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RELATIONSHIP BETWEEN EFFECTIVE MASS AND SUPERCONDUCTING CRITICAL TEMPERATURE IN THE ORGANIC SUPERCONDUCTOR κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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We report high pressure magnetotransport on the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The observation of Shubnikov-de Haas and magnetic breakdown oscillations has allowed the pressure dependences of the Fermi surface topology and quasiparticle effective masses to be deduced and compared with simultaneous measurements of the superconducting critical temperature T_c. The data strongly suggest that the enhancement of the effective mass and the superconducting behaviour are directly connected. The results are fitted by calculations of the linearised Eliashberg equations.

1. Introduction

In the BCS theory of superconductivity, the critical temperature T_c is expressed in terms of parameters such as the electron-phonon coupling function $\alpha^2F(\omega)$ and the Coulomb pseudopotential μ^*. Whilst these parameters are exactly defined in microscopic theories [1], it has proved difficult to determine them experimentally in the case of organic superconductors such as the BEDT-TTF charge transfer salts ([1-3] and references therein); even the pairing mechanism remains a contentious issue.

Instead of direct measurements of parameters characterising the superconducting state, the approach followed in this work has been to vary the bandstructure of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ using hydrostatic pressure and then to measure the resultant changes in Fermi surface (FS) topology, quasiparticle effective mass m^* and superconducting T_c simultaneously. In this way, T_c can be related to m^* (itself an input parameter in theoretical determinations of *e.g.* $\alpha^2F(\omega)$) in a consistent manner, enabling theoretical approaches to superconductivity to be tested. Since both m^* and T_c are determined by many-body interactions, an analysis of their relationship must give some insight into these interactions and clues to the form of the pairing mechanism. Studies such as this are aided by the simplicity of the FS in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, which consists of a quasi-two-dimensional (q2D) hole pocket and a quasi-one-dimensional (q1D) electron section [4] separated by a small gap (Figure 1).

2. Experimental

High purity single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ were grown by electrocrystallization of BEDT-TTF in distilled 1,1,2-trichloroethane and 10 % ethanol using KSCN/ CuSCN/ 18 Crown 6 as the source of the anion; the crystals are generally small (1x1x0.1 mm^3) black platelets, with the plane of the plate corresponding to the highly conducting 2D layers. Electrical contacts were made with silver paste to evaporated gold pads on both platelet faces, resulting in contact resistances of less than 10 Ω. Standard 4-wire AC techniques (5-150 Hz), with the current applied perpendicular to the sample q2D planes, were used for all measurements. To avoid sample heating, currents were generally 0.2-20 μA.

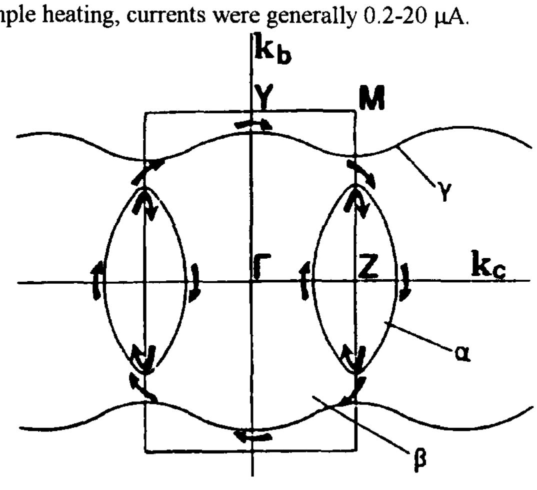

Figure 1 Schematic of Brillouin zone and Fermi surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ showing α and β orbits [4,5].

Magnetoresistance (MR) experiments under hydrostatic pressure were carried out using a non-magnetic clamp cell filled with a petroleum spirit medium providing pressures up to 16.5 kbar at helium temperatures. Pressure was applied at

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room temperature and then the cell was placed in a ^3He cryostat providing temperatures down to 500 mK in a 17 T superconducting magnet; cooling from room temperature to 4.2 K was accomplished over a period of around 12 hours, to ensure that the pressure was ideally hydrostatic at low temperatures. The temperature of the sample could be varied between 500 mK and 15 K and was measured using calibrated ruthenium oxide and carbon sensors, and the pressure in the cell at all temperatures was monitored using the resistance of Manganin wire with a known pressure and temperature coefficient

Figure 2 shows the MR of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at 0.7 K for a number of hydrostatic pressures [3]. The normal state conductivity of the sample increases with pressure and the upper critical field B_{c2}, observed as a steep drop in resistance to zero, decreases sharply.

A series of Shubnikov-de Haas (SdH) oscillations is observed in the MR, and both the amplitude and the frequency of the oscillations are visibly affected by pressure. These oscillations correspond to a k-space orbit about the q2D hole pocket of the FS; in common with others we label this the α-orbit (Figure 1) [5]. As the pressure is raised further (Figure 3)[3], a second series of oscillations with a higher frequency is observed in the MR, superimposed on the α-orbit oscillations. Similar oscillations have been observed at ~20 T at ambient pressure, and are attributed to magnetic breakdown[3,5]. Magnetic breakdown is due to electrons tunnelling between states of equal energy in adjacent sections of FS, thus describing a larger k-space orbit[3,5]. The inset in Figure 1 indicates the primary breakdown orbit (the β-orbit) in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ around the outer edges of both the q2D and the q1D FS sections.

The measured α-orbit SdH frequency increases from the ambient pressure value of 600 T to 775 T at 16.3 kbar, an increase in α-orbit k-space area of ~30 % [3]. By contrast, the frequency of the β-orbit increases by only 6 % over the same pressure range. This result is not unexpected as the β-orbit has the same area as the first Brilloun zone so that the slow increase merely reflects the compressibility of the material [6]. The breakdown field, which parameterises the strength of magnetic breakdown, may be deduced from the field dependence of the oscillatory MR using the Lifshitz-Kosevich formula and the coupled network magnetic breakdown model [3,5]; it is shown as a function of pressure in the inset to Figure 3. The breakdown field appears to extrapolate to zero at around 25 kbar, indicating that the q2D and q1D sections of FS unite at this pressure.

3. Effective masses

The effective masses associated with the α and β orbits were derived by fitting the temperature dependence of the SdH and magnetic breakdown oscillation amplitudes measured in the range 0.5-5 K at each pressure to the Lifshitz-Kosevich formula [5] and are shown in Figure 4. Two distinct regions are observed: above a pressure P_c~5 kbar the rate of change in effective mass with pressure is some eight times smaller than that below P_c. The variation of the superconducting T_c with pressure and its disappearence at P_c (Figure 3) appears to be connected with the rapid variation of the effective mass in this region [3]. The Dingle temperature T_D is found to be 0.57 K at ambient pressure by a direct fit to the field-dependent SdH data [6]; however, the product m^*T_D appears to be independent of pressure to within the experimental error [6].

The effective masses of carriers in ET charge-transfer salts measured using the SdH and dHvA effects are known to be much larger than those predicted by bandstructure calculations, suggesting that many body effects are important[7,8]. Within the theory of interacting Fermions a number of quasiparticle "masses" can be defined, reflecting the differing dynamical behaviour involved in various physical properties [9]. The simplest is the bare band mass m_b, which is derived from single particle bandstructure calculations. This is close in size to the optical mass m_{opt} which can be probed by an optical measurement of the intraband plasma response [9]. The effective mass m^* occurs in the thermodynamic density of states, and may crudely be thought of as arising from a quasiparticle displacing other quasiparticles as it moves through a medium. The backflow of quasiparticles leads to a contribution to the effective mass m^*. The dynamical mass m_λ is the mass which would be observed in the absence of quasiparticle interactions; it represents m_b renormalised only by electron-phonon interactions, whereas m^* contains contributions from both quasiparticle interactions and electron-phonon interactions. The temperature dependence of phenomena such as the SdH and dHvA effects determines the effective mass m^* whereas a microwave cyclotron resonance (CR) experiment measures m_λ [8,9].

Various quasiparticle masses have been derived for the α-orbit of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at ambient pressure[3]; $m_{b\alpha}$=0.64m_e was obtained from a fit of bandstructure calculations to low-temperature optical data[3], CR experiments give a value of $m_{\lambda\alpha}$=1.18m_e[8] and m^*_α=3.5m_e was measured using the SdH effect (Figure 4)[3]. The value m^*_α=3.5m_e represents an enhancement of a factor of ~3 over $m_{\lambda\alpha}$. The quasiparticle interactions thus appear to give a larger renormalisation of the quasiparticle mass than do the electron-phonon interactions ($m_{\lambda\alpha}/m_{b\alpha}$ is a factor ~2 smaller than $m^*_\alpha/m_{\lambda\alpha}$)). Note that the value of $m_{\lambda\alpha}/m_{b\alpha}$ =1+λ implies an electron-phonon coupling constant of λ≅0.7-0.8; this is similar in size to, but larger than, estimates of a total intramolecular λ≅0.3-0.5 for various BEDT-TTF salts derived by analysis of the frequencies of the phonons observed in infrared and Raman spectroscopy [10].

No CR data corresponding to the β-orbit have yet been observed. However, the ratios of the effective masses to the band masses are similar for the two orbits[3], indicating that the renormalisation of the bare band mass is relatively uniform over the whole FS.

Note also that the renormalisation of the effective masses will also serve to renormalise the quasiparticle scattering time

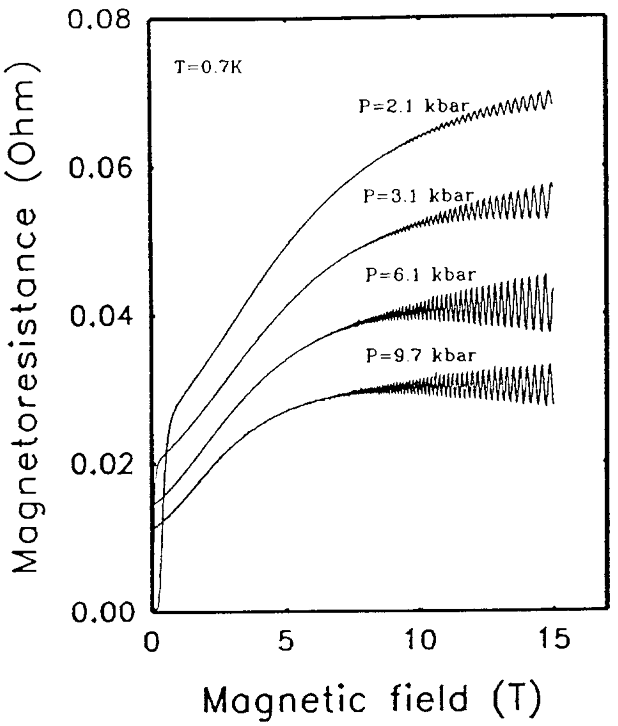

Figure 2. Magnetoresistance of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 0.7 K (magnetic field applied perpendicular to the conducting *bc* -planes) for four different pressures.

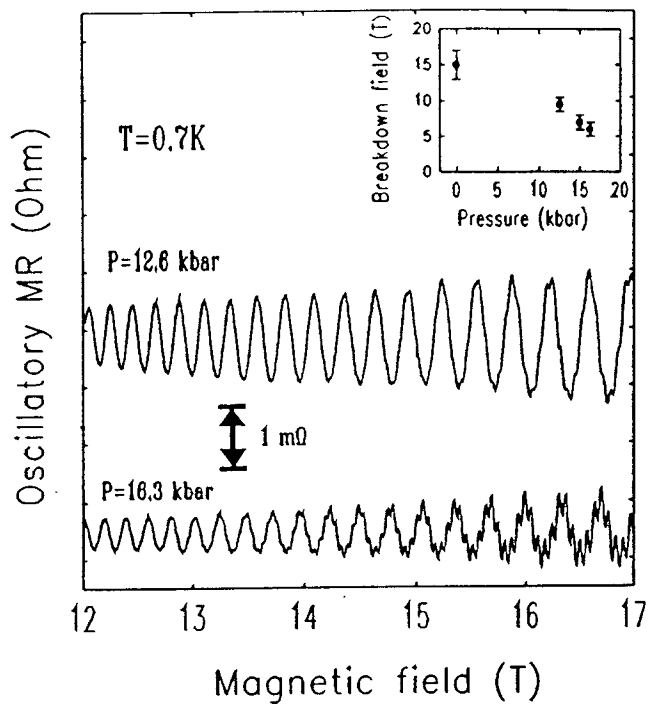

Figure 3. Oscillatory part of the MR (0.7 K; B normal to 2D planes) of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at two pressures. The inset shows the breakdown field versus pressure.

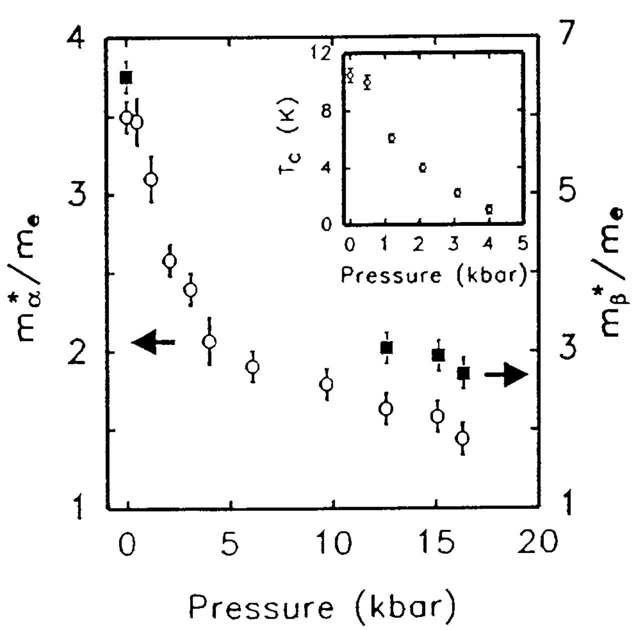

Figure 4. The effective masses of the α(hollow circles, left hand vertical scale) and β-orbits (filled squares, right hand vertical scale) of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ versus pressure. The inset shows the superconducting T_c versus pressure.

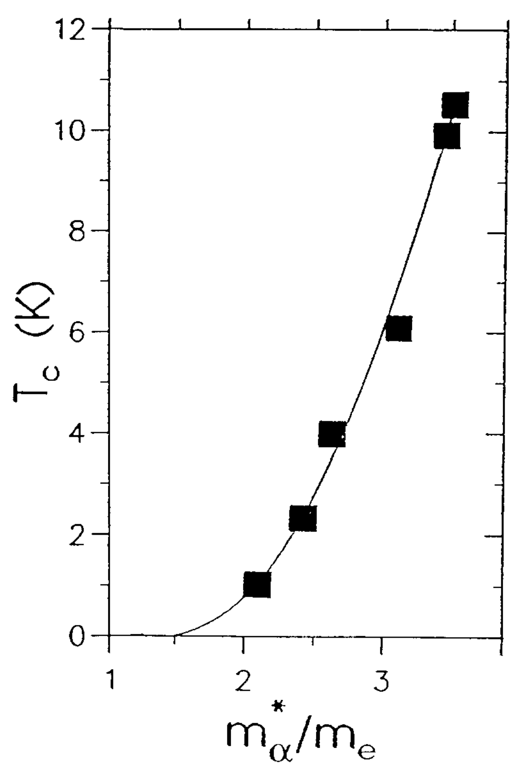

Figure 5. Comparison of the Eliashberg equation (curve) with experimental T_c versus m_α data (points) derived from the pressure experiments (see text for details).

τ by the same amount, for purely classical reasons; a heavy quasiparticle will have a slow Fermi velocity and thus a relatively long time will elapse between scattering events from fixed crystal defects [7]. As the effective mass decreases with increasing pressure, the Fermi velocity will increase and the scattering time decrease. This is the reason why the product m^*T_D appears to be independent of pressure; T_D is proportional to τ^{-1}, which in turn is proportional to m^{*-1} [7]. This effect was predicted some years ago by Toyota *et al.* [7].

The effects of many body interactions therefore appear to be very important in giving the large effective masses in ET charge-transfer salts[3,7,8]. It also seems that large effective masses are a prerequisite for superconductivity in ET salts (Figure 4) and that the mechanisms primarily responsible for producing the mass enhancement are due to interactions between quasiparticles, with electron-phonon interactions playing a smaller role[3]. The initial strong decrease in effective mass with pressure seen in Figure 3 could therefore represent suppression of a component of the quasiparticle interactions which depends critically on the bandwidth (see *e.g.* [11]); the bandwidth of course increases with pressure.

4. Superconductivity

Any model of superconductivity should potentially allow one to relate T_c to m^*, and, in a previous paper, we used a weak coupling BCS expression as a convenient parameterisation of the data [3]. However, the applicability of weak coupling BCS theory to κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is an open question[1-3], and so in this work we have calculated T_c by solving the linearised Eliashberg equations, an approach which should be valid for all coupling strengths [6]. An Einstein spectrum is used to simulate $\alpha^2F(\omega)$; this is not intended to be a rigorous representation of the excitation spectrum, but it is useful in understanding the spectral dependence of the physical quantities. The pressure dependence of the density of states at the Fermi energy is derived by assuming that it scales with the measured effective mass (Figure 4) [3,6]; the density of states is then used to determine the pressure dependence of μ^* and $\alpha^2F(\omega)$[6]. Fits to data are accomplished by specifying the Einstein phonon frequency and the ambient pressure values of λ and μ^*.

Figure 5 shows a comparison of the calculated T_c and experimental data from the pressure experiments, using an Einstein phonon energy of 5 meV and ambient pressure values λ=0.4 (*c.f.* 0.3-0.5 in [10]) and μ^*=-0.22. The fits depend fairly strongly on λ, and, irrespective of the phonon energy used, λ=0.4 seems to work best [6]. It should be noted that recent neutron scattering data [12] reveals a distinct peak in the low temperature phonon density of states at 5 meV. Systematic studies of other BEDT-TTF superconductors are under way to investigate this behaviour further.

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