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COMMUNICATIONS

Published on Web 05/21/2002

An Indication of Magnetic-Field-Induced Superconductivity in a Bifunctional Layered Organic Conductor, κ-(BETS)$_2$FeBr$_4$

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Received March 1, 2002

Hybrid systems consisting of the conducting layers of organic donor molecules and the magnetic layers of inorganic anions have been focused on as possible bifunctional materials, whose conducting properties can be tuned by controlling the magnetic state of the anion layers on an application of magnetic fields. The famous examples of magnetic conductors so far reported are the paramagnetic superconductor β''-(BEDT-TTF)$_4$(H$_2$O)Fe(C$_2$O$_4$)$_3$](C$_6$H$_5$CN)[1] and the ferromagnetic metal (BEDT-TTF)$_3$[MnCr(C$_2$O$_4$)$_3$][2] [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]. We have investigated BETS conductors, λ- and κ-(BETS)$_2$FeX$_4$ (X = Cl and Br) [BETS = bis(ethylenedithio)tetraselenafulvalene],[3] and reported several interesting properties, such as the novel magnetic-field-induced superconductivity under very high magnetic field (18 T < H < 41 T) in λ-(BETS)$_2$FeCl$_4$, which is caused by the Jaccarino−Peter compensation effect between the applied external magnetic field and the internal magnetic field by the Fe^{3+} spins.[4,5] On the other hand, we have reported the first antiferromagnetic (AF) organic superconductor, κ-(BETS)$_2$FeBr$_4$, which consists of the two-dimensional superconducting layers of the BETS semications and the insulating layers of the $FeBr_4^-$ anions.[6] The $FeBr_4^-$ anions exhibited metamagnetic behavior, that is, the Fe^{3+} spin system transformed into a forced-ferromagnetic state above 1.6 T when the field was applied parallel to the easy-axis of the AF ordering (//a axis). κ-(BETS)$_2$FeBr$_4$ showed the transition from the paramagnetic metal phase to the AF metal phase at the Néel temperature (T_N = 2.5 K), then underwent the transition to the AF superconducting phase at the critical temperature of T_c = 1.1 K. Here we report the magnetoresistance of κ-(BETS)$_2$FeBr$_4$ up to 15 T and the observation of the onset of the magnetic-field-induced superconductivity as the cooperative phenomena between the superconductivity and magnetism.

Plate-shaped crystals of κ-(BETS)$_2$FeBr$_4$ were prepared according to the literature.[6] The ac electrical resistivities were measured parallel to the a axis with electric currents along the a axis by a four-probe technique. The axis of the crystal was carefully oriented to the applied magnetic field because the magnetic-field-induced superconductivity is very sensitive to the inclination from the conducting plane. The resistivity measurements were performed up to 2 T to confirm the field-induced transition between the AF superconducting state and the forced-ferromagnetic metal state. As shown in the upper inset of Figure 1a, with an increase of the applied magnetic field at 0.58 K, the resistivity suddenly increased at about 1.6 T for the magnetic field applied parallel to the a axis (// easy-axis), and the system recovered its metallic state. This field of the superconducting destruction just corresponds to the metamagnetic transition field of the Fe^{3+} spin system. These results

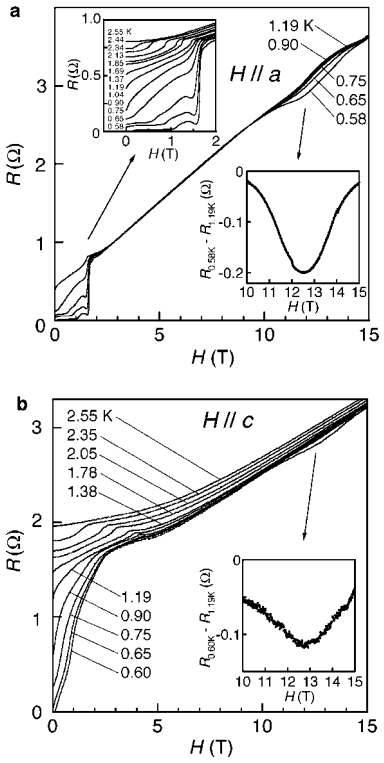

Figure 1. Magnetic field dependence of the magnetoresistance up to 15 T at the indicated temperatures in the figures with an application of the magnetic field in parallel with (a) the a axis and (b) the c axis. The upper inset of (a) is the data measured between 0 and 2 T. The lower insets are the resistivity differences between the data at 1.19 K and at the lowest measured temperature [(a) 0.58 K, (b) 0.60 K].

suggest that the internal field originated from the AF coupling between the π electrons and the ferromagnetically aligned Fe^{3+} spins, which was sharply induced at 1.6 T, destroyed abruptly the superconducting state. Therefore, this phenomenon is considered to originate from the bifunctionality of the π−d coupled magnetic organic superconductor.

In addition, a conspicuous resistivity decrease was observed just below the abrupt resistivity increase at 1.6 T. As mentioned before, the superconducting state was broken by the sudden appearance of the metamagnetically induced internal field. Namely, such an internal field created by the Fe^{3+} spins is considered to produce a negative magnetic field on the π-electron system through the AF exchange coupling between the d and π electron systems. Then, around the onset field of the metamagnetic transition, there should be a magnetic field where the applied external field (H_{ext}) is balanced with the rapidly growing internal field (H_{int}). And at this point the superconductivity tends to be stabilized because of the

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10.1021/ja026067z CCC: $22.00

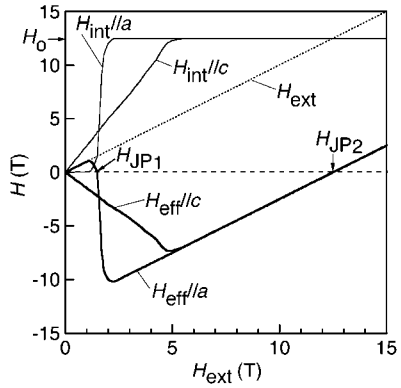

Figure 2. Schematic plot of the applied external magnetic field (H_{ext}) dependence of the induced internal field (H_{int}) by the Fe^{3+} spin system and the effective field (H_{eff}) on the BETS layers, which is obtained as $H_{eff} = H_{ext} - H_{int}$. The suffixes //*a* and //*c* denote that the external field (H_{ext}) that applied parallel to the *a* axis and *c* axis, respectively. The dotted line is H_{ext}, thin lines are H_{int}, and thick lines are H_{eff}. H_o is the internal field from the fully magnetized Fe^{3+} spin system. H_{JP1} and H_{JP2} indicate the fields for the Jaccarino−Peter compensation effect.

reduced effective field on the π electron system (H_{eff}). Thus, the resistivity minimum around 1.6 T suggests the compensation of H_{ext} by H_{int}. Figure 2 illustrates the relationship between H_{eff} ($= H_{ext} - H_{int}$) and H_{ext}. Here we assumed H_{int} to be proportional to the magnetization of the Fe^{3+} spins showing the metamagnetic transition as shown by the thin lines in Figure 2. When applying the external magnetic field parallel to the easy-axis (*H*//*a*), the sign of $H_{eff}//a$ is considered to be changed from positive to negative at 1.6 T (H_{JP1}) and then return to positive at the field ($H_{JP2} = H_o$) corresponding to the internal field (H_o) produced by the fully magnetized Fe^{3+} spin system. Consequently, there should be two zero-field points at H_{JP1} and H_{JP2} ($H_{eff} = 0$). Therefore, it may be possible to discover another field-induced superconducting state around H_o if T_c of this superconducting state is not too low to be detected. On the other hand, on the application of the magnetic field parallel to the hard-axis (*H*//*c*), initial effective fields are already negative because of large magnetization of Fe^{3+} spins, and only one compensation point will be expected at the same compensation field of H_{JP2} ($= H_o$).

To confirm the possibility of this field-induced superconductivity, we measured magnetoresistances under the magnetic field up to 15 T applied along the *a* axis (*H*//*a*) and *c* axis (*H*//*c*) on different crystals at the indicated temperatures in Figure 1. Stair-like resistivity anomalies were observed below 2.5 K ($= T_N$) and shifted to 1.6 T for *H*//*a* and 4.2 T for *H*//*c* with a decrease in the temperatures. The magnetic fields for such anomalies perfectly correspond to the fields of the AF transition of the Fe^{3+} spins determined by SQUID measurements reported before.[6] In contrast to the case of *H*//*a*, where the sharp "AF superconductor-to-ferromagnetic metal transition" was observed around 1.6 T (H_{JP1}), only gradual breaking of the superconducting state was observed for *H*//*c*. Of course, this anisotropic resistivity behavior comes from the interplay between the magnetic ordering and superconductivity. When increasing the magnetic field up to 15 T, further anomalies were observed at 10−15 T below 0.75 K for both *H*//*a* and *H*//*c* as shown in Figure 1. Although the lowest experimental temperatures were not sufficiently low, the resistivity changes between 1.19 K (the normal state) and the lowest measured temperatures [0.58 K (*H*//*a*), 0.60 K (*H*//*c*)] plotted in the lower insets strongly suggest the onset of the magnetic-field-induced superconductivity around 12.5 T ($= H_{JP2}$). This field of the magnetic-field-induced superconductivity just corresponds to the theoretically predicted field (12 T) by Cépas et al. on the basis of the splitting of the Shubnikov-de Haas frequencies.[7] The critical field of this field-induced superconducting state ($H_{JP2} = 12.5$ T) is about one-third of that of the first magnetic-field-induced organic superconductor λ-$(BETS)_2FeCl_4$ ($H_{JP} = 33$ T). These two salts have several similarities they have the layered structure consisting of the two-dimensional conducting layers and the insulating layers involving the magnetic iron atoms which show the AF transition at low temperatures. But their ground states are quite different. In the λ-$(BETS)_2FeCl_4$ salt, the strong π−d coupling suggested from many short contacts between Cl and chalcogen atoms resulted in the cooperative transition to the AF insulating state at T_N. On the other hand, such short intermolecular contacts were not observed in κ-$(BETS)_2FeBr_4$ and consequently the metallic state could be maintained during the AF transition of the anion layers and the AF superconducting state was realized. Therefore, the induced internal magnetic field on the BETS layers in κ-$(BETS)_2FeBr_4$ is considered to be weaker than that in λ-$(BETS)_2FeCl_4$, which is consistent with the smaller compensation field of κ-$(BETS)_2FeBr_4$. However, for *H*//*a*, the situation of κ-$(BETS)_2FeBr_4$ is more complicated because of the existence of the metamagnetic transition which makes this system a dual functional material and gives rise to the field-induced resistivity decreases suggesting the stabilization of the superconducting state at two characteristic magnetic fields of 1.6 and 12.5 T.

References

(1) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209−12217.
(2) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. N. *Nature* **2000**, *408*, 447−449.
(3) (a) Kobayashi, A.; Udagawa, T.; Tomita, H.; Naito, T.; Kobayashi, H. *Chem. Lett.* **1993**, 2179−2182. (b) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sasaki, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368−377. (c) Kobayashi, H.; Kobayashi, A.; Cassoux, P. *Chem. Soc. Rev.* **2000**, *29*, 325−333.
(4) (a) Uji, S.; Shinagawa, H.; Terashima, T.; Yakabe, T.; Terai. Y.; Tokumoto, M.; Kobayashi, A.; Tanaka, H.; Kobayashi, H. *Nature* **2001**, *410*, 908−910. (b) Balicas, L.; Brooks, J. S.; Storr, K.; Uji, S.; Tokumoto, M.; Tanaka, H.; Kobayashi, H.; Kobayashi, A.; Barzykin, V.; Gor'kov, L. P. *Phys. Rev. Lett.* **2001**, *87*, 7002−7005.
(5) Jaccarino, V.; Peter, M. *Phys. Rev. Lett.* **1962**, *9*, 290−292.
(6) (a) Ojima, E.; Fujiwara, H.; Kato, K.; Kobayashi, H.; Tanaka, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc.* **1999**, *121*, 5581−5582. (b) Fujiwara, H.; Fujiwara, E.; Nakazawa, Y.; Narymbetov, B. Zh.; Kato, K.; Kobayashi, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc.* **2001**, *123*, 306−314.
(7) (a) Cépas, O.; McKenzie R. H.; Merino, J. *Phys. Rev. B* **2002**, *65*, 100502−100505. (b) Uji, S.; Shinagawa, H.; Terai, Y.; Yakabe, T.; Terakura, C.; Terashima, T.; Balicas, L.; Brooks, J. S.; Ojima, E.; Fujiwara, H.; Kobayashi, H.; Kobayashi, A.; Tokumoto, M. *Phys. B* **2001**, *298*, 557−561. (c) Balicas, L.; Brooks, J. S.; Storr, K.; Graf, D.; Uji, S.; Shinagawa, H.; Ojima, E.; Fujiwara, H.; Kobayashi, H.; Kobayashi A.; Tokumoto, M. *Solid State Commun.* **2000**, *116*, 557−562.

JA026067Z