Large Positive Magnetoresistance of Insulating Organic Crystals in the Non-Ohmic Region

Yamaguchi Takahide,[1] Takako Konoike,[1] Kengo Enomoto,[1] Mitsuka Nishimura,[1]
Taichi Terashima,[1] Shinya Uji,[1] and Hiroshi M. Yamamoto[2]
[1]*National Institute for Materials Science, Tsukuba 305-0003, Japan*
[2]*RIKEN (The Institute of Physical and Chemical Research), Wako 351-0198, Japan*
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We report a large positive magnetoresistance ratio in insulating organic crystals θ-$(ET)_2CsZn(SCN)_4$ at low temperatures at which they exhibit highly nonlinear current-voltage characteristics. Despite the nonlinearity, the magnetoresistance ratio is independent of the applied voltage. The magnetoresistance ratio depends little on the magnetic field direction and is described by a simple universal function of $\mu_B B/k_B T$, where μ_B is the Bohr magneton. The positive magnetoresistance may be caused by magnetic-field-induced parallel alignment of spins of mobile and localized electrons, and a resulting blockade of electrical conduction due to the Pauli exclusion principle.

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Insulators induced by electron-electron Coulomb repulsions, e.g., Mott insulators, differ from band insulators in several respects; a significant feature of the former is their electron spin degree of freedom. Many of the layered organic crystals, $(ET)_2X$ (ET = bisethylenedithio-tetrathiafulvalene), are among such correlated insulators. Stacked ET molecules form two-dimensional (2D) layers, and their electronic properties are approximately described by 2D single-band extended Hubbard models [1]. The insulating behavior of θ-$(ET)_2MZn(SCN)_4$ (M = Cs and Rb, denoted as CsZn and RbZn salts) [2] is explained basically in terms of charge order at 3/4 filling due to long-range Coulomb repulsions [3–8].

Recently, highly nonlinear current-voltage ($I - V$) characteristics have been observed [9,10] in the CsZn and RbZn salts. The nonlinear characteristics are attributed to electric field induced unbinding of electron-hole pairs that are thermally excited in the background of the charge order [10]. An important point is that the charge order and the charge transport involve only a single energy level, i.e., the HOMO (highest occupied molecular orbital), in ET molecules. This suggests that the Pauli principle can be important for charge transport.

In this Letter, we report a large *positive* magnetoresistance ratio of the insulating CsZn salt in the non-Ohmic region. The magnetoresistance is considered to be electron-spin related and may be caused by magnetic-field-induced parallel alignment of spins of mobile and localized electrons both in the HOMO in ET molecules and a resulting blockade of conduction due to the Pauli principle. Our experimental results indicate that spin degrees of freedom have a strong influence on charge transport in the organic correlated insulators.

Single crystals of CsZn and RbZn salts were synthesized using a standard electrochemical method. The crystals were cooled in a ^{3}He cryostat or a dilution refrigerator, equipped with a superconducting magnet. We measured the $I - V$ characteristics using a two-point configuration; we checked that contact resistances of the electrodes are negligible [10]. A pair of electrodes were made of silver or carbon paste painted on a crystal surface or both ends of a crystal; they were separated by 10–140 μm. Details of the crystal dimensions and the measurement conditions are described in Ref. [10]. The data shown in this Letter were measured using a dc method. Note that the $a - c$ plane is parallel to the ET layers, and the b axis is perpendicular to them.

The in-plane (c axis) $I - V$ curves of a CsZn crystal measured at several temperatures in magnetic fields of 0 and 17.5 T are shown in Fig. 1. The $I - V$ curves are approximately linear at low electric fields, but they are highly nonlinear at high fields. The nonlinear $I - V$ curves are explained in terms of electric field induced unbinding of thermally excited electron-hole pairs. The conductivity is described by the Arrhenius law with an activation energy $\Delta(E)$ that corresponds to the binding energy of an electron-hole pair and is a decreasing function of the applied electric

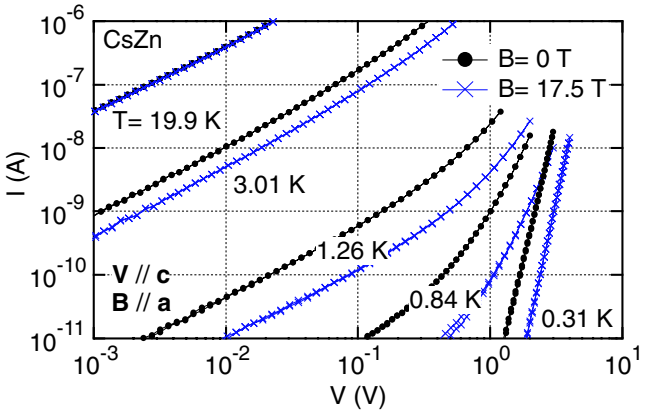

FIG. 1 (color online). In-plane (c axis) $I - V$ curves of a CsZn crystal at several temperatures in magnetic fields of $B = 0$ and 17.5 T ($B \parallel a$). The electrode spacing is 20 μm.

field E:

$$J/E = \sigma_0 \exp[-\Delta(E)/(2k_BT)], \quad (1)$$

where J is the current density. The E dependence of Δ reflects the nature of the Coulomb interaction between charges. The dependences of the $I - V$ curve on temperature and magnetic field observed for electrodes along the a axis are nearly the same as those observed for electrodes along the c axis, but the b-axis (out-of-plane) conductivity is much smaller than that of the c axis, which indicates the two-dimensional character of the charge transport [10].

As shown in Fig. 2, $d\ln(I)/d\ln(V)$ of the $I - V$ curves for $T = 1.08$ K are plotted as a function of voltage and current. The data for different magnetic fields lie on a single curve when plotted against voltage, but not when plotted against current. This means that the application of the magnetic field only shifts the $I - V$ curve along the current axis in the log-log plot. The $I - V$ curves for different magnetic fields fall on a single curve also at the other temperatures when shifted along the current axis. The shift indicates that σ_0 in Eq. (1) decreases with increasing magnetic field, which suggests that the mobility or the number of conduction paths of unbound free charges decreases with increasing magnetic field.

The dependence of current on magnetic field measured while voltage was kept constant is shown in Fig. 3. The voltage was chosen at each temperature so that the current would be measurable in a wide range of the magnetic field. Importantly, the $I/I(B = 0) - B$ curve (i.e., magnetoconductance curve) is independent of voltage, which is illustrated by the shift of the $I - V$ curve along the current axis in the log-log plot (Figs. 1 and 2). For $T = 0.135$ K, data for $B \parallel c$ and $B \parallel b$ are shown; the magnetoconductance curve depends little on the magnetic field direction, particularly at low magnetic fields. (A slight dependence on the magnetic field direction at high magnetic fields is described in detail below.) The finding that the transverse and longitudinal magnetoconductances are nearly the same despite the highly 2D charge transport indicates that the magnetoconductance is not caused by orbital effects but is spin related. Note that spin-related large magnetoresistance ratios have been often observed in systems containing magnetic elements such as Mn, but the CsZn and RbZn salts contain no magnetic elements.

A notable feature of the magnetoconductance is that the data fall on a single universal curve when plotted as a function of $\mu_B B/k_BT$ (Fig. 4). We find that the universal curve is described by a simple empirical function:

$$I(T, B)/I(T, B = 0) = [\cosh(\mu_B B/k_BT)]^{-1/2}, \quad (2)$$

or

$$I(T, B)/I(T, B = 0) = 1/[1 + (\mu_B B/2k_BT)^2]. \quad (3)$$

The latter can be written using the usual definition of the magnetoresistance ratio: $[R - R(B = 0)]/R(B = 0) = (\mu_B B/2k_BT)^2$, where $R \equiv V/I$ [11]. The magnetoconductance curves were measured along the a or c axis on ten crystals; regardless of the top or side electrodes, all of the curves fall on the universal curve in limited temperature ranges. It is worth noting that the scaling with B/T indicates that the temperature of the electronic system is identical to that of the thermometer placed near the crystal; namely, the nonlinearity of the $I - V$ curves is intrinsic and not due to current-induced heating. The insensitivity of the magnetoconductance to voltage also indicates that the nonlinearity is not a heating effect because heating effects would be larger at higher voltages and therefore they would cause the magnetoconductance effect to decrease with increasing voltage.

A deviation from the universal curve at high magnetic fields, as seen for the data at $T = 0.78$ K, increases with increasing temperature (left inset of Fig. 4). However, if we assume that the conductance consists of two parts, one that

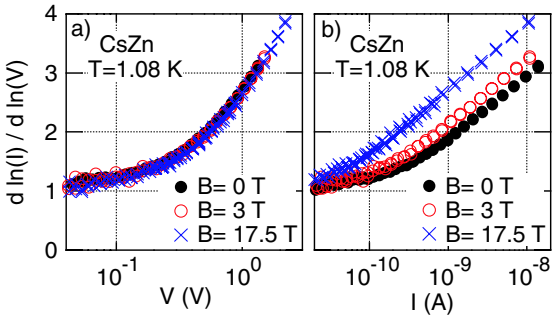

FIG. 2 (color online). $d\ln(I)/d\ln(V)$ for $T = 1.08$ K plotted as a function of voltage (a) and current (b).

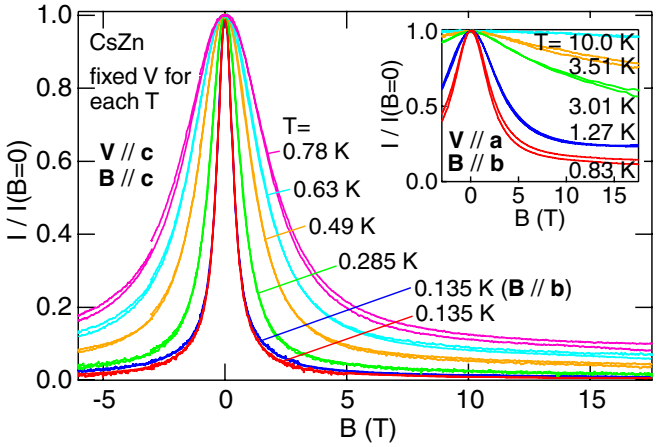

FIG. 3 (color online). Magnetic-field dependence of current measured while voltage was kept constant in a CsZn crystal. The current is normalized to the value obtained in zero magnetic field at each temperature. Both the voltage and magnetic field were applied along the c (in-plane) axis so that orbital effects would be minimized. For $T = 0.135$ K, data measured with $B \parallel b$ (out-of-plane) are also shown. Two curves for each temperature correspond to increasing and decreasing magnetic field. Inset: data for another CsZn crystal at higher temperatures; $V \parallel a$ and $B \parallel b$.

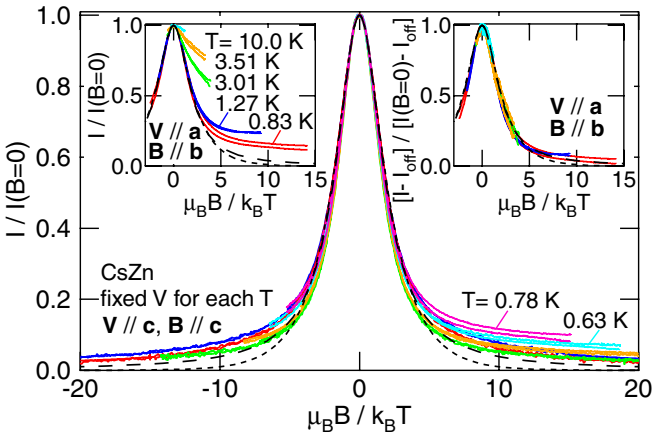

FIG. 4 (color online). Plots of the $I/I(B=0)$ shown in the main panel of Fig. 3 as a function of $\mu_B B/k_B T$. The curves for small B fall on a universal curve represented by $I/I(B=0) = [\cosh(\mu_B B/k_B T)]^{-1/2}$ (dotted line) or $I/I(B=0) = 1/[1+(\mu_B B/2k_B T)^2]$ (dashed line). Insets: plots of the $I/I(B=0)$ shown in the inset of Fig. 3 as a function of $\mu_B B/k_B T$ before (left inset) and after (right inset) subtracting a B-independent constant I_{off} at each temperature (see text).

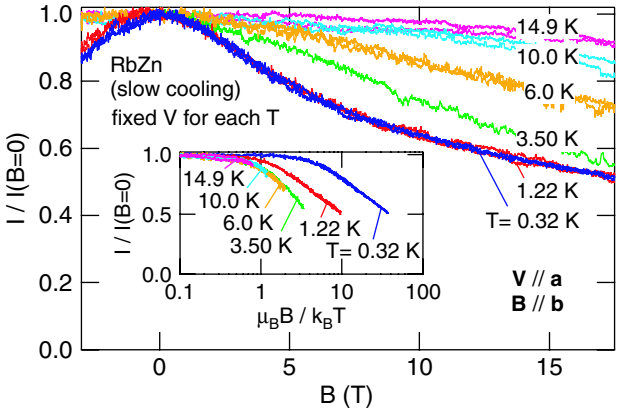

FIG. 5 (color online). Magnetic-field dependence of current measured while voltage was kept constant in a RbZn crystal. $V \parallel a$ and $B \parallel b$. Inset: the same data are plotted as a function of $\mu_B B/k_B T$.

depends on the magnetic field, and the other that does not depend on it, the B-dependent part of the conductance scales with $\mu_B B/k_B T$ up to relatively high temperatures. Namely, the B-dependent part, $[I(B) - I_{\text{off}}]/[I(B=0) - I_{\text{off}}]$, is described by the universal function of $\mu_B B/k_B T$ if we choose the value of B-independent current I_{off} for each temperature properly (right inset of Fig. 4). The temperature dependences of I_{off} vary for different electrode pairs, but typically, $I_{\text{off}}/I(B=0) = 0.07$–$0.1$ at $T = 0.8$ K and 0.8 at $T = 10$ K. A deviation from the universal curve was also observed in the low-temperature limit. This deviation occurs because the $I/I(B=0) - B$ curve depends little on temperature at low temperatures. The $I - V$ curve at $B = 0$ is also nearly independent of temperature in a similar low-temperature range. The temperature, T_L, below which the deviation from the universal curve was seen, varied from 0.1 to 0.3 K. There was a tendency for values of T_L obtained for the side electrodes to be lower than those obtained for the top electrodes.

Similar magnetoconductance effects were observed in both slowly and rapidly cooled RbZn salts. Because of lattice distortion, transfer integral parameters of the slowly cooled RbZn salt differ from those of the rapidly cooled RbZn salt [2,6]. The temperature and electric field at which the nonlinearity in the $I - V$ curve sets in increase in the order of CsZn, rapidly cooled RbZn, and slowly cooled RbZn, which is related to the increase in the zero-bias activation energy $\Delta(E \to 0)$ in that order [10]. Plots of $I/I(B=0)$ of a slowly cooled RbZn crystal as a function of B and $\mu_B B/k_B T$ are shown in Fig. 5. The data obtained for $T \geq 3.50$ K scale with $\mu_B B/k_B T$; if I_{off} are chosen properly, the data collapse on the curve represented by Eq. (2) or (3), indicating that the magnetoconductance effect has the same origin as that of the CsZn salt. At lower temperatures, however, $I/I(B=0)$ becomes temperature independent, and therefore, the data do not scale no matter how I_{off} are chosen: $1.22\ \text{K} < T_L < 3.50\ \text{K}$. The T_L increases in the order of CsZn, rapidly cooled RbZn, and slowly cooled RbZn. In addition, the value of $I_{\text{off}}/I(B=0)$ in the low-T limit increases in that order [12].

SQUID and EPR measurements showed that the spin susceptibility of the CsZn salt increases with decreasing temperature below 20 K [4]. This is considered as an intrinsic paramagnetic effect, not a paramagnetic effect due to impurities. The results of the EPR measurement, together with results of a ^{1}H-NMR measurement, suggest that many of the electrons singly occupying the HOMO are paired into spin singlet states, but there remain 1% unpaired localized electrons that behave as $S = 1/2$ paramagnetic spins with $1\mu_B$. The Zeeman energy $gS\mu_B B$ is approximately the same as $\mu_B B$ because the g values are 2.005 for $B \parallel a$, 2.014 for $B \parallel b$, and 2.002 for $B \parallel c$ [4].

We expect that the 1% localized spins are located along domain boundaries of charge order, because the spin singlet formation will be broken at such boundaries. As shown in x-ray measurements [3], a $2c$ superlattice structure grows with decreasing temperature, but its correlation length remains less than 20 nm at $T = 20$ K, indicating small domains of charge order. The optical conductivity and Raman spectra at $T \geq 6$ K are also consistent with the domain structures [8]. The free charges created by unbinding of electron-hole pairs have to cross some of the domain boundaries when they flow to electrodes, and therefore, they would most probably pass localized spin sites. Because of the Pauli principle, a free electron cannot pass a localized spin site if the electron's spin and the localized spin are aligned parallel. When the magnetic field is higher, more electrons are blocked because the magnetic field aligns the spins. The probability that orientations of two noninteracting spins are antiparallel is given by $p(T,B) = [\cosh(\mu_B B/k_B T)]^{-2}/2$. The observed universal function has a form similar to $p(T,B)$, implying

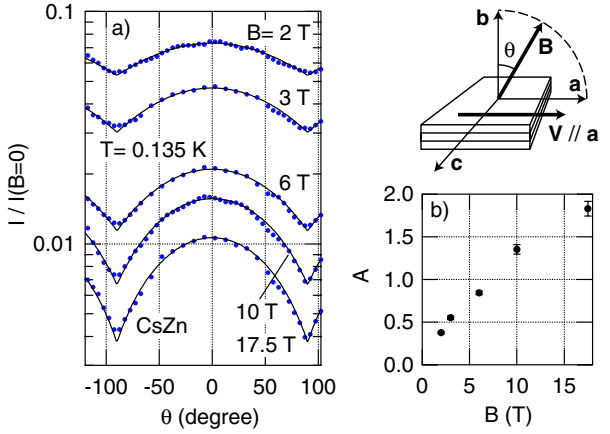

FIG. 6 (color online). (a) Dependence of $I/I(B=0)$ of the CsZn salt on the magnetic field direction. The voltage was applied along the a axis, and the magnetic field was tilted by θ from b towards a. The solid lines are fits to the formula, $I(B,\theta)/I(B,\theta=90°) = 1 + A(B)|\cos(\theta)|$. (b) The coefficient A plotted as a function of the magnetic field.

the blockade due to the Pauli principle. In the slowly cooled RbZn salt, long-range charge order was observed [2,6], but the existence of a small number of domain boundaries accompanied by paramagnetic spins is still likely, which is consistent with a Curie tail observed in the spin susceptibility [2,13]. The larger value of $I_{\rm off}/I(B=0)$ of the RbZn salt in the low-T limit than that of the CsZn salt may be attributed to a smaller probability of free electrons interacting with localized spins due to the larger domain size.

The blockade due to the Pauli principle requires both the charge order with some remaining spin degrees of freedom and the charge transport to involve only a single energy level in each ET molecule. This condition is satisfied: the HOMO energy level differs from the nearest levels by ≥ 0.9 eV in an isolated ET molecule [14], and the transfer integrals between ET molecules are ≈ 0.1 eV [2]. In addition, these energies are much larger than the Zeeman energy and the cyclotron energy in the magnetic-field range, $B \leq 17.5$ T. Moreover, voltage V_n across neighboring molecular sites while measuring $I/I(B=0)$ shown in Figs. 3–6 was $\leq 1 \times 10^{-5}$ V (CsZn) and $\leq 7 \times 10^{-3}$ V (RbZn); the energy eV_n is also very small.

The observed magnetoconductance effect is thus qualitatively explained, but a full understanding of it requires further study. For example, we cannot totally neglect orbital effects: the data for $T = 0.135$ K in Fig. 3 show that $I/I(B=0)$ for $B \parallel b$ is slightly larger than that for $B \parallel c$ at high magnetic fields. The dependence of $I/I(B=0)$ of the CsZn salt on the magnetic field direction is shown in Fig. 6(a). The voltage was applied along the a axis, and the magnetic field was tilted by an angle θ from b towards a. Similar behaviors were observed when $V \parallel c$ and the magnetic field was tilted from b towards c, or from b towards a. The data for each magnetic-field value can be fitted by the formula: $I(B,\theta)/I(B,\theta=90°) = 1 + A(B)|\cos(\theta)|$. The dependence of A on the magnetic field is shown in Fig. 6(b). Although A increases somewhat slower than linearly with B, the good fit of the cosine curve indicates that $I(B,\theta)/I(B,\theta=90°)$ is determined largely by the magnetic-field component perpendicular to the $a-c$ plane. Thus, orbital effects appear to play an additional role. We observed a decrease in A, i.e., a decrease in the field-direction dependence, with increasing temperature.

The in-plane magnetoconductance of the 2D electron system in silicon metal-oxide-semiconductor field effect transistors (MOSFETs) has been reported to exhibit a similar scaling [15]: the magnetic-field dependent part of the conductivity scales with B/T in the insulating phase near the metal-insulator transition. The insulating quasi-1D organic compounds, $TTT_2I_{3-\delta}$, also exhibit a magnetoresistance ratio with the form, $[R(B) - R(B=0)]/R(B=0) \propto (B/T)^2$ [16], which may be explained by the blockade due to the Pauli principle.

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