PRESSURE EFFECT ON THE MAGNETIC SUSCEPTIBILITY OF LOW DIMENSIONAL ORGANIC CON-

DUCTORS α,β-(BEDT-TTF)$_2$I$_3$ AND (TMTSF)$_2$X (X = ClO$_4$, PF$_6$, ReO$_4$)

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ABSTRACT

The pressure dependence of the static susceptibility of the α and β phases of (BEDT-TTF)$_2$I$_3$ and of (TMTSF)$_2$X for X = ClO$_4^-$, PF$_6^-$, ReO$_4^-$ was measured using a Faraday balance up to a pressure of 10 kbar. The fractional pressure dependence $\delta \ln\chi_s/\delta P$ is -2.0%/kbar and -3.3%/kbar for the α- and β-(BEDT-TTF)$_2$I$_3$ respectively and it is temperature independent. For (TMTSF)$_2$X $\delta \ln\chi_s/\delta P$ is about -3.0%/kbar at room temperature and increases to -4.8%/kbar on cooling. Both the magnitude and temperature dependence of the fractional pressure dependence in those two families are in contrast with the behaviour in TTF-TCNQ, where the magnitude is -8.%/kbar and decreases with decreasing temperature.

INTRODUCTION

The spin susceptibility χ of organic metals differs from the Pauli susceptibility of normal metals in several respects. It is temperature dependent, increases with temperature (in most organic metals) by about a factor of 2 between 100 K and 300 K; it is enhanced above the Pauli value by about a factor of 3 to 5 at ambient temperature; and it is strongly pressure dependent (see table1).

TABLE 1

	Perylene $(AgF_6)_{.75}$ $(PF_6)_{.25}$	TMTTF-TCNQ	TTF-TCNQ	$(TMTTF)_2$ BF_4	$(TMTSF)_2X$	$\alpha(BEDT-TTF)_2I_3$	$\beta(BEDT-TTF)_2I_3$
$\chi_s(300K)$ $(10^{-4}emu/mole)$	0.92	4.8	6.0	6.0	3.0-3.3	6.8	4.7
$\chi_s(300K)/\chi_{band}$	2-4	2-5	2-5	4-6	2-2.5	5	3
$\chi_s(300K)/\chi_s(100K)$	–	2	2	1.5	1.6	–	$\sim$ 1
$\delta \ln\chi_s/\delta P$ (300K) (%/kbar)	$4.2^{\pm}1.2$	$6.8^{\pm}1$	$8.0^{\pm}1$	$3.0^{\pm}1$	$3.0^{\pm}0.5$	$2.0^{\pm}.3$	$3.3^{\pm}.3$

The magnitude of spin susceptibility χ_s (see for example ref.[7]); the enhancement of χ_s at 300 K with respect to the expected value calculated from the assumed bandwith $\chi_s(300K)/\chi_{band}$ (see ref. [16]); the temperature dependence of the spin susceptibility given by the ratio of χ_s at 300 K and 100 K (see ref. [16]); and the pressure derivative $\delta \ln\chi_s/\delta P$ for the compounds studied up to now (Perylene$(AsF_6)_{.95}(PF_6)_{.25}$ (see ref. [3]), TMTTF-TCNQ, ref. [1], TTF-TCNQ, ref.[1], [2], $(TMTTF)_2BF_4$, ref. [2], and $(TMTSF)_2X$, $\alpha,\beta-(BEDT-TTF)_2I_3$, this work. $\delta \ln\chi_s/\delta P$ for TMTTF-TCNQ, TTF-TCNQ and $(TMTTF)_2BF_4$ is obtained by the ESR method. Note that the interchain couplings increase significantly from Perylene $(AsF_6)_{.75}(PF_6)_{.25}$ towards the $\beta-(BEDT-TTF)_2I_3$.

The Pauli susceptibility in "normal" metal displays none of these features. The spin susceptibility is one of the best-understood physical properties, and the smallness of its pressure dependence in "normal" metals appears to be universal.

The pressure-dependence of the susceptibility was measured in the past in the organic metals TTF-TCNQ [1,2], TMTTF-TCNQ [1], $(TMTTF)_2BF_4$ [2], and Perylene [3]. In all cases, it was found to be surprisingly large. The aim of the present set of measurements is to find out whether this strong pressure dependence is universal. Also, we want to find the temperature dependence of this pressure dependent. In the TTF-TCNQ series, there is a marked increase in the pressure-dependence with temperature.

The susceptibility χ increases with temperature in the TTF-TCNQ [4] and $TMTSF_2X$ series, and is nearly temperature-independent in $\beta-(BEDT-TTF)_2I_3$. We also aim to find out whether there is a correlation between the temperature dependence of χ and that of $\delta \ln\chi/\delta P$.

The understanding of χ is of great theoretical significance. There have been proposals attributing the enhancement of χ to Coulomb forces - the so-called "Big U" theories [5]. Also, polaronic effects have been proposed attributing the enhanced value of χ to electron-phonon interactions [6]. The detailed behaviour of $\delta \ln\chi/\delta P$ in different systems, and at different temperatures, should help to establish the theoretical understanding as well. Therefore, we have

performed measurements of $\chi(P,T)$ by a Faraday-balance method on two families of organic crystals, the $(TMTSF)_2X$ where $X = ClO_4$, PF_6 and ReO_4 and $\alpha,\beta-(BEDT-TTF)_2I_3$. During the last five years these compounds are of great interest because of their superconducting properties: $(TMTSF)_2PF_6$ is the first organic metal which shows superconductivity for $P > 10$ kbar, $(TMTSF)_2ClO_4$ is the first ambient pressure superconductor [7], while $\beta-(BEDT-TTF)_2I_3$ is the organic superconductor with the highest $T_c = 8$ K [8].

In the past, the spin susceptibility was measured by EPR, or by a Faraday balance. The EPR method can be used only when the EPR line is narrow, which is not the case in selenium compounds. The Faraday balance method is universal, but the difficulty is that it measures the total susceptibility, and in order to get the change in χ_s with pressure, one has to determine also the pressure dependence of χ_{dia} of the core, of the pressure fluid and delrin container. In the present set of measurements, we aim to find the factors affecting the accuracy of this method, and attain a high level of precision.

EXPERIMENTAL

Measurements of the static susceptibility at high pressures were carried out by the Faraday method using a CAHN R-100 microbalance, a superconducting solenoid with a field up to 5.7 T, and a miniature binary Cu-Be pressure clamp. Magnetic compensation of the diamagnetism of the pressure clamp was provided by a molybdenum cylinder. The pressure cell consists of a 0.4 mm thick tube of delrin (outer diameter 5.0 mm) which is sealed at both ends by a sealing ring made of unhardened binary Cu-Be, and two pistons made of hardened binary Cu-Be. The pressure transmitting fluid is a 50%-50% mixture of n-hexane/n-heptane. The pressure inside the pressure cell is measured at room temperature by the change in diameter $\emptyset$ of the pressure clamp at its center. This has been calibrated in a separate experiment against a manganin pressure gauge inside the cell. At the maximum pressure of 10.5 kbar, $\emptyset$ increases by 21 μm (with a resolution of 0.1 μm). The pressure in the pressure cell decreases upon cooling due to the large thermal contraction of the pressure fluid and the sample. The pressure at low T is determined by measuring the superconducting transition of a Pb manometer. The pressure at intermediate temperatures is determined by measuring $\Delta\chi=\chi(P)-\chi(0)$ for the diamagnetic pressure fluid with no sample present. $\Delta\chi$ is assumed to be T-independent and its decrease on cooling is attributed to pressure losses. According to this the pressure loss is linear down to 80-100 K and then levels off. Such a pressure scale is verified by measuring the metal-insulator phase transition temperatures T_p of compounds whose values of dT_p/dP are known from transport measurements (α-BEDT-TTF, $TMTSF_2ReO_4$) [9,10].

In order to evaluate the pressure dependence of χ_s, i.e. $\delta\ell n_{\chi_s}/\delta P \equiv \Delta\chi_s/\chi_s P$,

the pressure dependence of the core diamagnetism of the TMTSF and BEDT-TTF mole-
cules, of the pressure fluid, and of the delrin has been measured separately. At
room temperature their diamagnetism decreases at rates of 0.8±0.1 %/kbar, 0.8±
0.1 %/kbar, 0.8+0.1 %/kbar and less than 0.3 %/kbar, respectively.

For α,β-(BEDT-TTF)$_2$I$_3$ $\underline{ca}$. 45 mg and for the (TMTSF)$_2$X salts $\underline{ca}$. 80 mg of
electrochemically synthesized crystals were measured. In the case of α,β-(BEDT-
TTF)$_2$I$_3$ χ(T,P) was measured on single crystals. The (TMTSF)$_2$X salts were light-
ly compressed into a pellet in order to put them into the limited volume of the
pressure cell. Except for an increased low T Curie tail the χ(T) of the pellet
and of the single crystals is found to be identical.

RESULTS

Figures 1 and 2 show the temperature dependence of the total susceptibility
at ambient and high pressures for α,β-(BEDT-TTF)$_2$I$_3$ and (TMTSF)$_2$X family
respectively. Note that the data prints do not correspond to the same pressure
over the entire temperature range, because of the pressure losses on cooling.
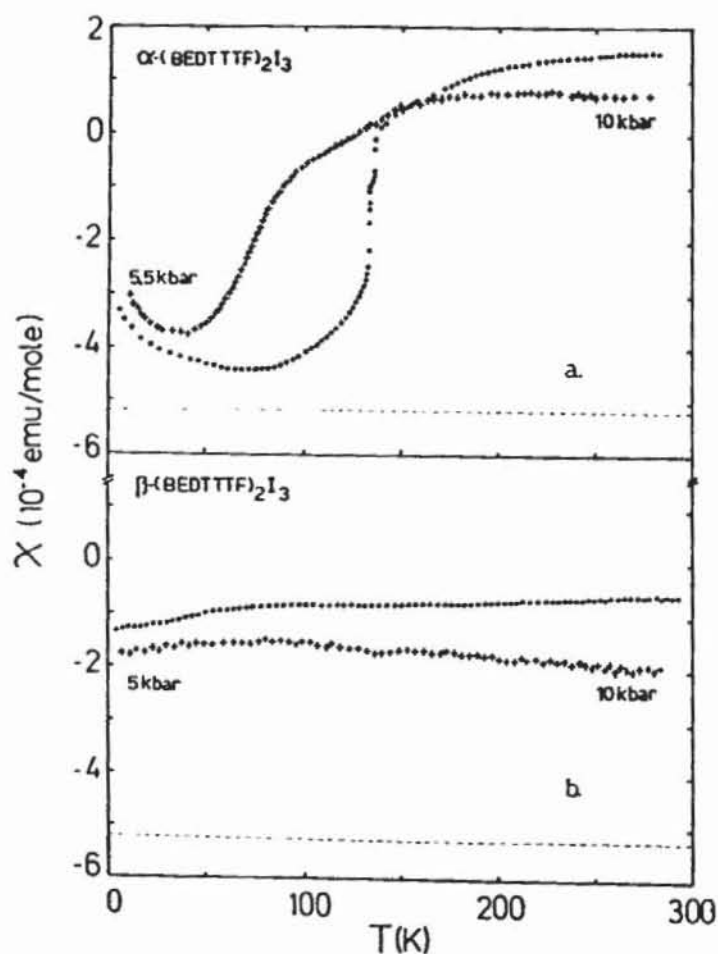The room temperature and helium temperature pressures are given on the figures.

Fig. 1. Static suscep-
tibility χ versus tem-
perature for single
crystals of α and β-
(BEDT-TTF)$_2$I$_3$ at am-
bient pressure and at
high pressure. Note
that the high pressure
data prints do not be-
long to the same pres-
sure over the entire
temperature range be-
cause of the pressure
losses on cooling. The
room temperature and
helium temperature
pressures are given on
the figures. The core
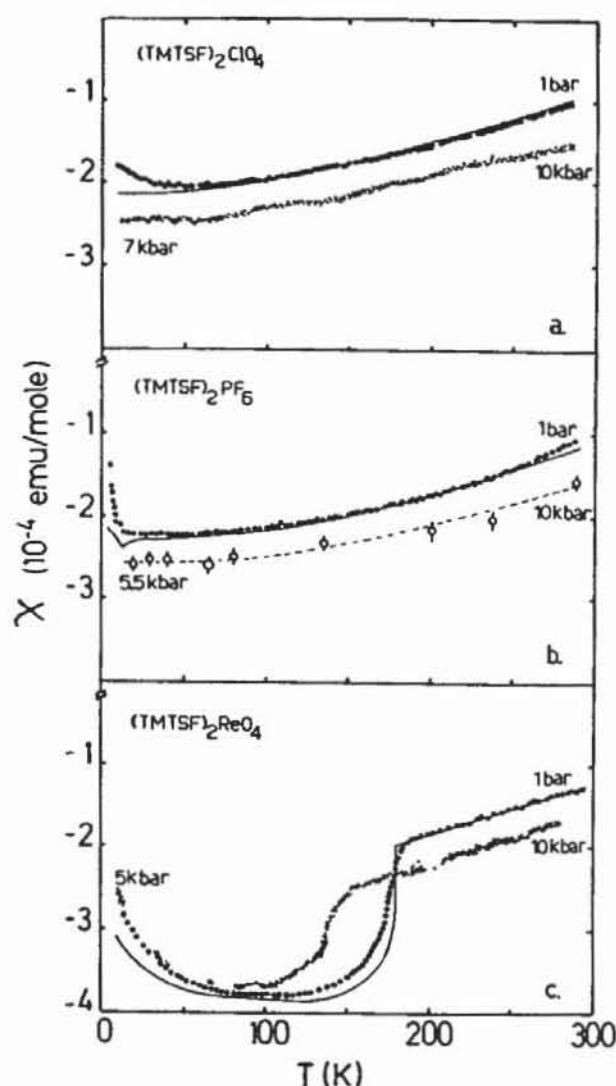diamagnetism is marked
with dashed line.

Fig. 2. Static susceptibility χ versus temperature for single crystals (full line) and pellets ($_o$) at ambient pressure and at high pressures (small points for $X = ClO_4$ and ReO_4 and open circles for PF_6). The dashed line for the latter compound is a guide for the eye. Note that the high pressure data points do not belong to the same pressure over the entire temperature range because of the pressure losses on cooling. The room temperature and helium temperature pressures are given on the figures. The Curie tails are substracted from the high pressure data for $X = ClO_4$ and PF_6. Corrections have not yet been made for the pressure dependence of χ_{dia} of the pressure fluid and core, i.e. the same empty clamp force has been subtracted for ambient and high pressures.

In figs. 1 and 2 corrections have not been made for the pressure dependence of χ_{dia} of the pressure fluid and core i.e. the same empty clamp force has been subtracted for ambient and high pressures.

In order to determine the pressure dependence of χ_s accurately we have measured $\Delta\chi = \chi(P)-\chi(o)$ at 290 K for all the compounds as a function of pressure up to 10.5 kbar. Fig. 3 illustrates it for $\beta-(BEDT-TTF)_2I_3$ and $(TMTSF)_2ClO_4$. The dotted line shows the contribution arising from the decrease in core diamagnetism under pressure. It is assumed that the core diamagnetism changes under pressure at the same rate as that of the BEDT-TTF and TMTSF molecules measured separately. The full line through the experimental points is the total χ, i.e. $\chi_s + \chi_{core}$ corrected for the diamagnetism of the pressure fluid. Thus the change in χ_s with pressure is the difference between the full and dashed lines. The values of $\delta ln\chi_s/dP \equiv \Delta\chi_s/\chi_s P$ are given in Table 1 completed with the pressure derivatives of compounds studied previously.
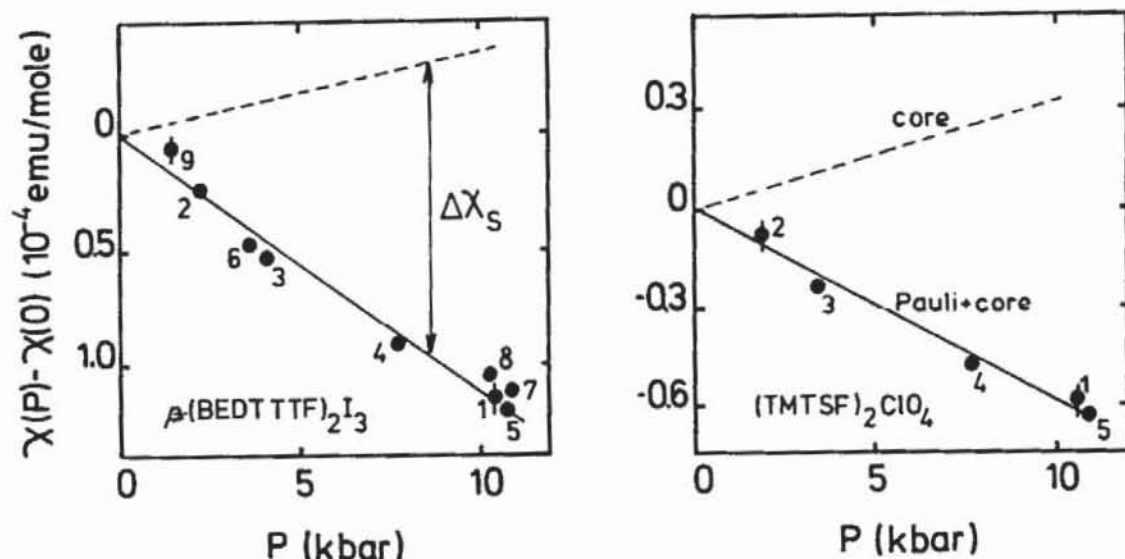
Fig. 3. $\Delta\chi = \chi(P) - \chi(0)$ versus pressure at 290 K for β-$(BEDT-TTF)_2I_3$ and $(TMTSF)_2ClO_4$. The dashed line shows the change of the core diamagnetism under pressure measured in a separate experiment, while the experimental points give the change in $\chi_s + \chi_{core}$ corrected for the diamagnetism of the pressure fluid. The change in χ_s with pressure is the difference between the dashed and the full lines. The numbers above the experimental points mark the sequence of measurements. The pressure derivative $\delta\ln\chi_s/\delta P \equiv \Delta\chi_s/\chi_s P$ is -3.3 ± 0.3 %/kbar and 3.0 ± 0.5 %/kbar for β-$(BEDT-TTF)_2I_3$ and $(TMTSF)_2ClO_4$ respectively.

Using the data of figs. 1 and 2 and knowing the pressure dependence of χ_{dia} of the pressure fluid and core electrons, and the pressure at all temperatures, we deduce the temperature dependence of $\delta\ln\chi_s/\delta P$. This is shown in fig. 4 for α, β-$(BEDT-TTF)_2I_3$, $(TMTSF)_2X$, X = ClO_4, PF_6, ReO_4 and for TTF-TCNQ and TMTTF-TCNQ.

The behaviour of the susceptibility in the three systems investigated so far, is qualitatively different. In TTF-TCNQ and TMTTF-TCNQ, both χ and $|d\ln\chi/dP|$ increase with temperature. In the Bechgaard salts, χ increases with T, while $|d\ln\chi/dP|$ decreases with increasing T. In BEDT-TTF_2I_3, both χ and $d\ln\chi/dP$ are nearly temperature independent. This qualitative difference is the salient feature of this work.

DISCUSSION

The temperature-independence of χ_s in BEDT-TTF_2I_3 is characteristic of "normal" metals. The value of χ_s is probably enhanced over the bare band value by about a factor of 3, however the available band calculations [11] are crude. Some enhancement of χ_s could be due to a Stoner factor, as in metals like Pd. However, more reliable values of $n(E_F)$ should be available before the enhancement factor can be established definitely. BEDT-TTF_2I_3 differs from TTF-TCNQ and $TMTSF_2X$ in several respects; the electronic band structure is two-dimensional rather than one-dimensional; also, the band-width is larger. Either factor could be responsible for the temperature-independence of χ_s.
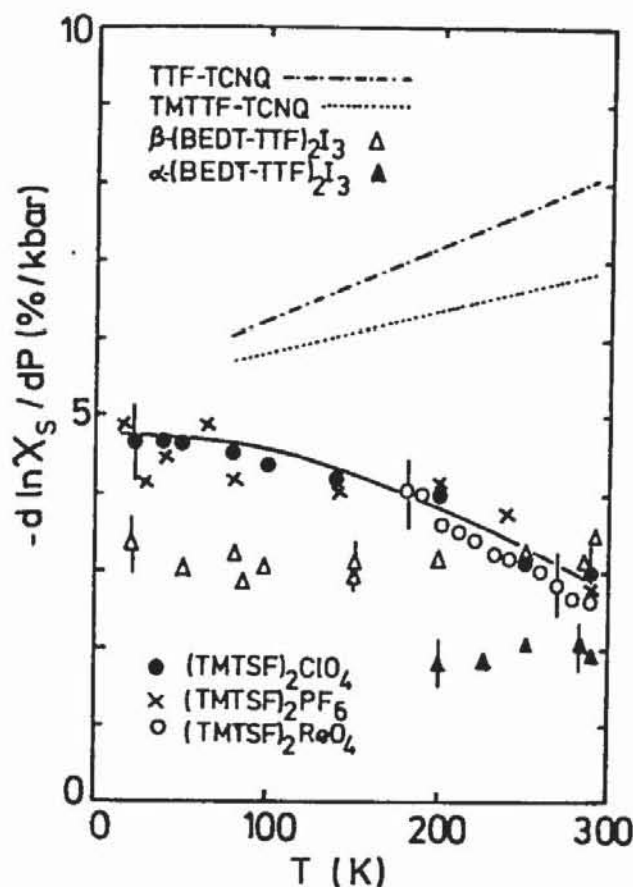
Fig. 4. Temperature dependence of the pressure derivatives deduced from fig. 1. and 2. after corrections for the change in the diamagnetism of the core and liquid. For comparison the pressure derivatives of TTF-TCNQ [1,2] and TMTTF-TCNQ [1] are given schematically.

The pressure derivative is $\delta \ln\chi_s/dP \simeq -3.0^{\pm}0.5\%/kbar$ for both $\beta-(BEDT-TTF_2)I_3$ and $(TMTSF)_2X$ family. Analysing χ_s within the tight binding formula

$$\chi_s = \mu_B^2 \,(\pi t_* \sin\pi\rho/2)^{-1}$$

$\delta \ln\chi_s/dP$ is determined by the pressure dependence of the bare bandwidth $\delta \ln t_*/dP$. However, the pressure dependence of the bare bandwidth was measured by Welber et al [12] for TTF-TCNQ and yields 2%/kbar. $(TMTSF)_2X$ [13] and $\beta-BEDT-TTF)_2I_3$ [14] have much larger bandwidths then TTF-TCNQ and an effective mass close to the free electron value, therefore, the pressure dependence of the bandwidth and spin susceptibility should be much smaller for these compounds, about 1%/kbar.

The decrease of $|\delta \ln\chi/dP|$ with T in $TMTSF_2X$ is a novel and surprising result. Within the framework of polaronic theory [6] we can attribute this behaviour to internal modes (i.e. bond twisting, bond bending, perhaps even C-Se stretching modes) that become excited at ambient temperature and thus give a contribution to χ_s without having a large pressure-derivative, since the frequency of internal modes is not strongly pressure-dependent. At low temperatures only low-frequency modes (external, i.e. rigid translations and librations) are excited, and the frequency of these modes is much more pressure dependent [15].

CONCLUSION

Organic metals differ from "normal" metals in having a large pressure dependence of the susceptibility, $-\delta\ln\chi/dP$ is typically 3-4%. This pressure-dependence has now been observed in the TTF-TCNQ family, the $TMTSF_2X$ family, (BEDT-TTF)$_2I_3$ and perylene. However, the variation of the pressure-dependence with temperature differs for different organic metals, increasing with T for the TTF-TCNQ family, decreasing with T for the $TMTSF_2X$ family, and being pressure independent in β-(BEDT-TTF)$_2I_3$. Theoretically, the Born-Oppenheimer approximation that applies in "ordinary" metals where the phonon frequency is very much smaller than the electronic bandwidth, may not apply for organic metals. More information about the phonon density of states, and the electron-phonon coupling will help to provide a better understanding of the susceptibility and its pressure dependence.

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