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Electron Tunneling Studies in the Charge Density Wave State of the Quasi Bidimensional Metal $\eta$-Mo$_4$O$_{11}$

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Abstract. — Electron tunneling studies have been performed on junctions made with the quasi bidimensional oxide $\eta$-Mo$_4$O$_{11}$ and a lead film separated by an insulating oxide layer. The density of states in the vicinity of the Fermi level has been obtained along two directions (parallel and perpendicular to the layers) in the temperature range 1 K-90 K. The data from the differential conductance as a function of dc bias voltage are consistent with gap openings taking place at $T_{p1} = 100$ K and $T_{p2} = 30$ K. Both electron instabilities are attributed to charge density waves and the anisotropy of the density of states is related to the anisotropy of the Fermi surface. For tunneling current in the plane of the layers, weak oscillations are found in the density of states at low temperatures. They are possibly due to the existence of several types of small electron and hole pockets induced on the Fermi surface by the charge density wave gap openings.

1. Introduction

Molybdenum bronzes and oxides have been extensively studied in the last decade in relation with their low-dimensional electronic properties and the onset of Peierls' instabilities leading to charge density wave (CDW) states [1]. Among these compounds, the Mo$_4$O$_{11}$ oxides are quasi bidimensional (2D) due to a crystal structure built with infinite layers of MoO$_6$ octahedra separated by MoO$_4$ tetrahedra [2]. Since the hybridized d-p band is partially filled and since the conduction electrons are confined into the MoO$_6$ layers, these compounds are metallic with quasi-cylindrical Fermi surfaces. The two phases, $\eta$-Mo$_4$O$_{11}$ and $\gamma$-Mo$_4$O$_{11}$ have neighbouring crystal structures and show a Peierls instability towards a metallic CDW state around 100 K. Only the monoclinic $\eta$-phase shows a second instability in the vicinity of 30 K. Up to now, the nature of this instability was not clear [3]. We report in this article electron tunneling studies performed on junctions made with single crystals of $\eta$-Mo$_4$O$_{11}$ and a lead counterelectrode separated by an insulating layer. The results establish that the low temperature instability is...
due to a gap opening, possibly of the CDW type. We also show that the residual density of states (DOS) is anisotropic.

The transport properties of $\eta$-Mo$_4$O$_{11}$ have been studied in detail by Guyot et al. [4,5], who established that the electrical resistivity is strongly anisotropic, the resistivity being two orders of magnitude larger along the $a^*$ axis perpendicular to the layers than in the layer plane. A strong anisotropy was also found between the $b^*$ and $c^*$ axis in this plane. X-ray diffraction and electron diffraction studies established that the anomaly which takes place at 100 K is due to a CDW transition, as shown by satellites found at $q_1 = (0, 0.23 b^*, 0)$ [4,6]. Furthermore Mössbauer studies supporting the existence of an anomaly in the Debye-Waller factor around 100 K corroborated this model [7]. Thermal conductivity as well as optical reflectivity changes below 100 K were also found to be consistent with a CDW instability [8,9]. Electrical resistivity studies under hydrostatic pressure showed that both transition temperatures $T_{p1} = 100$ K and $T_{p2} = 30$ K are pressure dependent [10]. But while $T_{p1}$ is found to increase with pressure, $T_{p2}$ is decreasing. Band structure calculations performed by the tight-binding method in a two-dimensional approximation are consistent with nesting properties of the Fermi surface along the $b^*$ axis and the $q_1$ vector found experimentally [11]. Further analysis of the band structure lead to the model of the so-called “hidden nesting” or “hidden one-dimensionality”, related to the presence of quasi one-dimensional chains of MoO$_6$ octahedra along the three crystallographic directions $b$ and $b + / - c$ [12,13]. Due to a weak hybridization between these three chains, the Fermi surface may be considered in a first approximation as the superposition of three quasi one-dimensional Fermi surfaces. The high temperature CDW transition at $T_{p1}$ is related to gap openings along $b^*$, as shown by X-ray results and electron diffraction [4]. Preliminary X-ray results indicate that the low temperature transition may be related to CDW satellites found at $q_2 = (\gamma, 0.42 b^*, 0.28 c^*)$ therefore corresponding to gap openings along other parts of the Fermi surface [13].

High magnetic field transport studies at low temperatures had shown the existence of Shubnikov-de Haas oscillations for magnetic fields perpendicular to the layers [5,6]. De Haas van Alphen oscillations were also found on the magnetization [5]. These results were consistent with the existence on the low temperature state Fermi surface ($T < T_{p2}$) of small electron and hole pockets with a size of the order of $10^{-3}$ the high temperature bidimensional ($b^*, c^*$) Brillouin zone. More recent magnetoresistance and Hall effect data in fields up to 26 T also show hysteretic phenomena between up and down-sweeps of the magnetic field [14]. This is attributed to an irreversible effect of the magnetic field on the CDW state. Studies of pulsed laser induced transient thermoelectric effect have also been performed recently between 4.2 K and 300 K [15]. The existence of several relaxation times is attributed to the complexity of the Fermi surface in the different CDW states. A model for the Fermi surface at low temperatures, with several types of electron and hole pockets is also proposed ( [15], see also Ref. [13], p. 167).

Electron tunneling studies can in principle give information on the change of the DOS near the Fermi level due to CDW gap openings. Such results have been obtained previously on NbSe$_3$ [16]. The temperature dependence of the Peierls gap can also be obtained by this technique. In the case of $\eta$-Mo$_4$O$_{11}$, it had been found earlier that the CDW satellite amplitude and therefore the Peierls gap show a BCS type law as a function of temperature [4]. In a quasi one-dimensional system such a law is expected to obey the mean-field theory of the Peierls transition. In this context it was relevant to perform electron tunnelling studies on $\eta$-Mo$_4$O$_{11}$ in order to study the two instabilities at $T_{p1}$ and $T_{p2}$ and the temperature dependence of the DOS.
Fig. 1. — Band scheme structure in a metal-insulating-semimetal junction.

2. Tunneling Effect: Special Aspects

2.1. Directivity of the Tunneling Effect. — Giaever first proved experimentally the possibilities given by the tunneling effect [17]. He demonstrated that a simple conductivity measurement at the terminals of a N-I-S sandwich (N being a normal metal, I an insulating layer and S a superconductor) provides the DOS of the superconductor around the Fermi level. The measurements established the existence of the BCS gap and a strong electron-phonon coupling inside lead.

An important factor in the calculation of the tunneling current is the evaluation of the transmission factor $D$ which is defined as being the probability current associated with the fraction of the incident wave which is transmitted. This calculation was largely developed in the literature [18]. If $\theta$ is the angle between the incident wave vector and the normal to the junction plane, in the frame of the WKB approximation, the transmission factor may be expressed in the following way:

$$D \propto D_0 \exp(-\alpha \theta^2)$$

where $D_0$ is the transmission factor in the case where the wave vector is normal to the junction plane. The transmission factor is multiplied by $1/e$ for $\theta$ changes of a few degrees. Therefore only the electrons which have their wave vector normal to the junction plane may cross the insulating layer.

2.2. Case of Multi-Valley Conduction Bands. — Esaki [19-21] considered the case of a M-I-SM junction, where SM is a semimetal, (as is shown in Fig. 1) and demonstrated that if the band edges of the semimetal are less deep than the conduction band edge of the metallic counterelectrode, the tunneling conductance reflects the DOS of the semimetal.

It follows that the tunneling spectroscopy in the case of a metal-insulator-semimetal provides the semimetal DOS along the crystallographic direction normal to the junction plane. This density will further be noted "DOS".

3. Experimental Technique

In order to verify the quality of the tunneling spectra, we have used a lead counterelectrode in which the superconductive DOS is well known. The superconducting phase is only used as a quality test and is then suppressed by applying a weak magnetic field. A typical characteristic of the tunneling conductance is shown in Figure 2.

Lead dots of 3000 Å thickness are evaporated through mylar masks into a vacuum environment ($10^{-6}$ Torr). The samples were first cleaved or washed in decinormal ammonia. We have studied four crystallographic directions $a$, $b$, $c$, and $b + c$. The $b + c$ direction has no geometrical relationship with the nesting wave vector $q_2$ but it was chosen because it is an easy cleavage direction. The quantity and the rate of lead evaporation is measured by using
Fig. 2. — Differential conductance in Pb/insulator/η-Mo₄O₁₁ junction measured with current parallel to \( b + c \) axis. The dashed line represents the superconducting lead DOS at 1 K. The effects of the superconducting energy gap and of the phonons are seen. The full line represents the “DOS” of \( \eta \)-Mo₄O₁₁ along the \( b + c \) direction at 1 K. A magnetic field of 0.3 T is applied.

a quartz balance. We believe that a natural insulating interface, probably PbO, is created. Ohmic contacts are then realized onto the sample and the lead dots with silver paste. The collection of the tunneling resistance data \( dV/dI \) versus \( V \), for a temperature \( T \) and a bias voltage \( V \), is made by a lock-in detection system which allows an analogic measurement of the differential resistance.

4. Experimental Results

4.1. DIFFERENTIAL CONDUCTANCE ALONG THE \( a \) AXIS. — Figure 3 shows the curves of the normalized differential conductance \( N(V, T) \), at different temperatures.

\[
N(V, T) = \frac{dI}{dV}(V, T) \frac{dI}{dV}(V, 100)
\]

\( dI/dV(V, 100) \), the differential conductance at a temperature above \( T_p1 \), (100 K) is taken as a base line and inform us about the barrier deformations with a bias voltage.

\( N(V, T) \) is in fact the convolution product of the “DOS” with the first derivative of the Fermi function. However we will assume that at low temperatures \( N(V, T) \) gives the “DOS”, the derivative of the Fermi function being considered as a Dirac function. Figure 4 shows the differential tunneling conductance as a function of temperature at null bias voltage. This curve represents the condensation rate at the Fermi level. It varies between 50% and 80% from sample to sample. A steeper variation appears at temperatures below 30 K. This phenomenon may be related to the second CDW transition. One can note that these results are similar to those observed in NbSe₃ [16].

4.2. DIFFERENTIAL CONDUCTANCE ALONG THE \( b + c \) AXIS. — In this direction, as is shown in Figure 2, the “DOS” seems to be temperature independent as if it were a normal metal.
Fig. 3 — Normalized differential tunneling conductance versus applied voltage along the a axis at different temperatures.

Fig. 4 — Temperature dependence of the differential conductance for zero bias voltage, for current along the a axis.

Fig. 5 — Differential conductance enlarged versus applied voltage at different temperatures along the b + c direction with an applied magnetic field of 0.3 T. The dashed line represents the “DOS” at 1 K with an applied magnetic field of 1 T.

However, Figure 5 shows that the enlarged curves (×10 or ×20) exhibit below 30 K weak oscillations in the “DOS”. The magnitude of these oscillations is maximal at the lowest temperature reached, 1.2 K, and decreases quickly with increasing temperatures. The energies corresponding to these minima are −9, −4.5, −2, 0, 2, 4.5, and 9 meV. The “DOS” which was minimal at the Fermi level at 1 K becomes maximal at 4 K. A magnetic field of 1 T directed along the a axis has no influence on the “DOS”.
4.3. DIFFERENTIAL CONDUCTANCE ALONG THE $b$ AND $c$ AXIS. — The temperature changes of the "DOS" are comparatively weak along the $b$ and $c$ directions as shown in Figures 6 and 7. For both directions there is a relative maximum of the "DOS" at the Fermi level. Weak oscillations are also found at the same energies as along the $b + c$ direction. They are more visible along the $c$ axis than along the $b$ axis.

One should note that along the $c$ direction the "DOS" is influenced by the application of a magnetic field, as shown in Figure 8. This effect appears for fields above a threshold value of approximately 0.5 T.

Therefore, it is clear that the "DOS" is anisotropic since the properties are different along the $(b,c)$ plane and along the $a$ axis. The temperature dependence of the "DOS" is the strongest along the $a$ axis. An increase of the condensation rate takes place below 30 K. In all the explored directions of the $(b,c)$ plane, symmetrical minima are found at energies of $-9$, $-4.5$, $-2$, $2$, $4.5$, and $9$ meV.

Fig. 6. — Differential conductance versus applied voltage at different temperatures along the $b$ direction for a magnetic field of 0.3 T.

Fig. 7. — Evolution for various temperatures of the amplified "DOS" along the $c$ direction for a 0.3 T magnetic field.
Fig. 8. — Idem along the c axis for different magnetic fields at several temperatures. In this case the magnetic field is applied along the a axis.

We can remark that the oscillations of the “DOS” are stronger along b + c direction than along b or c. This is due to the fact that along this direction junctions are realized onto freshly cleaved crystals giving better tunneling junctions.

A minimum at the Fermi level is found in addition to other minima along the b + c direction.

5. Discussion

Tunneling spectroscopy provides the “DOS” in the valence and in the conduction bands near the Fermi level. Our data show that there is no true metal-semiconductor transition. This is due to the quasi bidimensional character of this compound and to an imperfect nesting of the Fermi surface. We will now correlate the experimental curves to simple band structure models.

5.1. Evolution of the “DOS” with Temperature

5.1.1. Evolution along the a Axis. — Along this direction, the condensation rate is the highest. The tunneling conductance varies monotonously with the bias voltage and there exists a unique extremum situated at the Fermi level. We can assume a simple band scheme at 1 K in which the “DOS” near the Fermi level is parabolic, as shown in the inset of Figure 9a. In this approximation $N(E)$ varies as $E^{1/2}$ both in the valence and conduction bands. Figure 9 represents the tunneling conductance at 1 K, 50 K, and 90 K calculated by means of the following relation (22):

$$\frac{dI}{dV}(V) \propto \int N(E) \frac{1}{kT} \frac{\exp \left( \frac{E - eV}{kT} \right)}{1 + \exp \left( \frac{E - eV}{kT} \right)} dE$$
Fig. 9. — a) Numerical simulation of the differential conductance at 1 K, 50 K, and 90 K for rigid parabolic band scheme. The two band extrema are located at $E_f$. b) Same as previously with no rigid bands changing with temperature up to $T = 100$ K according to a mean-field law.

$N(E)$ is the projection of the DOS near the band edges along the crystallographic direction investigated.

The computed curves show that there is a crossing of the curves which does not appear experimentally (Fig. 9a). We have therefore assumed that there is a band splitting which increases below $T_p$. In this model the extrema of the two bands follow a mean-field law:

$$E_{\text{val}}^{\text{max}} = \Delta_0 \left[ 1 - \left( 1 - \frac{T}{T_p} \right)^{1/2} \right] + \Delta_{\text{cross}}$$

$$E_{\text{con}}^{\text{min}} = -\Delta_0 \left[ 1 - \left( 1 - \frac{T}{T_p} \right)^{1/2} \right] - \Delta_{\text{cross}}$$
Δ₀ is the value of the pseudo-gap defined by the mean-field theory, and Δₜ₉اسي is the overlap energy of the bands at \( T = 0 \) K. The evolution with temperature of the different curves is shown in Figure 9b with Δ₀ = 15 meV, \( Tₚ = 100 \) K, and Δₜ₉اسي = 0 meV. The calculated curves are more similar to the experimental ones.

This simple band model therefore supports the fact that along the \( a \) direction, a band splitting takes place when \( T \) is lowered, the temperature dependence following a mean-field theory.

5.1.2. Evolution along the \( b, c \), and the \( b+c \) Axis. — Canadell and Whangbo [12] have calculated in a 2D approximation a band structure in the \((b,c)\) plane in the normal state above the first Peierls transition. They also obtained the Fermi surface which includes three sheets, shown in Figure 10a. They have noted that the Fermi surface can be obtained by the superposition of three quasi-1D Fermi surfaces. The nesting vector of the first CDW transition, 0.23 \( b^* \), would relate sheets of this Fermi surface. One may speculate, as in reference [15] that below \( Tₚ \) ellipsoidal electron and hole pockets are left by the CDW gap openings (Fig. 10b). The major axis of these pockets would be along the \( c^* \) axis.

The oscillations that we have observed are not due to a phonon spectrum since they change with an applied magnetic field. Along the explored directions the "DOS" varies little with temperature and the oscillations disappear above 25 K. A classical "DOS" is then observed. These oscillations may therefore be due to the existence of these small pockets.

Let us assume a simple model of two parabolic bands overlapping at the Fermi level at 1 K. The extremum of these bands would follow a mean-field law towards temperature as the expression given in Section 5.1.1. The calculated "DOS" is shown in Figure 11, with \( Δ₀ = 4.5 \) meV and \( Δₜ₉اسي = 2 \) meV. Two minima which correspond to the extremum of each bands appear at 1 K. It can be seen that there is no overlapping of the differential conductance in the vicinity of the Fermi level, this is due to a too large splitting of these bands towards temperature. The parameter \( Δ₀ \) which gives computed curves corresponding to the experimental data obtained along \( b \) or \( c \) direction is lower than the mean field prediction and takes the value 1 meV.

On the basis of our experimental results it seems that there are at least three couples of electron and hole bands in the \((b,c)\) plane. The extrema of these bands are symmetrical and situated at 2, 4.5 and 9 meV on both sides of the Fermi level.

The minimum of the "DOS" at the Fermi level found in the \( b+c \) direction at 1 K could be explained in the following way: along this axis the faces of the crystals are possibly not perfectly parallel to the \( a \) axis. Therefore the junction plane may contain an \( a \) axis component. The

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**Fig. 10.** — a) Schematic diagram showing the high temperature Fermi surface from Canadell et al. Shaded areas correspond to electron pockets. b) Proposed electron and hole remaining pockets at low temperatures [11, 12]. The arrows indicate the nesting wave vector associated with the first and the second CDW transition.
Fig. 11. — a) Representation of the two-overlapping band model at 1.2 K. The arrows in the second scheme represent the evolution of these bands towards temperature. b) Numerical simulation of the "DOS" corresponding to the band model proposed above with $\Delta_0 = 4.5 \text{ meV}$ (mean-field value) and $\Delta_{\text{cross}} = 2 \text{ meV}$. The value of the extrema of the differential conductance are corresponding to the values of the band edges weighted by the derivative of the Fermi function.

Simulation of the tunneling conductance, at different temperatures which takes into account two overlapping bands and two jointive bands at the Fermi level at 1 K is represented in Figure 12. The overlapping bands follow a mean-field law up to 30 K but with $\Delta_0 = 1 \text{ meV}$, while the jointive bands follow also a mean-field law up to 100 K. This last set of bands is weighted by a factor 1/2. The results seem to be in good agreement with the experimental data.

Our model may be compared to the one proposed by Sasaki et al. [15]. In this model there are three electrons and holes pockets. The bands all cross the Fermi level. The values of the extrema of the hole bands are 2.2 and 7.3 meV and for the electron bands are 0.4 and 2.2 meV.

We can note that if the energies are not identical to those proposed by Sasaki, they are of
Fig. 12. — Numerical simulation of the “DOS” obtained with two overlapping bands at 1 K changing with temperature up to 30 K according to a mean-field law, with $\Delta_0 = 1$ meV, superimposed on two bands with extrema at $E_F$ at 1 K changing with temperature up to 100 K according to a mean-field law, with $\Delta_1 = 15$ meV.

The temperature seems to influence all the bands because all the extrema of the “DOS” are vanishing when $T$ is increased. The existence of hole and electron pockets would be related to the second transition because above this temperature there are no oscillations. The change in the condensation rate along the $a$ axis may also be related to a second gap opening corresponding to a second CDW transition.

5.2. INFLUENCE OF A MAGNETIC FIELD: POSSIBILITY OF A MAGNETIC BREAKDOWN. — The effect of a magnetic field $B$ applied along the $a$ axis for different current directions studied in the $(b, c)$ plane was investigated. The field has modified the “DOS” only for current along the $c$ direction.

We have assumed that the “DOS” in a field of 0.3 T (this field is used in order to suppress the lead superconductivity) was identical to that obtained in zero field. This relies on the fact that the effect of $B$ is significant only above 0.5 T. Therefore this effect is not related to the quantization in Landau levels, since the Landau levels being periodic in energy, the position of the relative minima of the “DOS” would vary linearly with the magnetic field.

One notes that the extrema in the “DOS” appear approximately at the same positions, whatever the value of the field (Fig. 8). A possible explanation of the “DOS” modification would be the presence of a magnetic breakdown between different ellipsoidal pockets at the Fermi surface. Indeed, Blount [23] has proposed that in the presence of a magnetic field electrons or holes may “tunnel” across a gap $\Delta$ separating the pockets. The transition probability is written as:

$$P = \exp \left( -\frac{B_0}{B} \right)$$

with

$$B_0 = \frac{\alpha \Delta^2 m^*}{eE_F \hbar}$$

$\alpha$ is a coefficient of order of unity. For a value of the effective mass 0.1 $m_0$, a carrier concentration at low temperature of $8.8 \times 10^{18}$ cm$^{-3}$, $c^*$ being equal to 0.94 Å$^{-1}$ and an experimental
threshold magnetic field of the order of 0.5 T, we obtain a distance between pockets in the reciprocal space of 0.3 Å⁻¹.

At a temperature of 1 K the effect of a magnetic field is more significant on the "DOS" at an energy of 4.5 meV than for the other energies.

At a temperature of 4 K, the "DOS" at the Fermi level does not change until $B = 1$ T. On the other hand the minimum of the "DOS" for 0.3 T which is at roughly 6 meV is subdivided into two minima at 4.5 meV and 9 meV, the absolute minimum being at 4.5 meV.

Above 10 K the influence of the magnetic field is progressively weakened and disappears completely above 18 K. The characteristic energies are the same as those concerning the electrons and holes pockets. Therefore, these results may be due to a magnetic breakdown related to the presence of electrons and holes pockets at the Fermi surface.

The different effects of the magnetic field for different bias voltages would be explained by a slight variation of the effective mass around a mean effective mass $0.1 m_0$, this causing different threshold fields between the pockets. In the present case the pocket having the lowest effective mass would be at 4.5 meV from the Fermi level.

6. Conclusion

To our knowledge, it is the first time that one observes by tunneling studies the existence of electron and hole pockets in a charge density wave compound. We have been able to separate three symmetrical couples of electron and conduction bands with edges at 2, 4.5, and 9 meV from the Fermi level in the low temperature CDW state of $\eta$-Mo₄O₁₁. These bands are induced by the second low temperature CDW transition. Furthermore there might be a magnetic breakdown along the c axis, the threshold field being at roughly 0.5 T.

A band scheme simulation describing the behaviour of the tunneling conductance along the a axis corroborates that the Peierls transition acts on overlapping valence and conduction bands and tends to split these bands according to a mean-field law.

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