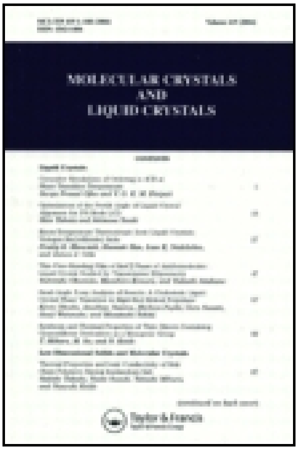

Molecular Crystals and Liquid Crystals

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L. J. Azevedo [a], E. L. Venturini [a], J. F. Kwak [a], J. E. Schirber [a], J. M. Williams [b a], H. H. Wang [b a] & P. E. Reed [b a]

[a] Sandia National Laboratories, Albuquerque, NM, USA

[b] Argonne National Laboratories, Argonne, IL, 60439

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ELECTRONIC PROPERTIES OF NEW ORGANIC CONDUCTORS

L. J. AZEVEDO, E. L. VENTURINI, J. F. KWAK AND
J. E. SCHIRBER
Sandia National Laboratories, Albuquerque, NM, USA
J. M. WILLIAMS, H. H. WANG, AND P. E. REED
Argonne National Laboratories, Argonne, IL 60439

Abstract We have undertaken a study of the electronic properties of a new organic conductor, $(BEDT\text{-}TTF)_2BrO_4$, using magnetic resonance techniues and also the organic superconductor $(BEDT\text{-}TTF)_2I_3$. Proton magnetic resonance experiments on $(BEDT\text{-}TTF)_2BrO_4$ have resolved individual proton lines without the aid of line narrowing techniques. The electron spin resonance line is very narrow and shows a frequency independent low temperature broadening in the low temperature regime. The ESR broadening is strongly pressure dependent, being suppressed to lower temperature with the application of pressure. We have used radio frequency techniques to monitor the pressure dependence of the superconducting transition temperature, T_c, in $(BEDT\text{-}TTF)_2I_3$ and find that T_c is suppressed to below 1K with the application of less than 0.5 kbar of pressure. In addition, we find a magnetic transition at 7K above a pressure of .5 kbar.

INTRODUCTION

The organic metal, $(BEDT\text{-}TTF)_2I_3$, has been of intense interest recently due to the discovery [1] that it superconducts at ambient pressure, the first sulfur-based organic superconductor to do so. Our motivation in investigating this material was to study the pressure dependence of its superconducting properties to compare with the well-characterized Bechgaard salts. A new material, $(BEDT\text{-}TTF)_2BrO_4$, has been synthesized[2] in crystalline form and we have studied the crystal structure,[2] the transport properties[3] and magnetic properties which we report here.

EXPERIMENTAL DETAILS

The single crystal samples, as verified by X-rays, were in the form of platelets of typical dimensions 0.2 x 0.4 x 1 $(mm)^3$. A radio frequency coil of these dimensions was constructed of teflon coated 50 micron copper wire. The teflon coating was necessary to minimize unwanted background proton signals. We found that the background proton signal was typically 10% or less of the total observed proton signal. The sample was carefully slipped inside the rf coil. This coil arrangement resulted in an optimal filling factor which is essential for performing nuclear magnetic resonance experiments on samples weighing less than a milligram. The rf coil and sample were then mounted inside a Be-Cu pressure vessel for experiments at high pressure. Pressures were accurate and reproducible to within 0.2 kbar. The helium gas pressure techniques are described elsewhere.[4] We have found that this pressure technique does no damage to samples upon repeated temperature and pressure cycling as verified by X-ray examination after the experiment. Temperature was measured by a calibrated Ge resistor for temperatures above 4 K and the vapor pressure of helium below 4 K. The low field electron spin resonance was measured by the use of a Q-meter circuit. Resonance frequencies ranged from 30 to 60 MHz corresponding to resonance fields from about 10 to 20 Oe.

The microwave ESR experiments were carried out in a cavity at ambient pressure over the temperature range 2-300 K. Absolute susceptibility, linewidth, and g-value were recorded at a variety of crystal orientations with respect to the applied and microwave fields. No hyperfine structure was observed in either series of samples.

RESULTS AND DISCUSSION

We first discuss the results of the ambient pressure experiments on (BEDT-TTF)$_2$BrO$_4$ and (BEDT-TTF)$_2$I$_3$. In Fig. 1 we show the microwave spin susceptibility vs. temperature from 2 K to 100 K of (BEDT-TTF)$_2$BrO$_4$. There is a monotonic increase in the susceptibility as the temperature is lowered. Above 50 K the susceptibility is nearly independent of temperature, characteristic of the Pauli susceptibility

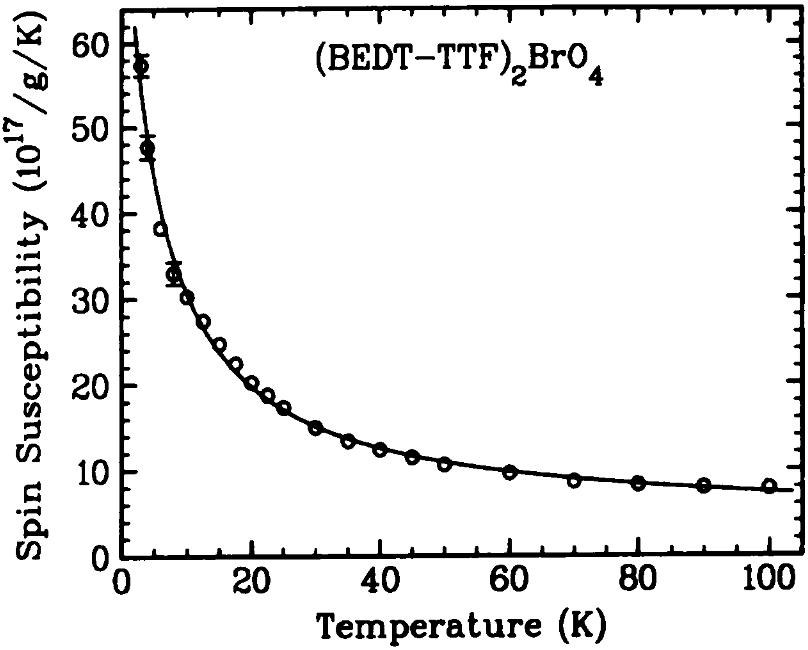

Figure 1. Microwave spin susceptibility vs temperature. The solid curve is a fit to a Curie-Weiss term plus a positive constant as discussed in the text.

of a metal. At lower temperatures the susceptibility rises sharply, dominated by a Curie-Weiss contribution. The solid curve in Fig. 1 is a least squares fit of the susceptibility data to a Curie-Weiss contribution plus a positive Pauli susceptibility. The Curie-Weiss constant is 4.9 K. The positive constant is indicative of antiferromagnetic ordering. In Fig. 2 we show the temperature dependence of the ESR linewidth at 9.8 GHz for (BEDT-TTF)$_2$BRO$_4$.

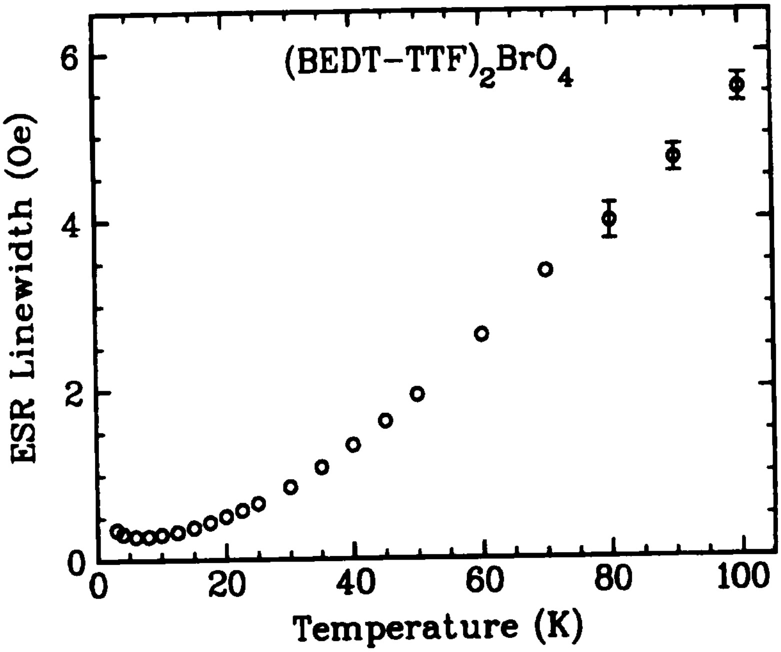

Figure 2. Microwave linewidth (derivative peak to peak) vs temperature.

There is a monotinic decrease of the linewidth with a minimum at a temperature of about 7 K and a small low temperature rise in the linewidth.

In Fig. 3 we show the temperature dependence of the ESR susceptibility at 9.8 GHz vs. temperature for $(BEDT\text{-}TTF)_2I_3$. The temperature independence of the susceptibility is consistent with that expected of a metal where one is measuring the Pauli spin susceptibility.

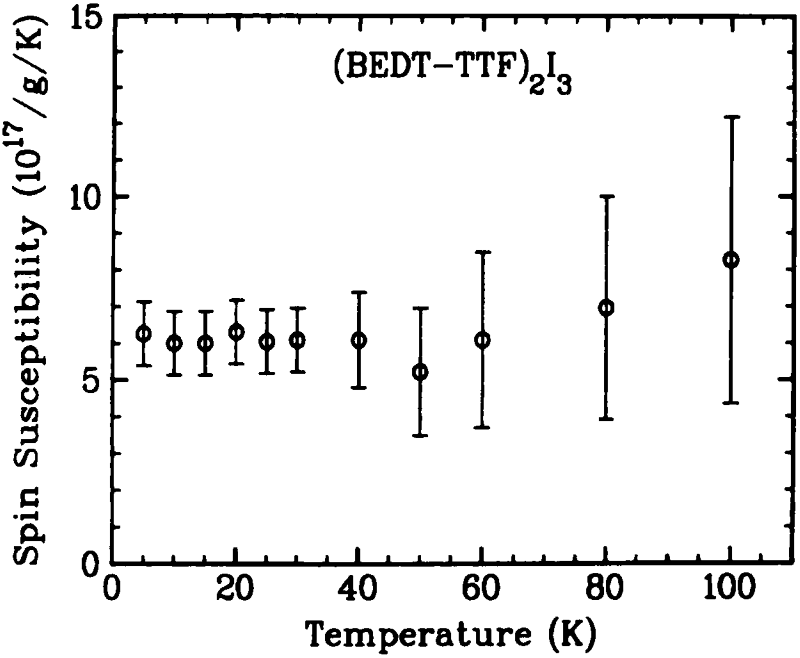

Figure 3. Microwave spin susceptibility vs temperature for $(BEDT\text{-}TTF)_2I_3$

In Fig. 4 we show the ESR linewidth of $(BEDT\text{-}TTF)_2I_3$ vs temperature. There is a decrease in the linewidth as the temperature is lowered which, together with the susceptibility data and the dysonian lineshape discussed below, is consistent with that expected for a Korringa dominated linewidth in a metal. The ESR signal is dysonian in this temperature range, i.e., the microwave skin depth is of the order of the sample dimensions. From a careful analysis of the lineshape for various microwave field directions with respect to the crystal axes we have determined that the microwave conductivity in $(BEDT-TTF)_2I_3$ is at least highly two-dimensional and agrees to within a factor of three of the dc conductivity. That is, the microwave conductivity is isotropic in a plane.

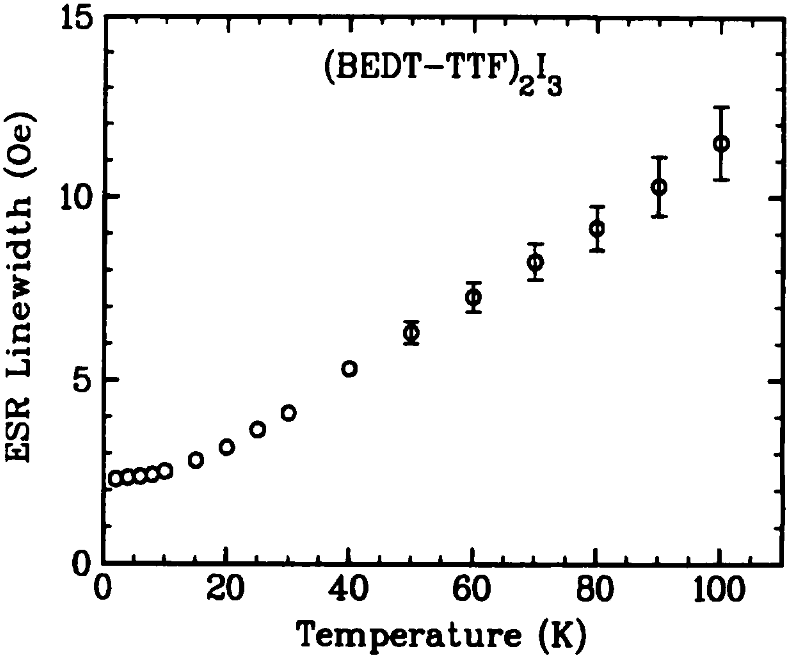

Figure 4. Microwave linewidth (derivative peak to peak)vs temperature for $(BEDT-TTF)_2I_3$

We now turn to the results of the pressure experiments on $(BEDT-TTF)_2BrO_4$ and $(BEDT-TTF)_2I_3$. Both low field ESR and NMR experiments were performed on single crystal samples of $(BEDT-TTF)_2BrO_4$. Figure 5 shows the low field (resonance field 10 Oe) ESR peak-to-peak linewidth as a function of temperature at several pressures. For temperatures above 6 K the low field ambient pressure linewidths agree with the microwave results depicted in Fig. 2 indicating that the ESR linewidth is frequency independent.

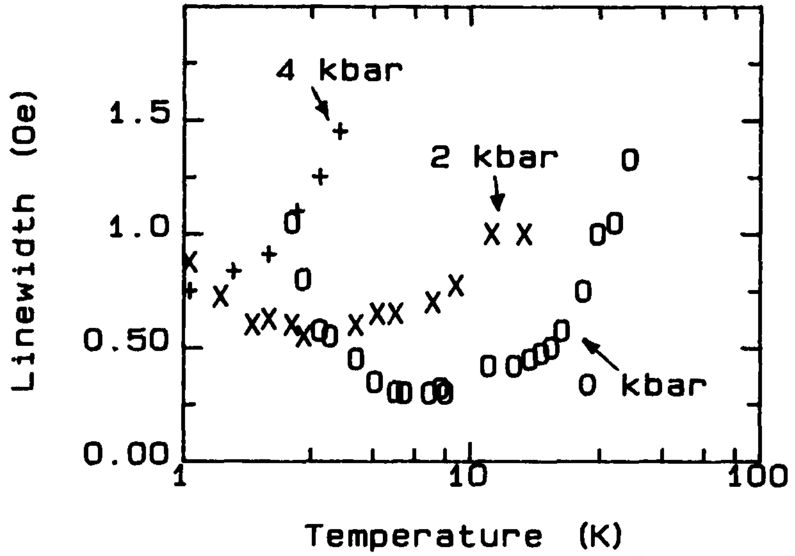

Figure 5. Low field ESR peak-to-peak linewidth (resonance field 10 Oe) vs temperature for 3 pressures in (BEDT-TTF)$_2$BrO$_4$

In the low temperature regime the microwave linewidth is less than the low field linewidth. The linewidth reaches a minimum of 0.3 Oe at 6 K and then increases strongly at lower temperatures. The decrease of the linewidth is similar to the ambient pressure results on (BEDT-TTF)$_2$I$_3$, which we interpret as that expected of a metal. However, as transport studies show,^{3} in this case there is evidence that (BEDT-TTF)$_2$BrO$_4$ is a semiconducting material at low temperatures. This points to the danger of interpreting the results of only one experiment and reaching an erroneous conclusion. The susceptibility of (BEDT-TTF)$_2$BrO$_4$ (not shown) decreases at lower temperatures indicative of a magnetic transition. With the application of pressure the transition is suppressed to lower temperature until at pressures above 4 kbar the transition temperature (defined as the minimum of the linewidth) is below 1 K. It is likely that the transition is a spin density wave transition based on the similarities with the other organic salts on this series. Finally, the ambient pressure microwave experiments on $(BEDT-TTF)_2BrO_4$ show a pronounced frequency dependence to the linewidth at temperatures below the transition.

In addition, we have measured the low field electron spin susceptibility using the Schumaker-Slichter method and find acceptable agreement with the low field measurements. The conductivity of $(BEDT-TTF)_2BrO_4$ is moderately

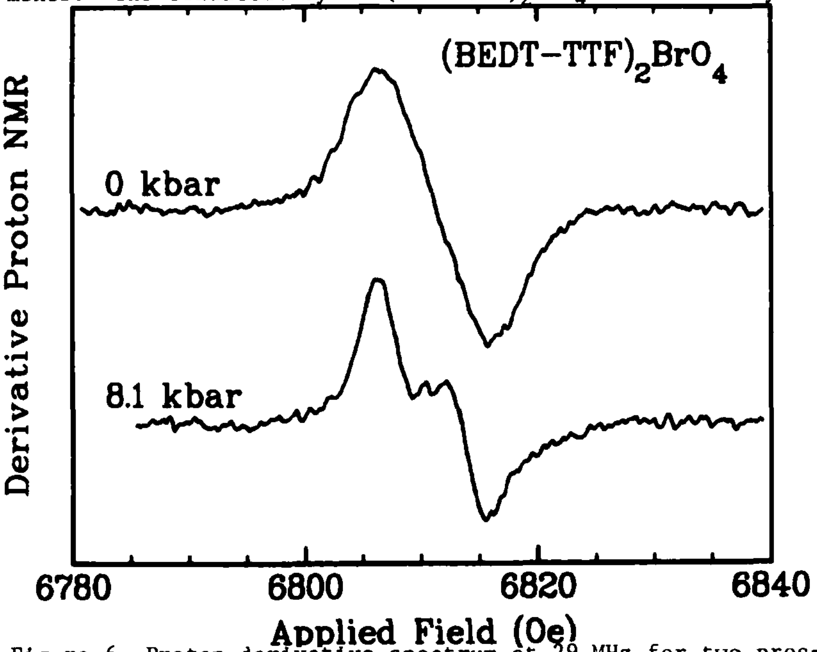

Figure 6. Proton derivative spectrum at 29 MHz for two pressures. The zero pressure data was taken at a temperature of 4.02 K and the 8 kbar at 1.02 K. There was no observed temperature dependence to the spectra for temperatures below 4 K over the whole pressure range.

activated below 200 K[3] and the low temperature log conductivity vs inverse temperature plot shows curvature similar to that observed in disordered materials such as Qn(TCNQ)$_2$. In Fig. 6 we show two derivative spectra of protons in (BEDT-TTF)$_2$BrO$_4$ at ambient pressure and at 8 kbar. Note that at high pressure the resolution of several individual proton lines. The increased resolution at high pressure is probably the result of hindered motion of the methylene groups. The resolution of individual proton lines without any line narrowing techniques implies that there can be localization of the electron spins. In Fig. 7 we show the pressure dependence of the

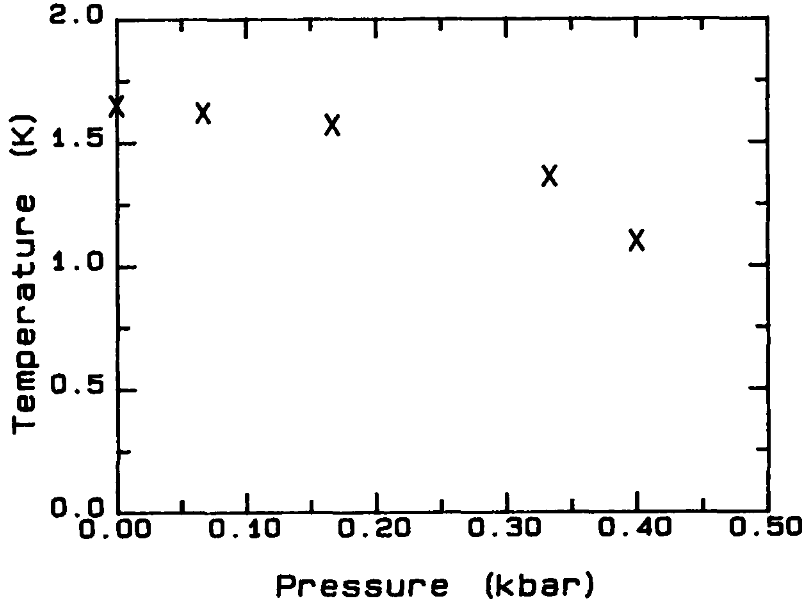

Figure 7. Pressure dependence of the superconducting transition temperature for (BEDT-TTF)$_2$I$_3$. The data point at 0.4 kbar is an upper limit: no superconductivity was observed down to 1.1 K.

superconducting transition temperature, T_c. At a pressure of 0.4 kbar T_c has been suppressed to below 1.1 K. This is an enormous pressure dependence compared to that measured on other superconducting organics. In this experiment T_c was measured by the contactless technique of monitoring the absorption in a coil. We define T_c as the onset of the superconducting transition. Four probe conductivity measurements on samples from the same batch confirm these values of T_c.[3] Above a pressure of 0.4 kbar we observe a magnetic transition, as measured by radio frequency absorption experiments whose onset is at 7 K. There is no pressure dependence to this transition up to at least 4 kbar of pressure.

Four probe conductivity measurements at 0.5 kbar show a small (about 10%) increase in the resistance of the sample in the 7 K temperature range. One interpretation of this effect is the partial loss of Fermi surface to a spin density wave.

CONCLUSIONS

We have found that the organic conductor $(BEDT\text{-}TTF)_2BrO_4$ has a magnetic phase transition at low temperature which is suppressed with the application of pressure. The proton spectra under pressure imply that the electron spins are localized and have small exchange interactions, consistent with the observed activated conductivity. In addition, the microwave ESR experiments do not show any evidence for a dysonian lineshape which would be expected for a metal. $(BEDT\text{-}TTF)_2I_3$ has a very large pressure dependence to T_c and we have discovered a magnetic phase transition at 7 K for pressures above 0.4 kbar which is most likely a partial destruction of the Fermi surface due to a spin density wave transition.

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3. See J. F. Kwak, these proceedings.

4. J. E. Schirber, Cryogenics, 10,418(70)