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Superconductivity in a New Family of Organic Conductors

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Evidence for superconductivity in $(BEDT-TTF)_4(ReO_4)_2$ [where BEDT-TTF is bis(ethylenedithiolo)tetrathiafulvalene] near 2 K for pressures above 4 kbar is reported. This is the first unambiguous observation of superconductivity in a sulfur-donor organic system. At higher pressures the transition temperature decreases rapidly, $dT_c/dP \sim -0.3$ K/kbar. At low pressures this material exhibits a first-order metal-insulator transition, postulated to result from a change in the arrangement of the anions which are ordered at room temperature.

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We report the discovery of superconductivity in a new family of organic conductors based on a sulfur-donor organic molecule. This is only the second organic system in which superconductivity has been observed. The overwhelming majority of organic conductors are unstable at low temperatures to periodic lattice distortions leading to an insulating ground state.¹ Over the past decade extensive studies on a wide range of structural and chemical types of organic linear-chain systems were carried out with the important aim of suppressing these instabilities and stabilizing a low-temperature metallic or superconducting state. Recently this goal was finally achieved for several members of the $(TMTSeF)_2X$ family of compounds (where TMTSeF is tetramethyltetraselenafulvalene and X is, for example, PF₆, TaF₆, ReO₄, ClO₄) with the observation of superconductivity near ~1 K for pressures above some critical pressure, $P_c \sim 1$ bar to 12 kbar.²⁻⁵ The reason why these particular compounds become superconducting is unclear, although it may be related to their atypical crystal and chemical structure. Indeed the related isostructural series of materials, $(\text{TMTTF})_2 X$ (the TMTTF molecule is identical to TMTSeF but with the Se replaced by S) has similar phase diagrams but with substantially higher P_c (~25-45 kbar) and no conclusive evidence of superconductivity.^{6,7} It is therefore clearly of interest to find other organic systems which are superconducting in order to better understand the mechanism for organic superconductivity and perhaps raise T_c .

Recently Saito *et al.*⁸ prepared a ClO₄ salt of bis (ethylenedithiolo) tetrathia fulvalene (BEDT-TTF) with inclusion of some solvent in the crystal structure. Concurrently we have electrochemically⁵ synthesized various salts of BEDT-TTF.⁹ Of interest here are the ReO_4 salts. A number of distinct crystallographic phases were obtained and characterized by x-ray crystallography, chemical analysis, and ESR. From tetrahydrofurane (THF) three phases were found; thin needles of chemical formula $(BEDT-TTF)_4$ - $(\text{ReO}_4)_2(\text{THF})$, and two phases growing as plates of form $(BEDT-TTF)_6(ReO_4)_4$ and $(BEDT-TTF)_4$ - $(ReO_4)_2$. All three phases could easily be identified from their distinct morphologies. Chemical and x-ray analysis show that neither plate phase includes solvent. The electrical properties and behavior under pressure of these phases are very different.

The 4:2 salt $(BEDT-TTF)_4(ReO_4)_2$ becomes superconducting below ~2 K for pressures above ~4 kbar. In Fig. 1 we present evidence for superconductivity in this compound from four-probe resistance measurements at 7 kbar as a function of magnetic field. The resistance drops to zero within experimental accuracy below the transi-



FIG. 1. Resistance [normalized to R(3 K)] vs temperature curves along the *a* axis of (BEDT-TTF)₄(ReO₄)₂ in zero field and for various magnetic fields applied along the transverse c^* direction.

tion; $T_c \sim 1.4$ K, defined as that temperature where *R* is half the normal value. At 4 kbar we observe an onset of superconductivity near 2 K although the transition is considerably broadened. The possibility that the superconductivity we observe is filamentary can be ruled out because we measure critical current densities of order 0.1 A/mm², which are comparable to those found in the (TMTSeF)₂X superconductors² for which the bulk nature of this phenomenon is well established⁵.

The structure of $(BEDT-TTF)_4(ReO_4)_2$ is shown in Fig. 2 and bears some similarity to that of the $(TMTSeF)_2 X$ salts.⁵ In particular the BEDT-TTF molecules are "zig-zagged" along the a axis, providing cages in which the ReO_4 anions sit and so determining the stoichiometry of the material; there is the possibility of strong S-S bonding between BEDT-TTF molecules along the b direction but direct interactions between these molecules in the c direction are clearly much weaker (note that the BEDT-TTF molecule contains twice as many S atoms as the TMTTF molecule). The structure belongs to space group $P\overline{1}$ with unit cell a = 7.78Å, b = 12.59 Å, c = 16.97 Å, $\alpha = 73.01^{\circ}$, $\beta = 79.89^{\circ}$, $\gamma = 89.06^{\circ}$, V = 1565 Å.³ However, there are two important differences compared with the structure of the $(TMTSeF)_2 X$ salts.^{5,10} Firstly, whereas the TMTSeF molecule is almost planar, the terminal



FIG. 2. Projected left-eye view of the structure of $(BEDT-TTF)_4(ReO_4)_2$ along the organic molecular stacking axis, *a*, showing the BEDT-TTF molecules (shaded and open circles correspond to S and C atoms, respectively; H atoms are not shown) and ReO₄ anions.

methylene (CH₂) groups at either end of the BEDT-TTF molecule are positioned well out of the plane of the rest of the molecule. Secondly, the ReO_4 anions are ordered at room temperature; in none of the TMTSeF or TMTTF salts is this the case.⁵

The room-temperature *a*-axis conductivity of $(BEDT-TTF)_4(ReO_4)_2$ at 1 bar is ~200 (Ω cm)⁻¹, comparable to the most conducting of the (TMTTF)₂X salts.¹¹ Conductivity was measured with use of a standard four-probe lock-in technique, with silver paint contacts of resistance a few ohms. Data at 1 bar are shown in Fig. 3; the material shows metallic behavior to 81 K where there is a metal-insulator (MI) transition. The resistance abruptly increases by two orders of magnitude at $T_{\rm MI}$ demonstrating that the transition is of predominantly first-order character. The resistance is activated below the transition with an activation energy, Δ , given by $2\Delta/kT_{\rm MI}$ ~13. Measurements of conductivity anisotropy in the a-b plane were made with the Montgomery geometry giving a value at 300 K of $\sigma_a/\sigma_b \sim 20$. This ratio varies little as the temperature is decreased to $T_{\rm MI}$, and is comparable with the generally agreed value of the analogous anisotropy ratio in the (TMTSeF)₂X salts.⁵ Measurements were made as a function of pressure in a simple Be-Cu piston cylinder clamp cell, with the sam-

ples contained in a Teflon cell filled with heptane. As pressure is increased the MI transition temperature falls and above ~7 kbar is suppressed. A resistance curve at 7 kbar is given in Fig. 3 with data below 3 K shown earlier in Fig. 1. The sample has a high resistance ratio of ~ 300 , indicative of good crystal quality. The resistance does not saturate at low temperatures but continues to fall to ~ 2 K below which temperature the resistance drops to zero as previously described. The normal resistance is restored with the application of a magnetic field. Data are shown in Fig. 1 for field applied along the c^* direction, giving a critical field of ~800 G. The critical field is about 2 times higher in the b^* direction. All these features are also seen in the $(TMTSeF)_{2}X$ materials to a similar degree. There is a substantial transverse magnetoresistance, but in contrast with the $(TMTSeF)_{2}X$ salts it is largest along the b^* direction. These results will be described in more detail elsewhere. Similar results have been seen in about a dozen crystals for various applied pressures and are summarized in the phase diagram shown in Fig. 4. In particular the superconducting transition temperature falls rapidly with pressure (dT_c/dP) ~ -0.3 K/kbar). This is a very unusual effect whose origin is unclear. The phase diagram suggests that T_c is somewhat depressed in the critical region (4-6 kbar) perhaps through competi-



FIG. 3. Resistance vs temperature curves for $(BEDT-TTF)_4(ReO_4)_2$ at 1 bar and 7 kbar. The resistance is normalized with respect to R(300 K, 1 bar) and a value of $d\sigma/dP$ of 20%/kbar has been used to normalize the high-pressure data.



FIG. 4. Phase diagram of $(BEDT-TTF)_4(ReO_4)_2$. The shaded region corresponds to that in which large hysteresis is observed on cooling and warming. The open circles correspond to onset of superconductivity.

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tion with anion ordering, a mechanism previously postulated in the (TMTSeF)₂X system.³ For pressures close to 6 kbar there can be a substantial increase in resistance well above T_c and the superconducting transition is considerably broadened. Moreover in this pressure region the resistance shows substantial hysteretic effects similar to those previously seen in $(TMTSeF)_{2}ReO_{4}$ (Ref. 12) and associated with anion ordering. Changes in the ESR spectrum at T_{MI} are also similar to those seen at anion ordering transitions in the $[TMTSe(T)F]_2X$ salts. It thus seems likely that the MI transition seen below ~ 7 kbar in the BEDT-TTF salt is associated with some kind of anion rearrangement, consistent with the high value of $2\Delta/kT$ mentioned above.

In summary, we have found superconductivity in a member of a new class of organic conductors based on a sulfur donor, BEDT-TTF. At low pressures $(BEDT-TTF)_4(ReO_4)_2$ exhibits a metal-insulator transition which we suggest is associated with some kind of anion rearrangement. Above and in a critical pressure regime (~4-6 kbar) superconductivity is observed with onset of superconductivity near 2 K at the lowest pressures. T_c is depressed in the critical pressure regime perhaps through competition with the low-pressure insulating instability and thus the possibility of higher superconducting transition temperatures in other BEDT-TTF salts cannot be ruled out. The variety of BEDT-TTF: X phases may permit the correlation of the existence of superconductivity with a particular structural type. This is an important distinction from the $(TMTSeF)_2 X$ family of compounds for which only a single phase is known.

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