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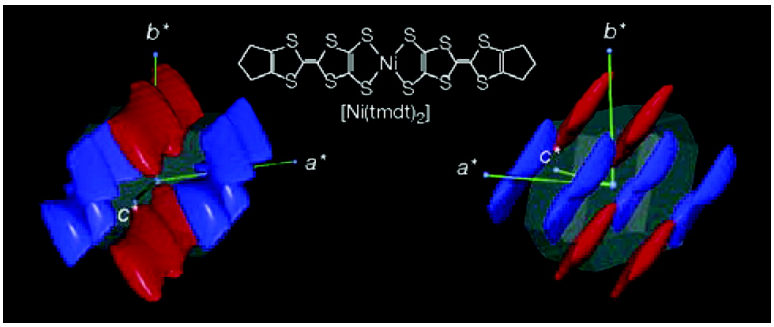

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Observation of Three-Dimensional Fermi Surfaces in a Single-Component Molecular Metal, $[Ni(tmdt)_2]$

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Recently considerable attention has been focused on unconventional conducting molecular systems such as nanowires,[1] molecular wire junctions,[2] and even DNA.[3] Though the number of intriguing reports on new types of molecular systems are rapidly increasing, there seem to be many systems where the origins of the charge carriers and/or transport mechanisms still remain unclear. We have reported that the single-component molecular crystal consisting of neutral metal complex molecules $[Ni(tmdt)_2]$ exhibits metallic behavior down to 0.6 K.[4,5] The crystal has a very simple structure with only one $[Ni(tmdt)_2]$ molecule in the unit cell, where all the centers of molecules are on the lattice points. In addition, the existence of many intermolecular contacts much shorter than the van der Waals contacts[5] suggests that in the crystal, the $[Ni(tmdt)_2]$ molecules assemble by interactions stronger than the van der Waals interactions, that is, metallic bonds. Needless to say, neutral molecular crystals and metallic crystals have been regarded as two typical but contrasting types of crystals. To prove the existence of a new class of single-component molecular crystals which possess simultaneously the character of molecular crystals and metallic crystals, experimental evidence for Fermi surfaces is essential.

To obtain direct evidence for the existence of Fermi surfaces in $[Ni(tmdt)_2]$, we have carried out experiments to measure magnetic quantum oscillations, namely de Haas−van Alphen (dHvA) oscillations, in high magnetic fields at low temperatures.[6,7] Single crystals of $[Ni(tmdt)_2]$ were prepared electrochemically from acetonitrile solution containing $((CH_3)_4N)_2[Ni(tmdt)_2]$. Black tiny platelike single crystals with maximum dimension of about 100 μm were grown on a platinum electrode.

Methods of torque magnetometry using sensitive piezoresistive cantilevers have been previously reported.[8] To measure tiny crystals (of order $130 \times 100 \times 20$ μm^3, and 0.5 μg in mass), we employed a commercially available microcantilever for atomic force microscope (AFM)[9−11] (see Figure 1a). A simple resistance bridge circuit was used to cancel the background resistance of the two piezoresistive sensing cantilevers on the AFM assembly. Measurements were carried out at temperatures down to 0.5 K in dc magnetic fields up to 45 T using the hybrid magnet at the National High Magnetic Field Laboratory at Florida. A total of four samples have been studied using a sample rotator, and all have given similar results. Representative experimental torque signals are shown in Figure 1b. Clear, angular-dependent dHvA oscillations were observed, which provided the first unambiguous evidence for the existence of Fermi surfaces in the single-component molecular crystal. Analysis of the temperature dependence of the amplitude of the dHvA oscillations through the Lifshitz−Kosevich formula led to the carrier effective masses,[12,13] which ranged between 1.0 and 1.6 free electron masses depending on field direction. We also found their impurity limited mean free paths through the Dingle temperature, $T_D = 4.7$ K. In certain directions, as shown in Figure 1b, the signal intensities of dHvA oscillations do not increase monotonically with increasing magnetic field, and the Fourier transform reveals the presence of more than two frequencies. This systematic angular-dependent Fermiological study allowed the mapping of the extremal areas A_k of the Fermi surface with respect to the three-dimensional Brillouin zone unit cell.[14] The dHvA signal is clearly seen in all directions, showing that $[Ni(tmdt)_2]$ is the 3D metal, as suggested from the tight-binding band calculations.[4,5]

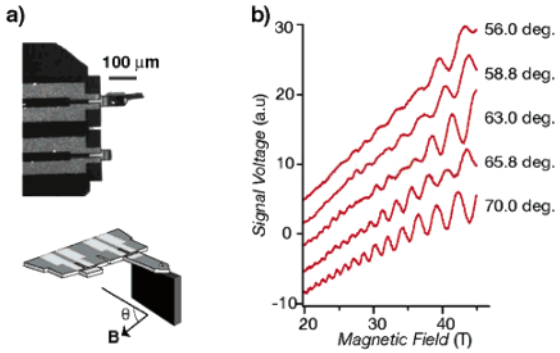

Figure 1. Torque magnetometry of $[Ni(tmdt)_2]$. (a) Microcrystal on AFM cantilever, (b) An example of raw torque magnetometer signals versus the applied magnetic field at 1.44 K. θ is the angle between the $-a^*$ direction and external magnetic field.

To compare the experimental results with electronic structure calculations, we have carried out local density approximation (LDA) calculations based on the ab initio plane-wave norm-conserved pseudopotential method with Troullier−Martins potentials and a cutoff energy at 110 Ry, which gave a band structure consistent with the previous calculations by Rovira et al.[15] We have recently found that the revised extended-Hückel tight-binding band calculations gave essentially the same topology for the Fermi surfaces.

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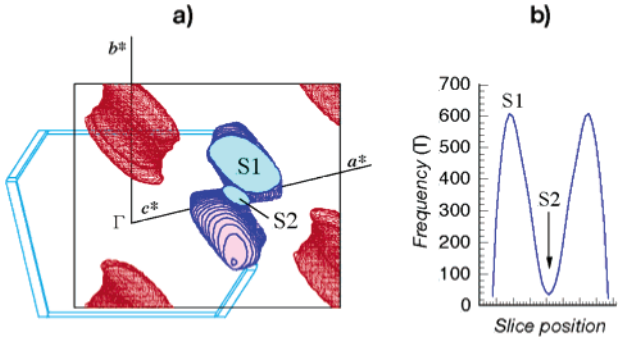

Figure 2. Hole (blue) and electron (red) Fermi surfaces and the first Brillouin zone of [Ni(tmit)$_2$]. (a) The extremal hole orbits for the field applied parallel to c^* and (b) the corresponding extremal cross section sizes (S1, S2) were calculated by slicing Fermi surfaces.

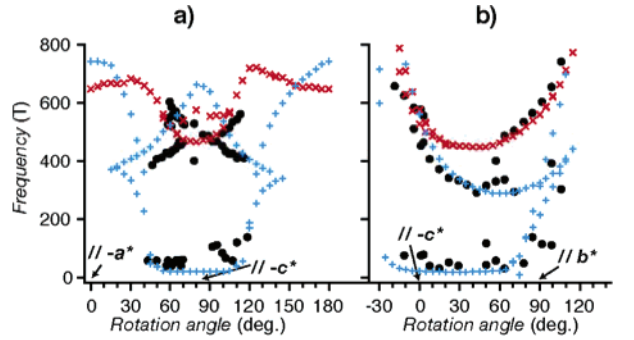

Figure 3. Observed and calculated angular dependences of the dHvA frequencies. The solid black circles represent the peaks after the Fourier transformation of the dHvA signals. The blue (+) and red (x) crosses in the latter correspond to the hole and electron Fermi surfaces, respectively. The magnetic field was rotated in the (a) a^*-c^* and (b) b^*-c^* planes, respectively.

An example of the extremal orbit is illustrated in Figure 2 with the calculated Fermi surfaces. The blue and red closed surfaces represent the hole and electron Fermi pockets, where the volume of each pocket occupies 3.5% of the first Brillouin zone. The angular dependence of the observed dHvA frequency and calculated value based on the LDA calculation are shown in Figure 3. The latter was estimated from the extremal areas of a series of calculated cross sections of Fermi surfaces for various magnetic field orientations in the a^*-c^* and b^*-c^* planes. The calculated angular dependence is brought into accord with the experimental observations, not only for the angular dependence, but also for the magnitude of extremal area. As shown in Figure 3, we observed multiple frequency branches. These features correspond well to the calculated topology of the hole and electron Fermi surfaces of [Ni(tmdt)$_2$].

The observation of the dHvA signal in [Ni(tmdt)$_2$] demonstrates that it is a single-component molecular crystal which not only shows metallic conductivity behavior down to low temperatures, but also exhibits high-quality quantum oscillations characteristic of a Fermi surface. These results unambiguously show the existence of 3D Fermi surfaces for both holes and electrons in this molecular crystal. There has been no metallic molecular system consisting of single-component molecules since the report on the intrinsic semiconducting behaviors of phthalocyanine and the condensed aromatic hydrocarbons such as violanthrone, isovioranthrone, and pyranthrone about a half century ago.[16,17] Hence, the discovery of the metallic properties of [Ni(tmdt)$_2$] and the rigorous confirmation of its metallic nature by the observation of dHvA oscillations marks a milestone in the design of the conducting properties for molecular systems.

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(7) In the metallic crystal, a magnetic field quantizes the charge carrier motion in a plane perpendicular to the applied magnetic field. Accordingly, the energy levels of electrons and holes are quantized into discrete Landau levels, whose separation increases proportionally to the applied magnetic field. This effect leads to oscillations in many properties including magnetization (dHvA effect), resistance (the Shubnikov−de Haas effect), specific heat, thermoelectric power, etc. When the Fermi surface is anisotropic, the magnetization will also have nonisotropic components that give rise to a magnetic torque ($\mathbf{M} \times \mathbf{H}$) term.
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(13) From the Lifshitz−Kosevich formula, the dHvA oscillation amplitude is proportional to the product $R_TR_DR_S$, where $R_T = (\alpha\mu_cT/B)/\sinh(\alpha\mu_cT/B)$, $R_D = \exp(-\alpha\mu_cT_D/B)$, and $R_S = \cos(\pi g\mu_b/2)$. Here $\alpha = 2\pi^2k_Bm_e/e\hbar = 14.69T/K$ and μ_c and μ_b are the effective cyclotron mass and band mass in units of the free electron mass, g is the g-factor, and T_D is the so-called Dingle temperature. For constant field (or for the average field over a small field interval), a fit of the expression vs temperature yields the Dingle temperature as a parameter of the fit.
(14) A Fourier transform of the oscillatory dHvA signal with respect to inverse field yields the area of the extremal carrier orbits on the Fermi surface according to $F = A_k4\pi^2e/h$, and a plot of the rotational data in terms of F vs angle yields information about the three-dimensional (3D) Fermi surface topology, as shown in Figure 2.
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