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Uniaxial-stress-induced superconductivity in organic conductors

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We report an interesting effect in organic conductors and superconductors: the inducement and/or enhancement of superconductivity by uniaxial compressive stress. Uniaxial stress induces superconductivity in a density-wave material and increases the transition temperature of a superconductor by a factor of 3. Analysis of the Shubnikov–de Haas effect shows an expansion of the in-plane unit cell with stress and an increase in effective mass when superconductivity is induced.

Superconductivity in organic conductors has been an active subject since the conjecture of Little concerning pairing mechanisms that might occur in highly anisotropic, linear chain organic materials.[1] Since Jerome and co-workers discovered superconductivity in $(TMTSF)_2PF_6$ under 6 kbar of hydrostatic pressure, the quest for higher T_c has become a driving force in organic conductor research.[2] The charge transfer complexes such as (BEDT-TTF)$_2X$ involve transfer of one electron from a pair of large BEDT-TTF organic donor molecules to the anion X. It is empirically observed that in those materials where superconductivity is present, the superconducting transition T_c scales with effective unit cell volume and with anion length.[3,4] Hence T_c may increase until instabilities set in and the material becomes insulating or impossible to synthesize under ambient conditions. At present, the highest transition temperature in charge transfer complexes series is κ-(BEDT- TTF)$_2$Cu[N(CN)$_2$]Cl, with a transition temperature of over 12 K.[5] Here a small pressure of 0.3 kbar is needed to stabilize the superconducting state over the insulating state.

The nature of superconductivity in such materials as κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Ref. 6) and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ (Ref. 7) is layered, and the critical fields and vortex dynamics are very anisotropic. When *hydrostatic* pressure is applied to these materials, T_c decreases very rapidly. For κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (T_c=10.4 K), $dT_c/dP=-3$ K/kbar,[8,9] and in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ (T_c=1 K) $dT_c/dP=-0.25$ K/kbar.[10] In both cases the effective mass determined from the Shubnikov–de Haas (SdH) effect also has a large negative dependence on pressure. Hence effective mass enhancement correlates with the existence and magnitude of T_c.

The purpose of the uniaxial stress study reported in this paper was to examine the role of anisotropy in the density-wave state of the material α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and the superconducting state of the isostructural material α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. These two compounds belong to the α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ (M=K, Tl, Rb, NH$_4$) isostructural family of charge transfer salts which has very thick ($\approx$7 Å) anion layers separating along the b axis the two-dimensional chevronlike arrangement of the donor molecules. The calculated Fermi surfaces for all four compounds are identical and consist of slightly warped cylinders at the corners of the Brillouin zone and two one-dimensional sheets running along the k_c direction.[4] There is no clear correlation in these salts between the M site in the anion complex, the unit cell volume, and the density-wave or superconducting ground state. Hence the fact that only α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ is a superconductor, and all others have density-wave ground states has remained a curious fact. Our study shows that uniaxial stress induces superconductivity in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and can therefore unify the ground-state behavior of these salts.

The method used to apply stress to these fragile single crystals has been previously described.[11] The concept is to

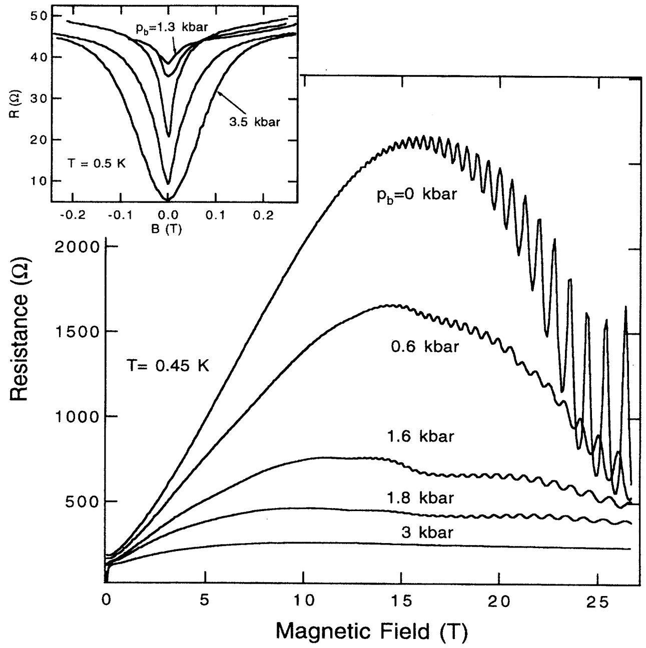

FIG. 1. Stress dependence of the magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$. Note the sharp drop around zero field in the 3 kbar trace. The fundamental Shubnikov–de Haas frequency α decreases linearly with stress at a rate of -20 ± 4 T/kbar (Ref. 13). Inset: detail of the magnetoresistance around zero field for a different sample in the 1.3–3.5 kbar stress range. Intermediate curves were measured at 1.6, 1.9, and 2.9 kbar.

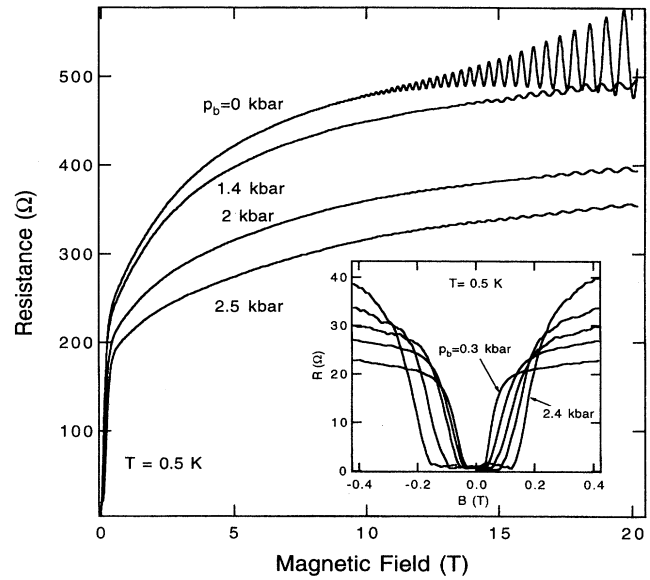

FIG. 2. Stress dependence of the magnetoresistance of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. Note the beat in the Shubnikov–de Haas oscillations at 15 T for the 2 kbar trace. The fundamental frequency α of the oscillations decreases linearly with stress at approximately -40 ± 8 T/kbar. Inset: detail of the magnetoresistance around zero field for a different sample in the 0.3–2.4 kbar stress range. Intermediate curves were measured at 1.0, 1.4, and 1.9 kbar.

encapsulate the single crystals in epoxy whose physical properties closely match those of the crystals and which compensates for the irregularities of the crystals' shape while allowing the stress to be transmitted unidirectionally. In the present experiment the magnetic field, compressive stress, and current were all along the cross-planar (b axis) direction of the samples studied. A standard four-terminal ac method with currents of 10 μA was used to monitor the resistance. In Fig. 1 the results for α-(BEDT-TTF)$_2$KHg(SCN)$_4$ are presented. Here, for zero stress, the characteristic magnetotransport behavior of the density-wave state is seen: finite zero-field resistance, large magnetoresistance with a maximum at about 15 T, SdH oscillations with a frequency $\alpha=668\pm6$ T, and a rapid drop in the resistance as the so-called "kink field" (about 22.5 T) is approached. As the stress is increased, the SdH frequency decreases linearly, the density-wave behavior decreases, and at about 1.3 kbar (coinciding with the total disappearance of the density-wave characteristics) a sharp drop in the zero-field resistance appears. By 3 kbar, a superconducting critical field behavior is well developed, and the magnetoresistance is strictly sublinear in magnetic field. Hence the density-wave state has been removed in favor of a superconducting state, in marked contrast to the metallic state induced with hydrostatic pressure.[12] We note also that there is a slow oscillation in the background magnetoresistance which appears at finite values of stress,[13] an effect similar to that seen in hydrostatic pressure measurements of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$.[14] We believe slow oscillations are a result of imperfect nesting of the quasi-one-dimensional bands.

In Fig. 2 similar measurements on α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ are presented. The critical field at ambient pressure is clear and, since there is no density-wave state, the magnetoresistance is always sublinear with field. Here again, the contrast with the effects of hydrostatic pressure (which rapidly destroys superconductivity) is profound. We find that T_c and H_{c2} increase by more than a factor of 3 over their ambient pressure values with uniaxial stress. Superimposed on the background magnetoresistance are SdH oscillations with a fundamental frequency α that decreases linearly with stress from a zero stress value of 588 ± 6 T; beating is also present for certain stresses.

The temperature dependence of the resistance for both materials vs stress is shown in Fig. 3. In the case of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ the resistance never completely reaches zero down to the lowest attained temperature (0.5 K), and the interpretation of the stress effect as induced superconductivity is complicated by the presence of another effect which is seen under ambient conditions at lower temperatures. Below about 0.1 K there is a drop in resistance, seen in all of the density-wave materials, which has been interpreted as filamentary superconductivity,[15] or as layered superconductivity in competition with the sheet resistance associated with the coexisting density-wave state.[16] This effect is very sensitive to current density, and nominally currents of 10 μA in a mm^2 sample destroy the effect. In contrast, our measurements were performed with 10 μA currents and the drops in resistance were always accompanied by a shift in the phase of the lock-in voltage. We have made an extensive investigation of the ambient pressure, low-

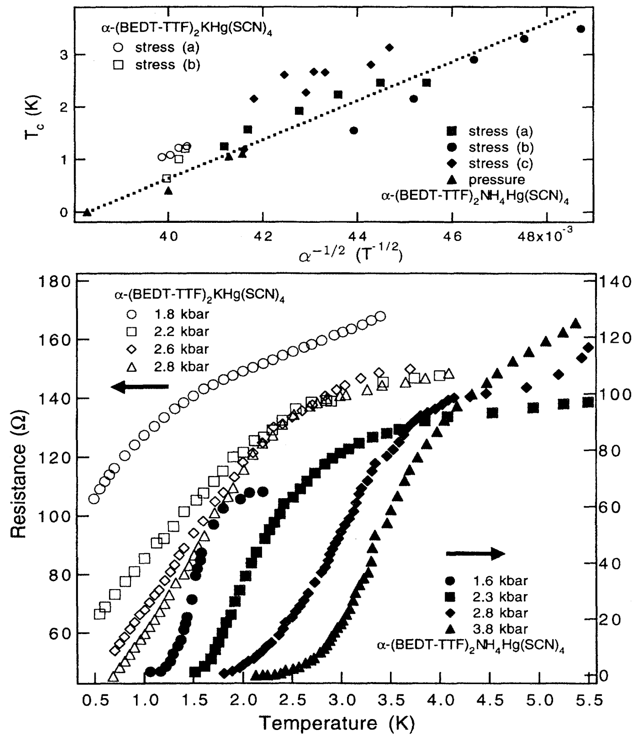

FIG. 3. Bottom graph: Resistance versus temperature of both salts for various stress values. Filled symbols are for α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, right-hand resistance scale; open symbols for α-(BEDT-TTF)$_2$KHg(SCN)$_4$, left-hand scale. Top graph: Plot of T_c versus the square root of the inverse fundamental SdH frequency ($\sqrt{1/\alpha} \propto 1/k_F$) for various samples. Slope of the dashed line is 376 K T$^{1/2}$. Hydrostatic pressure data for α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ from Ref. 10.

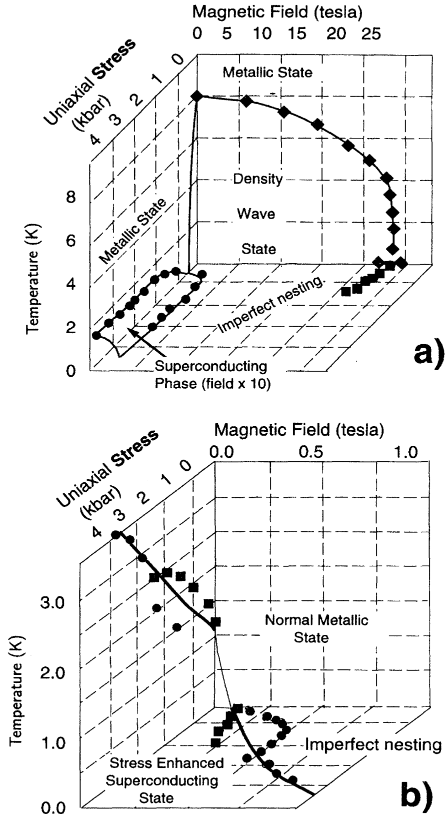

FIG. 4. Temperature–magnetic field–b axis stress phase diagrams: (a) α-(BEDT-TTF)$_2$KHg(SCN)$_4$. (b) α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. Different symbols (circles and squares) denote data from different samples. The points (diamonds) that mark the temperature-field density wave boundary in (a) are from Ref. 12.

temperature effect in α-(BEDT-TTF)$_2$RbHg(SCN)$_4$ and concluded that this effect is more closely related to weak antilocalization, which has a very explicit magnetoresistance near zero field.[17] The weak antilocalization curves that fit the low-temperature data well cannot be adjusted to fit the stress induced effects observed in α-(BEDT-TTF)$_2$KHg(SCN)$_4$. Rather, the resistance curves shown in Figs. 1 and 3 are characteristic of type-II superconductor behavior, although thermodynamic measurements are necessary to confirm the bulk nature of superconductivity. In the case of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, the enhancement of the ambient pressure superconducting state is unambiguous (see Fig. 4).

We may gauge the relation of T_c to the in-plane lattice expansion by plotting T_c vs the root of the inverse SdH frequency α which equals $\sqrt{2e/\hbar c}/k_F$ for the simple case of a circular orbit [see Fig. 3 (top)]. Here we find that *both* materials follow a systematic trend of increasing T_c with real space expansion in the a-c plane. This should be compared to a similar trend in other organic superconductors involving increasing unit cell dimensions.[4]

The uniaxial stress dependence of the effective mass (m^*) provides crucial information about the superconductivity enhancing mechanism. We have applied the Lifshitz-Kosevich formalism[18] to the temperature dependence of the SdH oscillations to obtain the stress-dependent effective mass. Here the background magnetoresistance, which changes with stress and temperature, has been taken into account in our determinations. For α-(BEDT-TTF)$_2$KHg(SCN)$_4$ there is a clear correlation between m^* and the appearance of superconductivity. The effective mass increases from a zero stress value of $1.4\pm0.1m_0$ to $1.7\pm0.1m_0$ by 1.6 kbar, when superconductivity has set in. Further increase in stress does not raise m^* further, although T_c is rising. A similar situation is observed in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, with m^* remaining locked at $2.1\pm0.1m_0$ throughout the stress range investigated, even though T_c increases threefold.

An increase of the density of states at the Fermi level (on which both T_c and m^* depend) with stress is consistent with a decrease in the conduction bandwidth (t_b). In the tight-binding model used for band structure calculations in these salts, t_b is proportional to the transfer integrals between the BEDT-TTF molecules. Uniaxial compressive stress applied in the cross-planar direction would stretch the in-plane dimensions (Poisson's effect), thereby lowering t_b. However, the rapid increase in m^* when superconductivity appears in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ cannot be ascribed to a band effect alone since the bare band mass is too small to begin with [less than m_0 for zero stress (Ref. 4)] and it is simply inversely proportional to t_b. The smooth decrease in α, which in a somewhat indirect way is a measure of the bandwidth, is proof that there is no sudden jump in t_b for any particular stress value.

The rapid increase in m^* must therefore be accounted for by many-body effects, which contribute to the effective mass measured in the SdH effect. We know from the stress induced slow oscillations in the magnetoresistance that the nesting condition of the open orbit band is most likely affected. Here small changes in lattice and band parameters may play a stronger role due to the sensitivity of the nesting condition to Fermi-surface topology. Hence stress must be influencing a system very close to an instability. The fact that the two isostructural materials studied have different ground states under ambient conditions reflects how close the nesting instability is. Since the nesting condition involves pairing and electron-phonon and electron-electron interactions, this may provide the connection between stress and superconductivity. The effect of stress in our experiment, which is to effectively "pull apart" the in-plane unit cell, may explain why hydrostatic pressure does not produce the same effects. More work will be necessary to identify the mechanism which enhances the superconducting ground state.

In conclusion, we have observed that uniaxial stress applied along the least conducting direction of α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ organic conductors unifies their ground-state behavior by greatly enhancing the tendency for superconductivity. This is in contrast to the effects of hydrostatic pressure on the same materials. Analysis of the SdH effect shows that stress expands the in-plane unit cell and increases the effective mass substantially prior to the appearance of superconductivity. The enhancement of the superconducting transition is consistent with the mass enhancement and the increase of the density of states at the Fermi level due to the decreasing bandwidth—but this alone cannot account for the large changes observed in T_c and m^*. We believe the most likely cause of the effect may be the influence of stress on the nesting condition which in turn is directly related to the pairing condition and electron interactions. Susceptibility, heat-capacity, and angular-dependent studies are needed to fully explore these new effects.

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[1] W. A. Little, Phys. Rev. **134**, A1416 (1964).

[2] For a general survey of organic conductor physics, see T. Ishiguro and K. Yamaji, in *Organic Superconductors*, edited by H. K. Lotsch *et al.*, Springer Series in Solid State Sciences Vol. 88 (Springer-Verlag, Berlin, 1990); many details of organic conductor chemistry and physics are treated by J. M. Williams *et al.*, *Organic Superconductors* (Prentice-Hall, Englewood Cliffs, N.J., 1992).

[3] J. M. Williams *et al.*, Prog. Inorg. Chem. **35**, 51 (1987).

[4] H. Mori *et al.*, Bull. Chem. Soc. Jpn. **63**, 2183 (1990).

[5] J. M. Williams *et al.*, Inorg. Chem. **29**, 3262 (1990).

[6] P. A. Mansky, P. M. Chaikin, and R. C. Haddon, Phys. Rev. B **50**, 15 929 (1994).

[7] J. S. Brooks *et al.*, Synth. Met. **70**, 839 (1995).

[8] J. E. Schirber *et al.*, Physica C **152**, 157 (1988).

[9] J. Caulfield *et al.*, J. Phys. Condens. Matter **6**, 2911 (1994).

[10] J. S. Brooks *et al.* (unpublished); X. Chen, Ph.D. thesis, Boston University, 1993.

[11] C. E. Campos *et al.*, Rev. Sci. Instrum. **66**, 1061 (1995). For other uniaxial stress studies on organic conductors see also M. Tokumoto *et al.*, Mol. Cryst. Liq. Cryst. **181**, 295 (1990); H. Kusuhara *et al.*, Solid State Commun. **74**, 251 (1990).

[12] J. S. Brooks *et al.*, Phys. Rev. Lett. **69**, 156 (1992).

[13] C. E. Campos *et al.*, Synth. Met. **70**, 803 (1995).

[14] S. J. Klepper *et al.*, Phys. Rev. B **48**, 9913 (1993).

[15] H. Ito *et al.*, Solid State Commun. **85**, 1005 (1993).

[16] H. Ito *et al.*, Synth. Met. **70**, 899 (1995).

[17] J. S. Brooks *et al.*, Appl. Supercond. **2**, 1 (1995).

[18] D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge University Press, Cambridge, 1994).