Scanning tunneling microscopy observation of sliding charge-density wave in blue bronze

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We investigated the sliding motion of charge-density wave (CDW) in $K_{0.3}MoO_3$ with scanning tunneling microscopy (STM). With fixed position of the tunneling tip, a sharp peak was found in the spectra of tunneling current for sample bias current exceeding the threshold for the CDW depinning. The peak frequency increased with the extra current carried by the CDW condensate. This peak is understood to be generated by the modulation of gap distance between the tunneling tip and sample atom due to the sliding motion of CDW. The velocity of CDW at the surface was obtained directly: $v_s = 5.7\times10^{-3}$ cm/s just above the threshold. The corresponding sliding velocity in the interior of the same sample was obtained as $v_b = 6.3\times10^{-4}$ cm/s from the narrow band noise frequency. It was confirmed that the CDW is easily depinned at the surface and begins to slide with much higher velocity than the interior of sample. Tunneling spectroscopy was also measured and the CDW gap structure was obtained as a preliminary result.

I. INTRODUCTION

Blue bronze $K_{0.3}MoO_3$ is one of quasi-one-dimensional conductors exhibiting the nonlinear transport due to the sliding of charge-density wave (CDW) condensate. As in other CDW materials such as $NbSe_3$, TaS_3, and $(TaSe_4)_2I$, various interesting phenomena associated with the sliding motion of CDW are observed in $K_{0.3}MoO_3$.[1] The observation of narrow band noise is the most characteristic one. The frequency of narrow band noise is related to the sliding velocity directly. We discussed previously[2] the metastable sliding state of CDW from the behavior of narrow band noise. Such metastable phenomena are mainly due to the degree of freedom of CDW deformation. The deformation of CDW is considered to be essential in the static structure and the dynamics of CDW. In connection with the deformable CDW, the behavior of CDW at the surface is now very interesting.

The scanning tunneling microscopy (STM) is one of most powerful methods investigating the local electronic state at the surface. STM measurements in the CDW materials with two dimensional structure have been reported.[3,4] The CDW superlattice structure was clearly observed as an STM image. More recently, the successful observation of CDW modulation in $NbSe_3$ with STM have been reported.[5] These experiments strongly suggest that the STM has possibilities observing both the structure of CDW and the sliding motion of CDW in quasi-one-dimensional conductors. As the STM has its noncontacting tunneling tip for a probe, we can observe the sliding motion of CDW with much less disturbance than the usual electric measurements.

We performed the STM measurement in $K_{0.3}MoO_3$ and found a modulation of tunneling current by the sliding motion of CDW.[6] In this article, we report on the direct observation of CDW depinning at the surface of $K_{0.3}MoO_3$ and discuss the sliding motion of CDW. A preliminary result of tunneling spectroscopy study is also reported.

II. EXPERIMENTAL

Figure 1 is a schematic picture of our measuring unit. The sample is pasted on the holder, whose position is adjusted coarsely by a screw. The tunneling tip of tungsten is attached to the tube-type actuator and the distance of the tip from the sample surface can be controlled finely by the actuator. Tunneling bias is applied to the gap between the tip and the sample through a series resistance. The tunneling current is monitored as the voltage signal appearing on the series resistance.

A single crystal of $K_{0.3}MoO_3$ was cut and cleaved along the $(\bar{2},0,1)$ plane to a rectangular shape. Electric leads for the transport measurement were attached to both sides of sample with indium metal by using an ultrasonic bonder. After the sample was pasted on the holder with epoxy adhesive, we cleaved again the sample to obtain a clean surface. The CDW chain (along the b axis) is parallel to the cleaved surface. In this unit, we can measure the electric transport while observing the STM signal simultaneously.

The temperature was controlled in a cell filled with thermal exchange helium gas. The cell was installed in a metal dewar, which was directly immersed in liquid nitrogen filled in another outer dewar. To avoid vibration of the unit, a

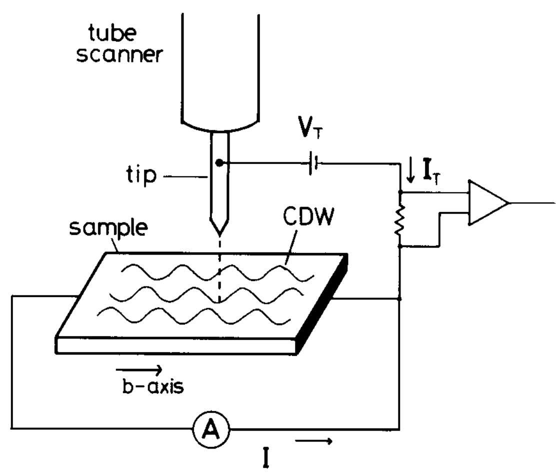

FIG. 1. Schematic picture of our measuring unit. Tip position is controlled with the tube type actuator. With the leads attached to both sides of sample, we can measure the electric transport while observing the STM simultaneously.

metal dewar was mounted on a vibration isolator, which is equipped with air suspensions. The outer dewar was laid directly on the floor. The temperature was monitored with a platinum resistance thermometer near the sample.

The electric transport was measured with the two probe method. In the narrow band noise measurement, the sample voltage was analyzed for the constant current with use of a fast Fourier transformer (FFT) analyzer.

In the tunneling measurement, the tip height was controlled to be constant and the variation of tunneling current was detected. With dc bias current applied to the sample through the leads, the tunneling current as a voltage signal was analyzed with the same FFT analyzer as for the narrow band noise. In the tunneling spectroscopy, the tunneling current was directly observed on a X–Y recorder against the tunneling bias voltage, which was swept with a triangular pulse.

III. RESULTS AND DISCUSSION

We first measured the current–voltage curve for characterization of the sample and obtained the threshold field for the CDW depinning $E_T = 88$ mV at 80 K. We could obtain the narrow band noise peaks in the voltage noise spectra for a bias current exceeding the threshold value. Two fundamental peaks and their harmonics were clearly found in the noise spectra. Their frequencies increase with the current carried by the CDW condensate as shown in Fig. 2. According to the classical washboard model, the well-known relation holds between the fundamental frequency F_1 and the CDW current density $J_{\rm CDW}$,

$$F_1/J_{\rm CDW} = 1/(en\lambda), \qquad (1)$$

where n and λ represent the electronic density condensed to the CDW and the wavelength of CDW, respectively. We previously obtained the ratio $F_1/J_{\rm CDW} = 11$ kHz/(A cm^{-2}) at 77 K in $K_{0.3}MoO_3$,[7] and this value is consistent with the calculated one 12.5 kHz/(A cm^{-2}) from the chemical formula. Fundamental frequencies in the present experiment are much higher than the expected value. Moreover, the precise linear relation does not holds in our present sample. If there are some portions of sample cross section, where the CDW is pinned, the calculated current density from the total cross section causes an underestimation for the real current density in the sliding part of the sample. Therefore, in the present sample the CDW is not sliding through the whole sample but through a limited area. The higher value of $F_1/J_{\rm CDW}$ is understood with such inhomogeneous CDW current flow. The existence of two fundamental peaks suggests that there are at least two portions where the CDW is sliding with different velocity from each other. The bend of F_1–$J_{\rm CDW}$ curve in Fig. 2 suggests that the existence of another portion, where the CDW is sliding with different velocity.

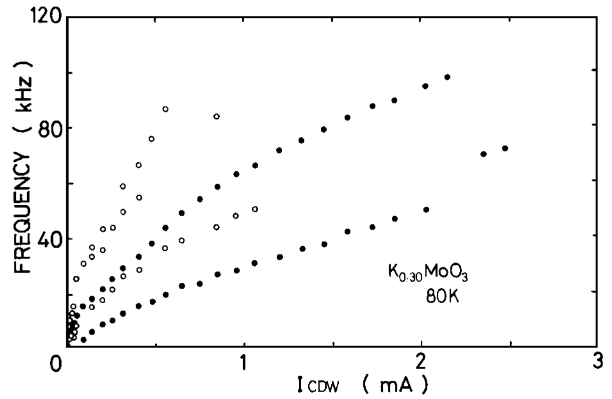

FIG. 2. Frequencies of narrow band noise vs current carried by CDW condensate. ● and ○ represent two different fundamentals and their corresponding second harmonics.

We investigated the tunneling current spectra with fixing the tunneling tip position at 80 K. As shown in Fig. 3, a new peak (indicated by arrows in the figure) appears in the tunneling current spectra for the sample bias current exceeding the threshold value ($I_c = 0.95$ mA). The peak frequency increases with increasing current. We can easily distinguish this bias current dependent peak from other extremely sharp peaks, because other peaks are observed even below the threshold current and neither their shape nor amplitude changes with varying bias current. These spurious peaks are attributed to the system noise generated mainly by the STM controller. Figure 4 shows the peak frequency against the CDW current. The peak frequency rapidly increases just above the threshold current and shows the tendency of saturation for large bias current.

According to the simple tunneling theory, the tunneling current is owing to the overlap between the electronic wave functions in tip metal and sample, and is expressed as

$$I_T = I_0 \exp(-d/d_0), \qquad (2)$$

where d is the gap distance between the tip and the nearest

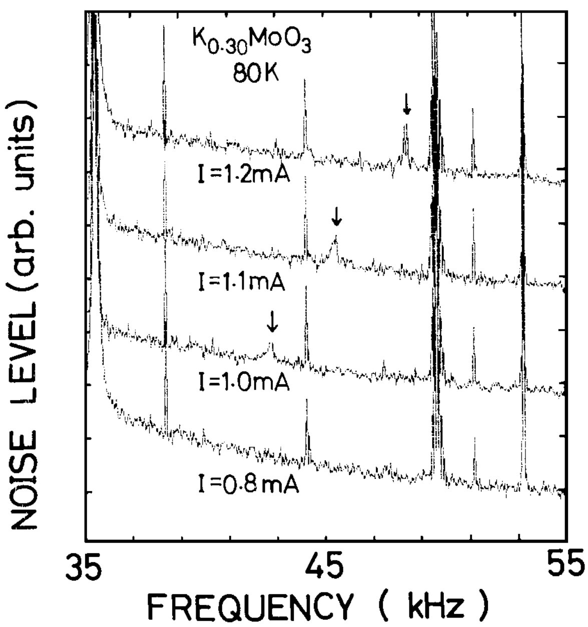

FIG. 3. Spectra of tunneling current under bias current. The position of tunneling tip was fixed and the tunneling current was analyzed. For current exceeding the threshold value ($I_c = 0.95$ mA), a new peak (indicated by arrows) appears in the current spectra.

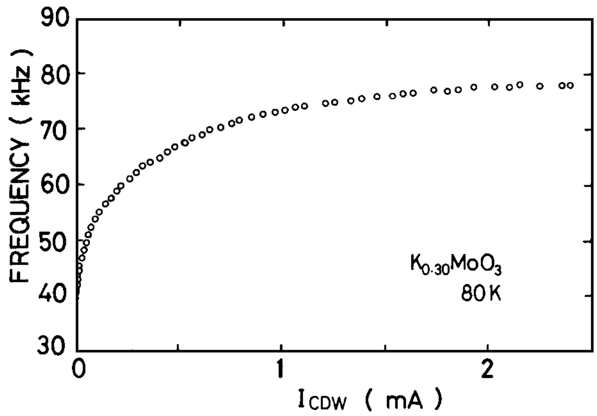

FIG. 4. Peak frequency in tunneling current spectra vs CDW current.

atom of the sample. The length d_0 characterizes the extension of electronic wave functions. The characteristic current I_0 is simply described by the tunneling bias voltage V_T as

$$I_0 \propto \int N_t(E+eV_T)N_s(E)[f(E)-f(E+eV_T)]dE, \tag{3}$$

where N_t and N_s are the densities of electronic states for the tip metal and the sample, respectively.If the sample is a normal metal with constant electronic density of states, the tunneling current is proportional to the tunneling bias voltage for small bias. But our sample is a Peierls-type semiconductor. In the CDW phase, the tunneling current–voltage curve is expected to show a gap structure similar to that of a superconductor.[8] At $T=0$ K no current can flow for the bias voltage lower than the Peierls gap. At finite temperature, the tunneling current is associated with the thermally activated normal carriers. The tunneling bias used in the present experiment is 50–100 mV and less than the Peierls gap 100 mV estimated from the temperature dependent Ohmic resistivity. This condition was also confirmed in the tunneling spectroscopy as discussed later. Therefore, it is understood that the CDW condensate is not converted to normal electrons in our bias condition. Accordingly, we can observe the CDW with a relatively small disturbance. Then the tunneling current is mainly determined by the gap distance d.

The CDW state is described with the electronic charge density modulation as

$$\rho(x)=\rho_0+\rho_1\cos(Qx+\phi), \tag{4}$$

where Q represents the wave number of CDW. The phase ϕ denotes the position of rigid CDW. Correspondingly, the lattice displacement $\mathbf{u}$ is also described as

$$\mathbf{u}(x)=\mathbf{u}_1\cos(Qx+\phi). \tag{5}$$

The sliding motion of CDW with the velocity v, represented by $\phi=-Qvt+\phi_0$, modulates the distance d periodically. Then the tunneling current is modulated with a time period $\tau=(2\pi/Q)v$; the tunneling current is expected to be modulated with a frequency $f=1/\tau$. This frequency is exactly the same as the narrow band noise frequency [Eq. (1)]. The local density of thermally activated electrons might give another contribution to the modulation of tunneling current, because it has the same spatial modulation period as the CDW through the electrostatic screening.

The observed peak frequency in our tunneling current spectra increases with the extra current carried by the CDW and is the same order as the narrow band noise frequency. Therefore, the origin of the peak is naturally explained with the above mentioned mechanism. Behavior of this peak supplies the most direct evidence for the sliding motion of CDW at the surface. We estimate the sliding velocity at the surface v_s from the peak frequency of tunneling spectra; $v_s=5.7\times10^{-3}$ cm/s at $I_{\mathrm{CDW}}=0.1$ mA and $v_s=7.8\times10^{-3}$ cm/s at $I_{\mathrm{CDW}}=2$ mA. The sliding velocity of CDW in the interior of sample v_b is calculated as $v_b=6.3\times10^{-3}$ cm/s at $I_{\mathrm{CDW}}=0.1$ mA and $v_b=5.1\times10^{-3}$ cm/s at $I_{\mathrm{CDW}}=2$ mA correspondingly, from the low frequency component of fundamental frequencies of narrow band noise (Fig. 2). These results show that just above the threshold the CDW begins to slide at the surface of sample, while the CDW is pinned or sliding but with very low velocity in the interior region of sample. The extra current is mainly carried by the CDW near the surface just above the threshold. It might be probable that the surface energy pin the CDW. However, our present result shows clearly that the CDW can slide easily at the surface.

The width of the peak in the tunneling current spectra is much narrower than that of the narrow band noises, but broader than those of system noise. The modulation of tunneling current is generated at the gap point between the tip and the sample. If the wavelength of CDW is uniform and the sliding velocity is constant, the peak must have an infinitesimal width. We averaged the spectra of tunneling current for ~1 min. The observed width is equivalent to the fractional sliding velocity fluctuation of 4×10^{-3}. The stability of the current generator used in the present experiment, better than 1×10^{-4}, cannot explain the observed width. Therefore, the width of peak suggests the existence of fluctuation of local sliding velocity. However, another explanation may be given that the observed width corresponds to the spatial variation of wave number Q in the deformed CDW. The precise discussion for the width needs more detailed experiments.

We also measured the tunneling spectroscopy. In this measurement, the tip position was again fixed and the tunneling current I_T was observed for one-shot triangular pulse of bias voltage V_T. A typical I_T–V_T curve for the CDW phase is shown in Fig. 5. The distinct nonlinear curve can be seen in the figure. At room temperature, I_T–V_T curve is nearly a straight line, showing the constant electronic density in the metallic phase of $K_{0.3}MoO_3$. The nonlinear tunneling resistance, observed below the transition temperature (180 K), indicates the existence of the Peierls gap. The condition of low tunneling bias voltage used in the sliding experiment is confirmed with the curve in Fig. 5. But the differential conductance dI_T/dV_T, which corresponds roughly to the electronic density of states in the sample, does not show the sharp peak at the Peierls gap edge. So we cannot obtain the precise gap value from the I_T–V_T curve. Alternatively, we estimate the gap 2Δ as the width of dV_T/dI_T curve and show its temperature dependence in Fig. 6. The obtained gap

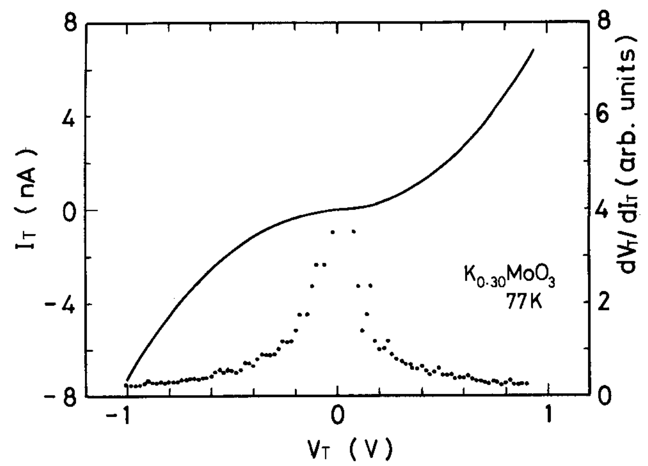

FIG. 5. Tunneling current I_T vs tunneling voltage V_T (—) and dV_T/dI_T vs V_T (●). The distinct nonlinear tunneling resistance is observed.

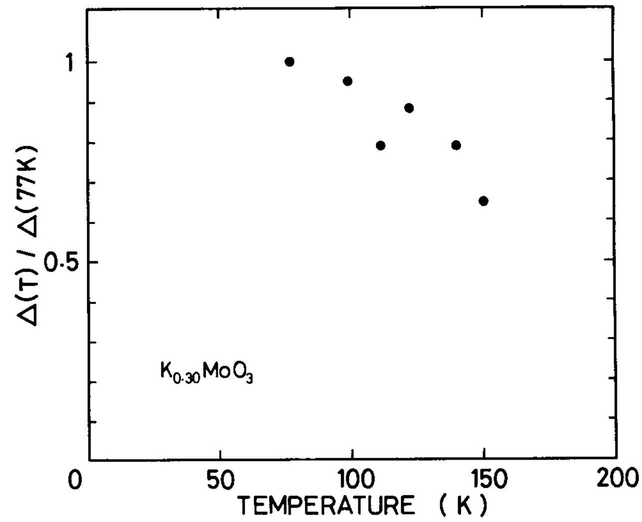

FIG. 6. Temperature dependence of the normalized Peierls gap $\Delta(T)/\Delta(77\ \mathrm{K})$ estimated from the tunneling spectroscopy measurement. The gap decreases with increasing temperature toward the transition temperature (180 K).

2Δ is ~ 130 meV at 77 K and roughly in agreement with the estimated value 100 meV from the temperature dependent resistivity. Because there is large ambiguity in determination of the gap value from the tunneling experiment, the absolute value of Peierls gap is not discussed in detail here. But the relative gap decreases toward the transition temperature with increasing temperature and this temperature dependence is reasonable for the CDW phase. The similar I_T–V_T curve have been reported recently in another quasi-one-dimensional conductor $NbSe_3$.[5] The absence of sharp peak at the gap edge may be essential in the tunneling spectroscopy in the quasi-one-dimensional conductor. More experiments are eagerly desired.

IV. CONCLUSIONS

We investigated the CDW phase of $K_{0.3}MoO_3$ with the STM. We analyzed the tunneling current with fixing the tip position and found a relatively sharp peak in the tunneling current spectra for bias current exceeding the threshold value for CDW depinning. This peak is understood to be generated by the modulation of tunneling gap distance due to the sliding CDW and supplies the direct evidence for the sliding motion of CDW at the surface. The sliding velocity at the surface was obtained from the peak frequency. The velocity of sliding CDW is one order larger at the surface than in the interior of sample, just above the threshold current. It was confirmed that the CDW is easily depinned at the surface.

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