDW occurs is reduced. These results are consistent with those reported by Ong *et al.*[12]

With 5 at.% Ta the CDW at 59 K is no longer visible. However, the upper transition is still present and the resistivity shows a small and gradual increase as temperature is lowered. This increase has previously been noted by On *et al.*, but is not yet explained. It may result from a remnant of CDW formation or from localization effects in this highly anisotropic "dirty" metal.

As can be seen in Fig. 1, the Ti is more effective in suppressing the CDW with a large change at only 0.1 at.%. Ti is expected to cause a greater effect because it is a charged impurity. This implies it will be a stronger scatterer than the Ta and perhaps affect the nesting of the Fermi surface, the carrier density, and hence k_F, more than the Ta. Again, we note the increasing resistivity shown to liquid-helium temperature.

It is also worth mentioning that thermopower studies on these samples indicate the absence of a lower transition for 5 at.% Ta or 0.1 at.% Ti doping.[17]

In order to see the effect of the impurities on the existence of superconductivity the low-temperature resistance of the samples was measured. These data are plotted, normalized to the 4.2-K value for the resistance, in Fig. 2. Here it is seen that the concen-

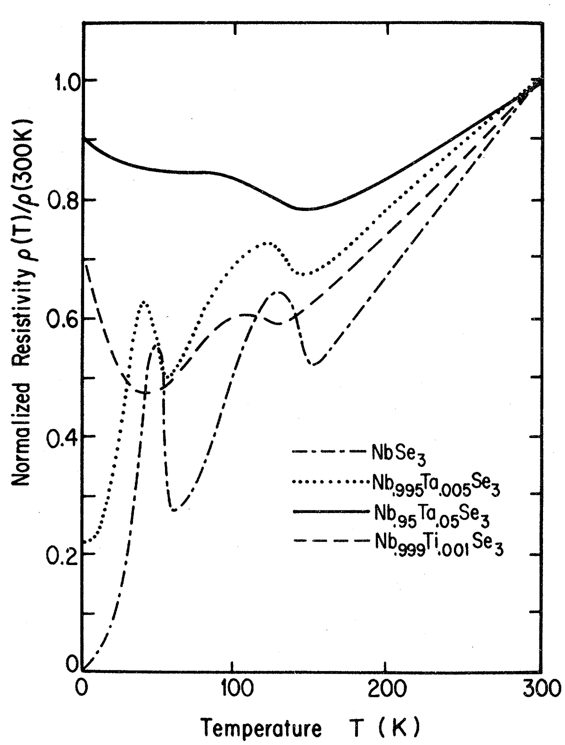

FIG. 1. Normalized resistivity as a function of temperature for pure and doped samples of $NbSe_3$.

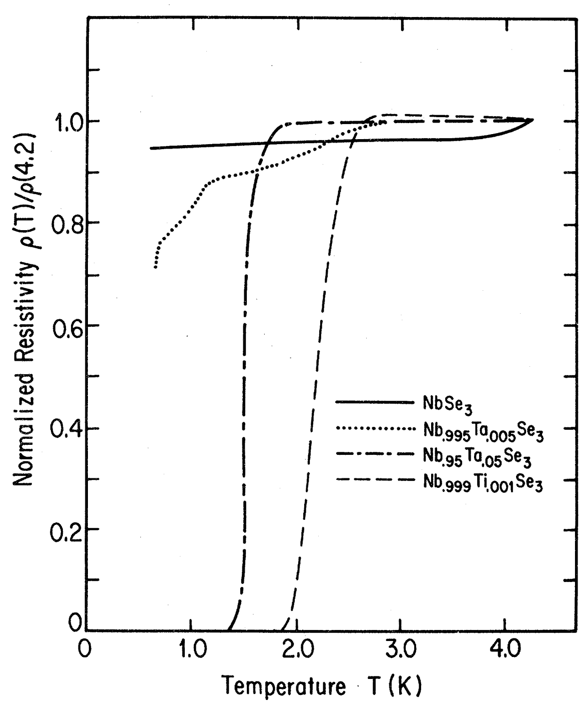

FIG. 2. Low-temperature resistivity of pure and doped samples of $NbSe_3$ showing the superconducting transition of Ti and 5 at.% Ta samples and the absence of a homogeneous transition in the 0.5 at.% Ta sample.

trations of impurities which correspond to suppressing the CDW have strong, complete superconducting transitions. Thus one has further verification of the suppression of superconductivity by CDW in this material. The pure $NbSe_3$ shows a knee in the resistance below 0.5 K. Since others have reported a resistance for $NbSe_3$ which is current-density dependent at low temperatures,[6,14] we have plotted in Fig. 3(a) the normalized resistivity for a variety of current densities. It can be seen that the resistance is ohmic for current densities up to 5×10^{-3} A/mm^2 and becomes increasingly more resistive for higher densities. For comparison, Fig. 3(b) shows data for the 0.1 at.% Ti sample. It can be seen that the critical current is about a factor of 10^3 greater in the Ti-doped sample.

This behavior is indicative of a very filmentary type of superconductivity in pure $NbSe_3$. This agrees with our preliminary results from magnetic susceptibility data where with 5 at.% Ta the magnetization versus field curve was found to be linear to several gauss. Buhrman *et al.*[14] on the other hand, see curvature in the *M* vs *H* curve in the milligauss range for pure $NbSe_3$. Thus from the magnetization at low temperatures one also sees that the doped $NbSe_3$ is a "better" bulk superconductor by a factor of 10^3. We then point out that an impurity concentration as low as 1-ppm Ti could account for what is seen in "pure" $NbSe_3$ if the impurities were inhomogeneously distributed in filaments with a higher concentration of ~0.1 at.%. Microprobe analysis of several of our samples indicate that inhomogeneities are often a problem.

In order to further investigate the superconducting state in the 5 at.% Ta-doped $NbSe_3$, the upper critical field was studied. In Fig. 4 the critical field is plotted as a function of temperature for fields oriented parallel and perpendicular to the conducting axis. The anisotropy of the critical field is seen to be independent of temperature. This is suggestive of the anisotropy being due to an anisotropic effective mass rather than sample-size limitations. To further verify this point, the critical field as a function of angle is plotted in Fig. 5. For an anisotropic effective mass one expects the angular dependence to go as[18]

$$\left(\frac{H\sin\theta}{H_\perp}\right)^2+\left(\frac{H\cos\theta}{H_\parallel}\right)^2=1\ , \qquad (1)$$

but if the anisotropy is due to sample-size limitations where the thickness of the sample is much less than the coherence length, the expected form is[19]

$$\left(\frac{H\sin\theta}{H_\perp}\right)+\left(\frac{H\cos\theta}{H_\parallel}\right)^2=1\ . \qquad (2)$$

The least-squares fit gives the former as a better fit. From the initial slopes of H_{c2} vs T one can calculate the coherence length parallel and perpendicular to the conducting *b* axis. This gives $\xi_\perp=1.2\times10^{-6}$ cm, while $\xi_\parallel=4.4\times10^{-6}$ cm, thus with the smallest sample dimension being of the order of 10^{-4} cm, one can safely say that the anisotropy is not due to sample-size limitations. From the measured anisotro-

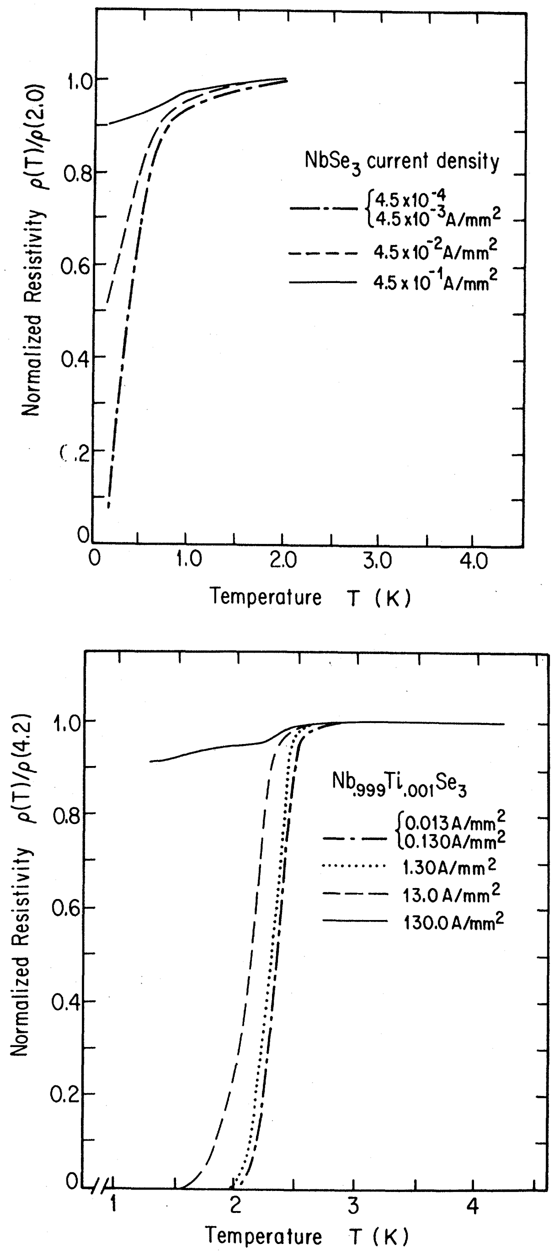

FIG. 3. (a) Normalized resistivity of pure $NbSe_3$ at low temperatures showing the effects of small currents. (b) Current dependence of the resistive superconducting transition of Ti-doped $NbSe_3$.

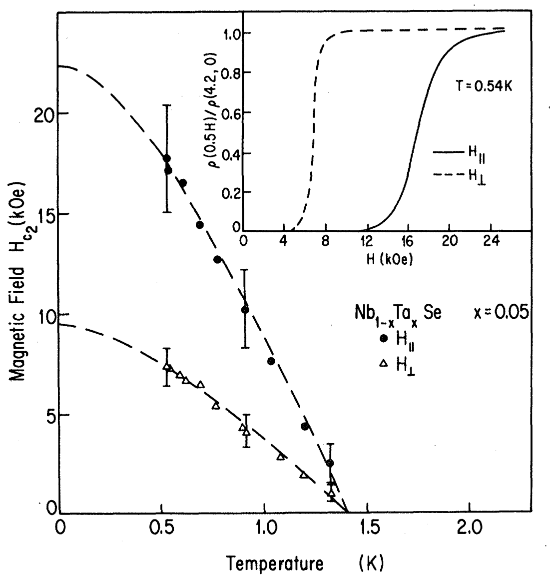

FIG. 4. Critical magnetic field parallel and perpendicular to the highly conducting direction for Ta-doped $NbSe_3$. Inset shows the resistive transitions as a function of magnetic field.

py in the critical field one obtains $m_{\perp}/m_{\parallel}=14$, which is in rough agreement with the value of 20 that Ong and Brill[20] found in the conductivity. It is also in agreement with the minimum value reported by Fleming *et al.*[21]

There is also a lack of curvature in H vs T which has been seen in materials where the sample size plays a part in the anisotropy.[22] The fact that the temperature dependence of the critical field has the same form for the parallel and perpendicular orientations remains, however, the best evidence for the effective-mass model.

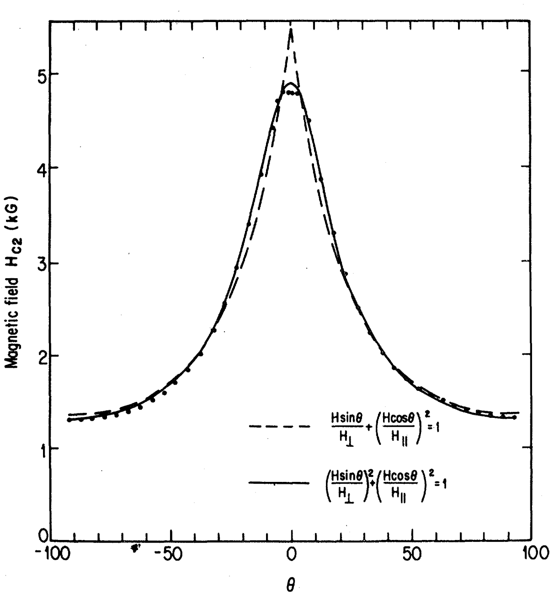

FIG. 5. Angular dependence of the critical magnetic field of 5 at.% Ta-doped $NbSe_3$ at 1.2 K. θ is parallel to the b axis.

The suppression of superconductivity by CDW's has been studied by several theorists. The theory of Bilbro and McMillan[2] considered a CDW gap opening up over only a fraction N_1/N of the Fermi surface. Their result for the transition temperature is

$$T_c^{N_2/N}T_{\rm CDW}^{N_1/N}=T_{c0}\ , \tag{3}$$

where $T_{\rm CDW}$ is the charge-density-wave transition temperature, T_{c0} is the superconducting transition temperature in the absence of the CDW, and T_c the superconducting transition temperature in the presence of the CDW. Since the CDW gap in $NbSe_3$ opens up over only part of the Fermi surface this theory should be applicable; however, including an anisotropic electron-phonon interaction which might be expected due to measured conductivity anisotropies—could be expected to change this equation. This result can be fitted to the pressure data of Haen *et al.*[6] and reasonable agreement is seen in the region where the assumption of a linear pressure dependence of $T_{\rm CDW}$ is valid (Fig. 6). Almost all of the reduction in T_c results from decrease in N_1. They found that for the lower CDW transition the transition temperature initially varied as $(59-4p)$ K where p is the pressure in kilobars. From the fractional increase in the resistance at $T_{\rm CDW}$ one can assume that the fraction of the Fermi surface destroyed by this CDW goes as $N_1/N=0.6-0.18p$; this has recently been confirmed by Briggs *et al.*[6] However, Briggs *et al.*[6] no longer find the same pressure depen-

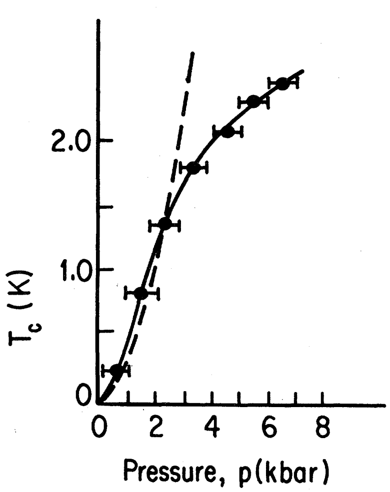

FIG. 6. Pressure dependence of T_c from the data of Ref. 6 (solid line) compared with the Eq. (3) (dashed line, see text).

dence for T_{CDW} or T_c. This could be due to the fact that the earlier measurements were done isotropically (in liquid) while the more recent ones were done using Teflon as the pressure medium.

The superconducting transition temperature when there is no CDW present is approximately 2.5 K. Thus Eq. (3) becomes

$$T_c^{(1-N_1/N)}(59-4p)^{N_1/N}=2.5$$

and one has T_c as a function of pressure. This is plotted in Fig. 6 and reasonable agreement is seen. Thus it appears that most of the change in T_c can be accounted for by the reduction in the density of states at the Fermi surface caused by the CDW gap. It is not necessary to have large changes in the electron-phonon interaction to account for the observable behavior.

Using the data of Monceau *et al.*[6] or our data on the T_c of Ti- and Ta-doped samples in conjunction with Eq. (3), one obtains a T_c of 10–20 mK for pure $NbSe_3$ at ambient pressure.

This number is not unreasonable with respect to the measured resistivity at low temperatures; however, no superconductivity has been seen to 10 mK (Haen *et al.*). The theoretical prediction can be off because it assumed an isotropic electron-phonon interaction which is not necessarily the case in $NbSe_3$.

We note that if pure $NbSe_3$ is assumed to have a superconduction transition temperature of ~ 1 K in the presence of the CDW transitions then from Eq. (3) it should have a T_c of ~ 15 rather than ~ 2.5 K when the CDW's are destroyed.

One question which remains unanswered is how the CDW's are destroyed by the impurities. Disorder can smear and suppress CDW transitions and nonmagnetic impurities can act as pair breakers (electron-hole pairs) for CDW's in much the same way that magnetic impurities suppress a superconducting transition.[23] However, in more recent experiments we have found that $NbSe_3$ samples which have been radiation damaged with doses which produce a much higher residual resistivity than the Ta- and Ti-doped samples *do* undergo CDW transitions and are not superconducting at low temperatures. We therefore suggest that scattering or momentum smearing are not the cause of the CDW suppression in these doped samples. A possible explanation is that the band structure of $NbSe_3$ makes the Fermi surface unusually sensitive to the electron density. Thus a sizable amount of isoelectronic atoms (Ta) or a small amount of nonisoelectronic atoms (Ti) could alter the delicate nesting of flat regions or saddle points on the Fermi surface. This would be consistent with the sensitivity for the CDW transitions to pressure.[6]

In summary, impurity doping of $NbSe_3$ suppresses the CDW, thereby allowing a transition to a superconducting state at low temperatures. The competition between superconductivity and CDW's results largely from a competition for the density of states at the Fermi level. It is seen that the Bilbro-McMillan theory for this competition fits $NbSe_3$ in a semiquantitative way. The knee in the resistance as a function of temperature for the pure samples can be explained by filamentary superconductivity caused by very small (1 ppm) amounts of impurities in the material. The contrast to bulk superconductivity is evidenced from the current density studies in the Ti-doped and pure $NbSe_3$. There is an intrinsic anisotropy in the superconducting properties of these materials resulting from anisotropic band masses as can be seen in the angular dependence of the critical field. Since the anisotropy in the critical field is of the same order of magnitude as that previously measured for the conductivity of the pure samples, it is seen that the anisotropy of this material is not greatly effected by the destruction of the CDW's. Comparison with radiation damage studies indicates that the effect of the impurities is not simply accounted for by an increased scattering.

We would like to acknowledge useful discussion with W. G. Clark, G. Gruner, T. Holstein, and P. Pincus. Research supported by National Science Foundation Grant No. DMR7908560 (P.M.C.), by ONR under Grant No. N00014-76-C-1078 (W.W.F.), and at USC under Grant No. DMR 79-05418. P.M.C. receives support from the A. P. Sloan Foundation, and W.W.F. from IBM.

[1]L. R. Testardi, Rev. Mod. Phys. 47, 637 (1975).
[2]G. Bilbro and W. L. McMillan, Phys. Rev. B 14, 1887 (1976).
[3]L. P. Gorkov, Zh. Eksp. Teor. Fiz.Pis'ma Red. 17, 525 (1973) [JETP Lett. 17, 379 (1973)]; L. P. Gorkov and O. N. Dorokhov, J. Low Temp. Phys. 22, 1 (1976).
[4]J. Friedel, J. Phys. Lett. 36, L-279 (1975).
[5]J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).
[6]P. Haen, G. Waysand, G. Bock, A. Waintal, P. Monceau, N. P. Ong, and A. M. Portis, J. Phys. (Paris) 37, C4-179 (1976); P. Monceau, J. Peyrand, J. Richard, and P. Molinie, Phys. Rev. Lett. 39, 161 (1977); A. Briggs, P. Monceau, M. Nunez-Regueiro, J. Peyrand, M. Ribault, and J. Richard, J. Phys. C 13, 2117 (1980).
[7]D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. 41, L95 (1980).
[8]J. Chaussy, P. Haen, J. C. Lasjaunias, P. Monceau, G.

Waysard, A. Waintat, A. Meerschant, P. Molinie, and J. Rouxel, Solid State Commun. 20, 759 (1976).
[9]T. Tsutsumi, T. Takagaki, M. Yamamoto, Y. Shiozaki, M. Ido, and T. Sambongi, Phys. Rev. Lett. 39, 1675 (1977).
[10]R. M. Fleming, D. E. Moncton, and D. B. McWhan, Phys. Rev. B 18, 5560 (1978).
[11]P. Monceau, N. P. Ong, A. M. Portis, A. Meerschant, and J. Roux, Phys. Rev. Lett. 37, 602 (1976).
[12]N. P. Ong, J. W. Brill, J. C. Eckert, J. W. Savage, S. K. Khanna, and R. B. Somoano, Phys. Rev. Lett. 42, 811 (1979).
[13]P. Haen, J. M. Mignot, P. Monceau, and M. Nunez-Regueiro, J. Phys. (Paris) 39, C6-703 (1978).
[14]R. A. Buhrman, C. M. Bastuscheck, J. C. Scott, and J. D. Kulick, in *Inhomogeneous Superconductors—1979,* edited by D. V. Gubser, T. L. Francavilla, S. A. Wolf, and J. R. Leibowitz, AIP Conf. Proc. No. 58 (AIP, New York, 1980).
[15]W. W. Fuller, P. M. Chaikin, and N. P. Ong, Solid State Commun. 30, 689 (1979).
[16]R. H. Dee, A. J. Berlinsky, J. F. Carolan, E. Klein, N. J. Stone, B. G. Turrell, and G. B. Street, Solid State Commun. 22, 303 (1977); R. H. Dee, D. H. Dollard, B. G. Turrell, and J. F. Carolan, *ibid.* 24, 469 (1977).
[17]P. M. Chaikin, W. W. Fuller, R. Lacoe, and N. P. Ong (unpublished).
[18]R. C. Morris, R. V. Coleman, and R. Bhandori, Phys. Rev. B 5, 895 (1972).
[19]M. Tinkham, Phys. Rev. 129, 2413 (1963).
[20]N. P. Ong and J. W. Brill, Phys. Rev. B 18, 5265 (1978).
[21]R. M. Fleming, J. A. Polo, and R. V. Coleman, Phys. Rev. B 17, 1634 (1978).
[22]L. J. Azevedo, W. G. Clark, G. Deutscher, R. L. Greene, G. B. Street, and L. J. Suter, Solid State Commun. 19, 197 (1976).
[23]J. Zittartz, Phys. Rev. 164, 575 (1967).