**Anomalous Variation of the Normal State Resistance of
 κ -(BEDT-TTF) $_2$ CuN(CN) $_2$ Br with Temperature and
Hydrostatic Pressure. Small Polaron.**

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Classification
Physics Abstracts
71.38, 72.20, 72.60, 72.80L, 74.70 K

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OCT 14 1991
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Abstract

Several radical organic cation conductors have resistances, $R(T)$'s, which attain maxima as functions of temperature. In some cases, κ -(BEDT-TTF)₂CuN(CN)₂Br for instance [Sushko et al., *J. Phys. I. France*, **1** (1991) 1375], the maxima are suppressed by hydrostatic pressure, and with sufficient pressure $R(T)$ becomes classified as metallic in the sense that $dR/dT > 0$. These variations with temperature and pressure can be understood quantitatively in terms of two equivalent models: (a) one in which the electronic density of states $g(\epsilon)$ is constant except that it is zero for $E_f \leq \epsilon \leq E_g$ and (b) the small polaron. The effect of pressure in this case is essentially to oxidize some cation or anion.

Recently reported measurements of the variation of the normal-state resistances with temperature of some radical organic cation compounds show that these materials cannot be classified throughout the temperature-range as semiconductors in the sense that $dR/dT < 0$ or as metallic conductors in the sense that $(dR/dT) > 0$. Rather, as the temperature is decreased, $R(T)$ is such that the compounds appear to be semiconductive until at some temperature $R(T)$ attains a maximum and then decreases rapidly. This behavior has been observed with $(\text{TMTSF})_2\text{ReO}_4$ (1), $(\text{DMET})_2\text{AuBr}_2$ (2), $\kappa\text{-(BEDT-TTF)}_2\text{Cu(SCN)}_2$, (3-5), $\beta\text{-(BEDT-TTF)}_2(\text{I}_3)_{0.95}(\text{IBr})_{0.05}$ (6), and (most recently) $\kappa\text{-(BEDT-TTF)}_2\text{CuN(CN)}_2\text{Br}$ (7,8).

An explanation of this "puzzling normal state anomaly" (8) is particularly challenging because of the observation that the maximum can be suppressed by hydrostatic pressure, and at some pressure the conductor can be made to have $(dR/dT) > 0$ throughout the range of measurements. With $\kappa\text{-(BEDT-TTF)}_2\text{Cu(SCN)}_2$, the suppression was reported by Murata et al. (6), Parker et al. (9), and Kang et al. (10); with $\kappa\text{-(BEDT-TTF)}_2\text{CuN(CN)}_2\text{Br}$ the suppression has been characterized quantitatively by Sushko et al. (8).

This general behavior has been predicted by Thorn (11) and colleagues (12, 13) in terms of the Fermi energy.

Cariss et al. (13 see also 14) showed that a phenomenological model presented by Thorn (11) could be used to describe quantitatively the variation of $R(T)$ with the maximum for $\kappa\text{-(BEDT-TTF)}_2\text{Cu(SCN)}_2$. They also showed that the variation is consistent with the small polaron theory (15, 16). In the present report, it is shown that the measurements of the variation of the resistance with varying temperature and hydrostatic pressure by Sushko et al. using $\kappa\text{-(BEDT-TTF)}_2\text{CuN(CN)}_2\text{Br}$ are also described quantitatively by these two models. The results imply that the essential effect of pressure is oxidative in this instance.

The phenomenological model of a conduction band/valance band conductor derived by Thorn (11) is based on a two dimensional solid. However, its essential nature is one in which the density of states for both bands are assumed to be constant but with $g(\epsilon) = 0$ for $E_f \leq \epsilon \leq E_g$. This is exactly the case for the two dimensional solid wherein $g(\epsilon)$ is evaluated by the usual, elementary procedure (17). Because the conductivity, $\sigma(T)$, can be relatively insensitive to the detailed structure of $g(\epsilon)$, the assumption should be a valuable one for several cases over a limited range of temperatures. If in addition, one assumes that the scattering of electrons is proportional to T^{-n} , then it is found (11) that the conductivity is given by

$$\sigma = CT^{(1-n)} \ln \left\{ \left(\frac{(e^{\beta E_f} + 1)(e^{-\beta(E_g - E_f)} + 1)}{2} \right) \right\} \quad (1)$$

with $\beta = (kT)^{-1}$.

Thorn and Thorn (13) have shown that this equation describes quantitatively the variation of $\sigma(T, \delta)$ of $YBa_2Cu_3O_{7-\delta}$, $\sigma(T, x)$ of $YBa_2Cu_{3(1-x)}Fe_3O_{7-\delta}$, and $\sigma(T)$ of other superconducting oxides. The application of this equation to the oxide superconductors and to $(TMTSF)_2ClO_4$, $(TMTSF)_2ReO_4$, and $\kappa-(BEDT-TTF)_2Cu(SCN)_2$ reveals that these materials can be classified as consisting of a composite with a narrow-band conductor ($E_f \sim 10^{-4}eV$) and a thermally activated conductor having an activation energy of $\sim 10^{-2}eV$.

A theory in which equations have been derived having the same features as those contained in equation (1) is that of the small polaron (15, 16). In this theory the current is transported via polarization so that

$$j = \Omega^{-1} \frac{dD(t)}{dt} \quad (2)$$

in which Ω is the appropriate volume and $D(t)$ is a temporally varying dipole moment at a given site in the solid. The equation for the small polaron consist of two additative parts: one attributable to thermally activated hopping between sites and one attributable to narrow-band tunneling:

$$\sigma = \sigma_h + \sigma_t; \quad (3)$$

$$\sigma = C_h T^{-3/2} E^{-1/2} e^{-\beta E} + C_t T^{-1} [\sinh(\beta\omega)]^{-1/2} e^{-g/\sinh(\beta\omega)} \quad (4)$$

in which E is the activation energy for thermal hopping, ω is the "frequency" in units of energy of the longitudinal optical phonon along the hopping bond, and g is the electron-phonon coupling constant involved in the phonon-electron charge exchange. Thorn (18) has shown that this equation describes $\sigma(T)$ for $YBa_2CuO_{7-\delta}$.

Using data obtained from the curves in Figure 1 of Sushko et al. in least squares' analyses with the equation for the first model, one obtains the curves shown in Figure 1. The least squares' parameters are listed in Table I. Although the parameters are inter-correlated, in general one observes that the values for the Fermi energy are of the order of 10^{-4} - 10^{-3} eV, the values for the gap energy E_g are of the order of 10^{-2} eV, and the values for the first increase and those for the second are nearly constant, respectively, as the hydrostatic pressure is increased. Thus with increasing pressure, the electronic density and the attendant Fermi energy increase. This agrees with the fact that the range in $\sigma(T; E_f, E_g, n)$ from "semiconductor-like" to "metal-like" is attributed mostly to $1 \times 10^{-4} \leq E_f \leq 18 \times 10^{-4}$ eV (see Table I); it cannot be attributed to the interval $1 \leq n \leq 2$. A relation

between E_f and hydrostatic pressure was predicted to exist in general (see especially the abscissa of Figure 4 in Reference (11)). In the present case it is given by

$$E_f = (1.16 \pm 0.57) \times 10^{-4} + (3.02 \pm 0.19) \times 10^{-9} p^2 \quad (5)$$

in eV. Whether the p^2 -dependence has any particular significance remains to be determined.

Using the same data by Sushko et al. in least squares' analyses with the equation for the small polaron, one finds the curves shown in Figure 2. The values for the parameters are listed in Table II.

The curves shown in Figures 1 and 2 have the same structures as those reported by Thorn and Thorn for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_{3(1-x)}\text{Fe}_{3x}\text{CuO}_{7-\delta}$ as the oxygen and iron contents are varied respectively. (As pointed out by Thorn and Thorn, the variation of iron is equivalent to the variation in oxygen content.) The curves for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and for $\kappa\text{-(BEDT-TTF)}_2\text{CuN(CN)}_2\text{Br}$ cover the same range in temperature. Whether this fact that they have the same temperature range is significant remains to be determined.

In the case of the oxides, the small polaron can be associated with the chemical equilibria (see 18):

and

in which cs refers to a cation site, as refers to an anion site, and as_1 and as_2 refer to two, adjacent anion sites.

The similarities of the two sets of curves establish a close relationship, heretofore unrecognized, between the two materials: the oxides and the radical organic cation compounds. Indeed, the curves can be considered to be a signature for the small polaron in both cases.

What happens when pressure is applied to this organic compound is that the energy of compression contained in $\Delta(pV)$ "oxidizes" some cationic or anionic species in the sense:

and/or

The effect is similar to that observed when pressure is applied to some of the lanthanide dichalcogenides wherein pressure causes the "oxidation": $Ln^{2+}cs \rightarrow Ln^{3+}cs + e_f$. The "metal" volumes of the "oxidized" (compressed) species are less than those of the initial state (19-21, see also 11). In the organic compound, there are three species that can be "oxidized" by pressure, sulfur, copper, and possibly nitrogen.

The description given above is satisfactory for this particular case. However, the total situation is more complex because as stated in 1987 (11) "...it is possible that pressure can transfer charge in such a way to make the material less conductive...." Such occurs with $(BEDT-TTF)_2Cl_2 \cdot 2H_2O$, $(S,S, DMEDT-TTF)_2ClO_4$ and probably $(TMTSF)_2ClO_4$. In these cases, reduction appears to occur in the sense that

The change in the electronic structure can be accompanied by hysteresis; this implies that a structural change occurs, as one might expect, when there occurs such a large change in electronic structure.

In a measurement with κ -(BEDT-TTF)₂(I₃)_{0.95}(IBr₂)_{0.05}, Murata et al. found a similar effect but at temperatures near 10 K. In this case iodine can be "oxidized." In the measurements with (DMET)₂AuBr₂, the effect is near 100 K. Comparing the results found by Sushko et al. with those found by Murata et al., one observes that the source is not exclusively in the radical cation, κ -(BEDT-TTF)₂⁺; oxidation can occur in both the cation and anion. Further systematic studies of the kind effected by Sushko et al. are needed. Especially significant would be structural studies at varying hydrostatic pressure to determine which ions are being oxidized or reduced.

Acknowledgement

I thank J. M. Williams for bringing the article by Sushko et al. to my attention and for the opportunity to do this study. I express my appreciation of the efforts of V. Bowman and J. Bormet for processing the manuscript. Work at Argonne National Laboratory is sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials and Chemical Sciences, under Contract W-31-109-ENG-38.

References

1. Parkin, S. S. P., Jérôme, D., Bechgaard, K., *Mol. Cryst. Liq. Cryst.*, 79 (1982) 213.
2. Kikuchi, K., Honda, Y., Ishikawa, Y., Saito, K., and Ikemoto, I., *Solid State Commun.*, 66 (1988) 405.
3. Urayama, H., Yamochi, H., Saito, G., Nozawa, K., Sugano, T., Kinoshita, M., Sato, S., Oshima, K., Kawamoto, A., Tanaka, J., *Chem. Lett.* (1988) 55.
4. Oshima, K., Urayama, H., Yamochi, H., and Saito, G., *J. Phys. Soc. Jpn.*, 57 (1988) 730.
5. Gärtner, S., Gogu, E., Heinen, I., Keller, H. J., Klutz, T., and Schweitzer, D., *Solid State Commun.*, 65 (1988) 1531.
6. Murata, K., Tokumoto, M., Anzai, H., Honda, Y., Kinoshita, N., and Ishiguro, T., *Synth. Met.*, 27 (1988) A263.
7. Williams, J. M., Kini, A. M., Geiser, U., Wang, H. H., Carlson, K. D., Kwok, W. K., Vandervoort, K. G., Thompson, J. E., Stupka, D. L., Jung, D., and Whangbo, M.-H., *Proceedings of the International Conference on Organic Superconductors*, South Lake Tahoe, CA, 1990 (Plenum, New York) p. 39.
8. Sushko, Yu. V., Bondarenko, V. A., Petrosov, R. A., Kushch, N. D., and Yagubskii, E. B., *J. Phys. France*, 1 (1991) 1375.
9. Parker, I. D., Friend, R. H., Kurmoo, M., Day, P., Lenoir, C., and Batail, P., *J. Phys.: Condens. Matter*, 1 (1989) 4479.
10. Kang, W., Jérôme, D., Lenoir, C. and Batail, P., *J. Phys. Condens. Matter*, 2 (1990) 1665.
11. Thorn, R. J., *J. Phys. Chem. Solids*, 48 (1987) 355.
12. Thorn, R. J. and Thorn, C. E., *J. Phys. Chem. Solids*, 50 (1989) 153.

13. Cariss, C. S., Porter, L. C., and Thorn, R. J., *Solid State Commun.*, 74 (1990) 1269.
14. Toyota, N. Sasaki, T., *Solid State Commun.*, 74 (1990) 361.
15. Holstein, T., *Ann. Phys.*, 8 (1959) 325, 343.
16. Böttger, H. and Bryksin, V. V., *Hopping Conduction in Solids*, VCH Publishers, Deerfield Beach, FL, 1985; *Phys. Stat. Sol.*, 78 (1976) 9, 415.
17. See Kittel, C., *Introduction to Solid State Physics*, John Wiley & Sons, Inc., N.Y. 1955.
18. Thorn, R. J., *Physica C*, 190 (1992) 193.
19. Jayaraman, A., Bucher, E., and McWham, D. B., *8th Rare Earth Research Conference* (Edited by T. Henric and R. Lindstrom) p. 33 (1970a).
20. Roovymans, J. C. M., *Solid State Commun.*, 3 (1965) 421.
21. Jayaraman, A., Narayanamurti, V., Bucher, E., and Maines, R. G., *Phys. Rev. Lett.*, 25 (1970) 1430.

Figure Captions

Figure 1 - Results of the least squares' analyses of the variation of conductivity with temperature at the indicated hydrostatic pressures (in bars) obtained through the use of equation (1). (Data are from Sushko et al. (8)).

Figure 2 - Results of the least squares' analyses of the variation of conductivity with temperature at the indicated hydrostatic pressures (in bars) obtained through the use of the small polaron equation (4). (Data are from Sushko et al. (8)).

Table I Least Squares' Values for Parameters in Equation (1). Data from Sushko et al. (8).

Pressure (bar)	$E_f \times 10^4$ (eV)	$E_g \times 10^2$ (eV)	n	$C \times 10^{-3}$
1	$1.76 \pm 0.43^*$	2.70 ± 0.15	2.13 ± 0.13	1.99 ± 1.55
250	3.10 ± 1.08	2.85 ± 0.20	2.36 ± 0.20	7.16 ± 8.51
435	5.93 ± 1.06	2.43 ± 0.07	2.20 ± 0.10	2.56 ± 1.45
750	18.5 ± 1.58	2.19 ± 0.37	1.89 ± 0.51	35.8 ± 1.1

*The uncertainties are somewhat misleading because of the intercorrelation among the parameters. They do not reflect the differences between the experimental values and the calculated least squares' values. These generally are 0.02 or less as indicated in the figure.

Table II Least Squares' Values for Parameters in Equation for the Small Polaron (Equation 4). Data from Sushko et al. (8).

Pressure (bar)	$E \times 10^2$ (eV)	$g \times 10$	$C_h \times 10^{-3}$	$C_{tu} \times 10^{-2}$	$W \times 10$ (eV)
1	$2.94 \pm 0.10^*$	3.55 ± 0.90	2.60 ± 0.20	0.54 ± 0.21	1
250	2.60 ± 0.12	4.41 ± 0.84	2.05 ± 0.20	1.98 ± 0.81	1
435	2.35 ± 0.11	7.93 ± 0.96	1.77 ± 0.16	2.86 ± 0.54	2
750	2.59 ± 0.90	1.46 ± 1.16	2.05 ± 1.16	1.28 ± 1.19	0.6

*The uncertainties are somewhat misleading because of the intercorrelation among the parameters. They do not reflect the differences between the experimental values and the calculated least squares' values. These generally are 0.02 or less as indicated in the figure.

NORMALIZED CONDUCTIVITY

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