Observation of Superconductivity in the Organometallic Intercalation Compound $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$

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Intercalation of phosphorus-doped $SnSe_2$ with bis(cyclopentadienyl) cobalt $\{Co(\eta^5\text{-}C_5H_5)_2\}$ produces superconducting $SnSe_2\{Co(\eta^5\text{-}C_5H_5)_2\}_{0.33}$ with a critical temperature of 6 K; magnetisation measurements show a hysteresis loop with a maximum at 40 G, indicating type II superconducting behaviour; the lower critical field (B_{c1}) is estimated at 10 G at 4.2 K and the critical current density (I_c) is *ca.* 500 A cm^{-2} at 2.5 K; the diamagnetic susceptibility corresponds to 13% of perfect diamagnetism.

In recent years, molecular solid state chemistry has experienced rapid growth, through the discovery of molecular organic crystals and extended inorganic lattices that exhibit metallic conductivity and even become superconducting at low temperature. Of particular interest are materials with layered structures, *viz.* ceramic copper oxide superconductors,[1] the molecular organics BEDT–TTF [bis(ethylenedithio)-tetrathiafulvalene],[2] and the dichalcogenides of niobium and tantalum.[3]

We have demonstrated previously that bis(η-cyclopentadienyl)cobalt can be intercalated into single crystalline samples of layered tin dichalcogenides.[4] We have used both UV and *X*-ray photoelectron spectroscopy to characterise the unusual mixed valence behaviour of this material and to

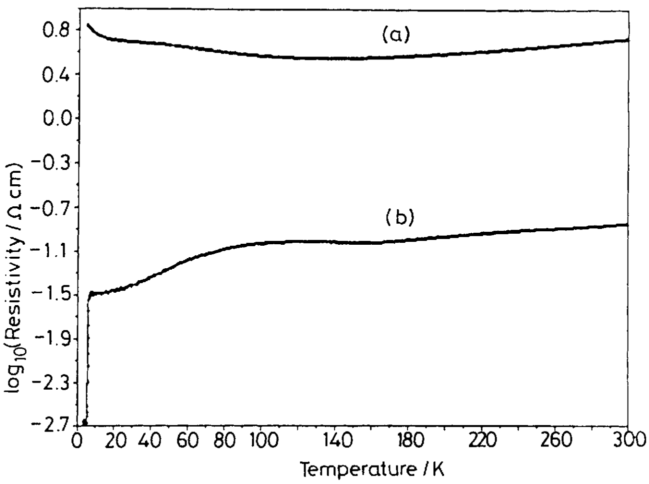

Figure 1. Plot of $\log_{10}$ (resistivity/Ω cm) *vs.* temperature for single crystals (a) $SnSe_2$ and (b) $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$.

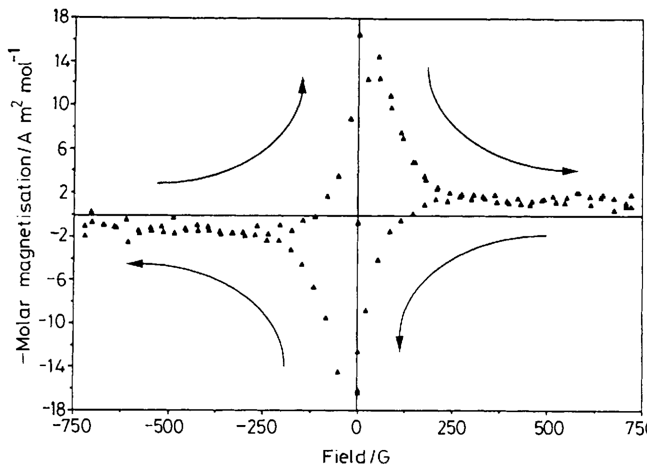

Figure 2. Plot of molar magnetisation *vs.* applied magnetic field for $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ at 2.5 K.

elucidate the changes in band filling as we cross the series of intercalates $SnS_{2-x}Se_x\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$. Our valence band UV-PES experiments indicated that the intercalate $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ has a partially filled conduction band characteristic of metallic behaviour.

In this communication we report conductivity and magnetic susceptibility measurements on $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ which reveal a transition to a superconducting state below 6 K.

Single crystals of phosphorus doped (1% molar) $SnSe_2$ were grown by vapour phase transport using I_2 as the transport agent (4 mg cm^{-3}).[5] Crystalline samples of the intercalate $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ were prepared by heating crystals of $SnSe_2$ (typically 4.0 × 2.0 × 0.1 mm) in a concentrated solution of bis(η-cyclopentadienyl)cobalt in MeCN for 21 days at 60 °C. After the reaction was complete the crystals were washed with MeCN and dried *in vacuo*. The final elemental composition and homogeneity of the samples were determined by elemental microanalysis and powder *X*-ray diffraction ($\Delta c = 5.56 \pm 0.01$ Å). The intercalate was found to be air sensitive and all manipulations and measurements were carried out under an inert atmosphere.

The single crystal 4-probe electrical conductivity of n-type $SnSe_2$[6] was measured in the temperature range 2—300 K [Figure 1(a)]. The gross features of the temperature dependence of the resistivity can be modelled assuming a mechanism for conductivity in which the number of carriers (n) has an $\exp(-A/kT)$ dependence, whereas their mobility (μ) has a $T^{-\alpha}$ dependence. A fit for the generalised equation (1)[7] gives the activation energy (A) of 4×10^{-4} eV and α *ca.* 2.0. This small activation energy is consistent with an extrinsic semiconductor. The band gap measured optically by transmission through a single crystal is 1.3 eV.

$$\sigma(T) = \sigma_0 e^{-A/kT} T^{-\alpha} \quad (1)$$

On intercalation of bis(η-cyclopentadienyl)cobalt, the room temperature conductivity for single crystals increases significantly from 0.2 to 9 Ω^{-1} cm^{-1}. On cooling the resistivity initially falls linearly to a minimum value near 150 K, before increasing to reach a maximum near 100 K. At 6.1 K the resistivity drops sharply from 2.5×10^{-2} Ω cm to zero [Figure 1(b)]. The width of the transition is *ca.* 0.6 K. This temperature dependence of the resistance has also been observed in the organic superconductor $(BEDT\text{–}TTF)_2Cu(NCS)_2$.[8]

Superconductivity was confirmed by the observation of a magnetic response appropriate to a type II superconductor. After cooling to 4.2 K in zero applied magnetic field, an initial diamagnetic response was observed as shown in Figure 2. At 4.2 K the magnetisation falls to a low value above 300 G (1G = 10^{-4} T), the presence of flux trapped within the sample is shown on returning to zero applied field. Below 3 K extensive hysteresis of the magnetic moment is observed as the motion of the flux lines is hindered.

The initial diamagnetic response of the sample after cooling in zero applied field had a magnitude equivalent to 13% of the total calculated diamagnetism using Pascal constants. Previous studies on the $TaS_2\{pyridine\}_{0.5}$[9] superconductor indicated that the Meissner effect is dependent on the sample orientation with respect to the applied magnetic field. In this case it is highly likely that the sample was not randomly orientated in the magnetic field. In addition, our *X*-ray photoelectron experiments on this sample indicate that not all the bis(η-cyclopentadienyl)cobalt is oxidised on intercalation[4] and so the material will have residual paramagnetic response, we therefore conclude that the value of 13% flux exclusion will be a minimum limiting value. The application of the Critical State Theory of the magnetic moment gives a critical current density at 4.2 K of 200 A cm^{-2}, rising to 500 A cm^{-2} at 2.5 K.

The discovery of superconductivity in other intercalation complexes such as $TaS_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.25}$ and $NbSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.25}$[10,11] has been reported previously, and these observations raised many questions regarding the dimensionality of the superconducting state in these complexes.[12] However the pure host lattices also exhibit a superconducting transition at lower temperatures.

The observation of a superconducting transition for $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ is remarkable since the pure host lattice is a large band gap semiconductor. Intercalation of bis(η-cyclopentadienyl)cobalt induces a transition to a metallic phase which becomes superconducting below 6.1 K. To our knowledge $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ has the highest reported T_c for an organometallic intercalate.

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