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OBSERVATION OF THE MEISSNER EFFECT IN THE HIGH-T_c (PRESSURE-) PHASE OF THE ORGANIC SUPERCONDUCTOR β-$(BEDT\text{-}TTF)_2I_3$

H. Veith, C.-P. Heidmann, F. Gross, A. Lerf and K. Andres
Walther-Meissner-Institut für Tieftemperaturforschung
D-8046 Garching, FRG

and

D. Schweitzer, Max-Planck-Institut für Medizinische Forschung
D-6900 Heidelberg, FRG

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It is shown that the recently found superconducting state below 6 K in β-$(BEDT\text{-}TTF)_2I_3$ under a pressure of 1.5 kbar is diamagnetic and exhibits Meissner effects of up to 24 %, indicating that superconductivity is a true volume effect in these crystals. In contrast, no traces of diamagnetism are found in iodine doped α-$(BEDT\text{-}TTF)_2I_3$, for which resistively observed superconducting transitions in the vicinity of 3 to 5 K have also been reported.

The discovery of superconductivity (SC) in the charge transfer salt $(BEDT\text{-}TTF)_2I_3$ /1-3/ promised to be especially interesting since this compound can crystallize in several different structures /4/. Experience has since shown that the occurrence of SC not only depends on structure /4/, but also sensitively on pressure /5/ as well as on the iodine stoichiometry /6,11/. While the α-phase exhibits a metal-insulator transition at 137 K /7/, the β-phase remains metallic and becomes SC below 1.2 K. Upon application of mild pressures, T_c first decreases somewhat /8/, then abruptly increases to around 8 K at a critical pressure of about 1 kbar and subsequently decreases again with increasing pressure /5/. It is also reported that part of this "high-T_c" SC phase can be retained at zero pressure after suitable pressure - and temperature cycles /9/, or else obtained from the iodine-richer ε-phase by vacuum-annealing of ε-phase crystals /6/.

Most of these observations were made by means of resistivity measurements and thus yield little indication about the volume fraction of the SC-phase. This information can only be obtained from specific heat measurements, or, albeit less accurately, from observing the Meissner effect (i.e. the degree of magnetic flux expulsion in the SC state). Meissner effects, on which we report in this note, are generally reduced by the omnipresent flux pinning effects, especially in non-homogeneous samples. They usually yield, nevertheless, a lower bound on the SC volume fraction of the material in question, with the exception of some rather special microscopically inhomogeneous distribution of SC regions (see below). They are thus useful in deciding whether a resistively observed transition is caused by only a minute SC volume fraction or not.

Our Meissner effect apparatus consists of a simple d.c. SQUID magnetometer in a cryostat of the top-loading type, in which the samples can be moved between two oppositely wound search coils. The measuring field is generated by a SC solenoid with a heatable NbTi shield inside it for field stabilization. The search coils are wound on the outside of an insert dewar and always remain at 4.2 K, while the temperature of the samples inside can be varied by a regulated heated gas flow from 1.2 K up to 30 K. Measurements are taken in constant fields as a function of temperature. Besides the Meissner effect, the diamagnetic SC shielding signal resulting from switching on a field can also be observed in the following manner: The sample is pulled out of the field region, warmed up, then cooled down again in the He-gas stream and pushed back into the field region. Both Meissner and shielding signals are compared to those of a perfect SC (tin) of similar sample size and shape. Measurements under pressure were done in a small ice-bomb. It consists of a Be-Cu cylinder (0.5 cm dia., 1.5 cm long) with a 0.2 cm bore for sample space and threaded on top for a 0.3 cm screw so that it can be sealed by means of Teflon tape. When filled with water, the cell generates a pressure around 2 kbar (at 4.2 K).

Lower freezing pressures can be generated by mixing the water with suitable amounts of glycerine.

The crystals used were grown in the conventional way by electrochemical deposition. It is known that the α-phase of (BEDT-TTF)$_2$I$_3$ grows easier than the β-phase. Using trichloroethane as a solvent, however, we were also able to grow β-phase crystals only /10/.

Fig. 1 shows results obtained on a crystal of β-(BEDT-TTF)$_2$I$_3$ under pressure of 1.5 kbar which are typical of crystals grown in the abovementioned way. Plotted are the observed Meissner and shielding susceptibilities, as percentage of those observed for a similar size tin sample, in different applied fields, versus temperature.

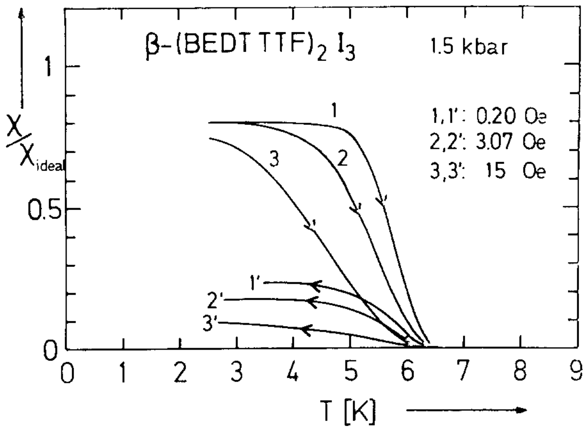

Fig. 1: Observed d.c. diamagnetic shielding (curves 1, 2, 3)- and Meissner (curves 1' 2' 3') susceptibilities in β-(BEDT-TTF)$_2$I$_3$ in different applied fields.

Since the SC state of the crystals is very anisotropic, with critical supercurrent densities in the c*-direction much smaller than in the other two principal directions, the field orientation was always chosen approximately parallel to the c*-direction. From past experience, flux pinning effects are minimized for this orientation, especially in small fields. It can be seen that the SC transition is fairly broad and that both the Meissner and the shielding signals are strongly field dependent even in small fields. This is undoubtedly due to the combined effect of both an inhomogeneous SC state which is also strongly type II in character. It should be mentioned that the results obtained on β-phase crystals grown in the previously described manner (i.e. using tetrahydrofurane as a solvent during electrolysis) are very similar to those shown in Fig. 1. Previous measurements of the lower critical field in the zero pressure SC state of the same material have indicated a value of H_{c1} as low as 0.36 Oe /3/. In other words, the decrease of the diamagnetic shielding susceptibility in fields above $\sim$ 1 Oe is in part due to the effect of flux penetration in the type II state and in part due to the breakdown of Josephson supercurrents connecting superconducting and normal regions. The fact that the shielding signals in Fig. 1 never exceed 80 % of full diamagnetic shielding may also result from a misalignment between the field- and the c*-direction.

The largest Meissner effect is observed in the lowest applied field and amounts to 24 %. This would normally indicate that the SC volume fraction must be at least that large. In view of the nearly twodimensional nature of the SC state in this crystal, however, we have to add one possible exception to this interpretation: If, say, only individual a-b planes (or adjacent groups of planes) were SC and were separated (in the c*-direction) by larger groups of normal-conducting a-b planes, then demagnetization effects could mimic a fractional Meissner effect which could be considerably larger than the actual SC volume fraction of the crystal.

We have also investigated the influence of iodine stoichiometry by exposing the β-phase crystals to iodine vapor before pressurizing and cooling them. We find that for an one hour-exposure, the SC transition sharpens and slightly shifts up in temperature, while the size of the transition remains unchanged. This is shown in Fig. 2. After removing the pressure from both the as grown as well as the iodized samples, we have never observed any leftover diamagnetic traces of the 6 K-SC transition.

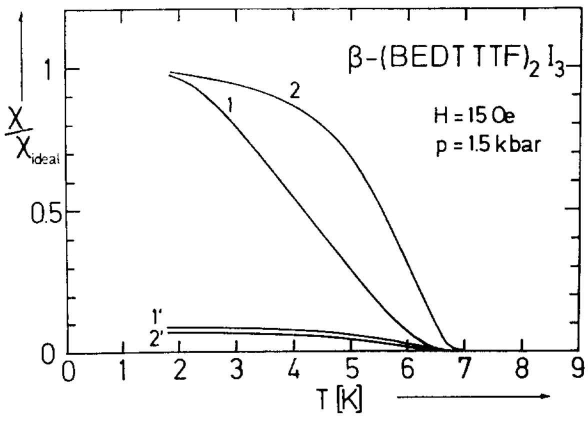

Fig. 2: Observed d.c. diamagnetic shielding (curves 1, 2)- and Meissner (curves 1' 2') susceptibilities of an as grown (1, 1') and iodine treated (2, 2') crystal of β-(BEDT-TTF)$_2$I$_3$ in a field of 15 Oe.

Guided by the previous observation of traces of SC in iodine-doped crystals of the α-phase of (BEDT-TTF)$_2$I$_3$ /11/, we have also searched for diamagnetic signals in α-phase crystals so treated, both at zero pressure as well as at 1.5 kbar. Iodine exposure times at room temperature ranged from 1/2 to 1 1/2 hours. During this treatment, the platelet-like crystals typically started warping themselves after about the first 15 min. However, no diamagnetic traces of SC transitions were ever observed in the temperature range above 1.2 K.

In summary, we have shown that the previously observed "high-T_c" superconductivity in β-(BEDT-TTF)$_2$I$_3$ under pressure is a genuine property of a large fraction of the crystal volume, at least when the above-mentioned rather special microscopic distribution of SC and normal regions is exempted. The homogeneity of the SC state can be improved somewhat by increasing the iodine content of the crystals. The question as to the cause of the sudden increase in T_c at the critical pressure in the β-phase, however, still remains to be answered.

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