行政院國家科學委員會專題研究計畫　成果報告

電荷密度波(CDW)的高能 X-光散射研究(2/2)

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計畫主持人：杜昭宏

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（計畫名稱）

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一 緣由與目的

There has been a great deal of interest in the relationship between various diverse and exotic low-temperature phases of strongly correlated electron systems, including the antiferromagnetic insulating and unconventional superconducting phases of high-T_C cuprates, the charge ordered insulating insulating and ferromagnetic metal phases of the manganites, the orbital-ordered and ferromagnetic metal phases of the ruthenates, and the charge-density wave (CDW) and superconducting phases of 2H-$NbSe_2$. Among these, a particular interest is the exotic phase behaviour that is expected between fully ordered and disordered phases as one tunes the interactions in these systems using some control parameter other than temperature. It is therefore the projective of this study to explore the quantum phase transition in the charge-density waves (CDWs). For achieving this goal, we chose the electric field as the control parameter and a single crystal $K_{0.3}MoO_3$ as the sample.

二 英文摘要

We study the transport property and the internal structure of charge density waves (CDWs) in $K_{0.3}MoO_3$ simultaneously by two-probe measurement and multiple X-ray diffraction. We report the first experimental observation of all three types of dynamical motions, from creeping to plastic flows, and eventually into the moving solid phase. The transitions are identified through measuring the phase of the structure-factor triplet, which describes the internal deformation of CDW due to the applied electric field. Comparisons with other experiments are made and related issues and open questions are discussed at the end.

Keywords: charge-density waves (CDWs), multiple x-ray diffraction, x-ray scattering, creeping phase, plastic flow, moving solid

三 結果與討論

The homogeneous phase in low dimensional materials, such as $K_{0.3}MoO_3$, $NbSe_3$, 2H-$NbSe_2$ and TMTSF molecules, undergo a phase transition to charge density waves (CDWs) at low temperatures. The instability toward spontaneous formation of charge-density modulations is driven by electron-phonon interactions, or sometimes electron-electron ones. Among many other interesting aspects of CDW, transport property has attracted lots of attentions from both experimental and theoretical sides [1]. It is generally believed that the current is suppressed at small biased voltage, where the CDW is pinned by impurity potential. Above some threshold voltage, the sliding motion along the applied electric field starts and the current increases significantly. It has been known that this dynamic behaviour involves the phase slippage of the density waves [2]. In addition, the dynamics of the disordered state driven by an external force in a periodic media is also of the characteristic in common in many physical systems, such as the density waves and the vortex lattices [3, 4].

An interesting question naturally arises: How does the internal structure of density modulations change in the presence of the applied electric field? In particular, in the non-equilibrium sliding motion, the robust periodic structure, originally developed in static limit, might become unstable [5]. In this Letter, we address this issue by applying the technique of multiple (three-wave) X-ray diffraction to measure how the internal structure of CDW changes with respect to the applied electric fields. From the extracted phase $\delta_3(V)$ of the three-wave diffraction, we found the dynamical motion of CDW undergoes a crossover from creeping to plastic flow and eventually enters the moving solid phase [3, 4]. As far as we know, this is the first experimental report that all three types of dynamical motions are observed.

The key quantity we studied in this Letter is the phase δ_3(V) of the three-wave diffraction at different biased voltages. To set up a three-wave diffraction experiment, the crystal is first aligned for a reflection vector *G*, the so-called primary reflection. It is then rotated around the reciprocal lattice vector *G* with azimuthal angle, to bring in the secondary reflection *L*, which also satisfies the Bragg's law. Namely, the reciprocal-lattice points of both *G* and *L* reflections are brought onto the surface of the Ewald sphere simultaneously. During the azimuthal rotation, the same three-wave (*O*, *G*, *L*) diffractions occur at these two positions, denoted as IN and OUT, where the reciprocal lattice point *L* enters and leaves the Ewald sphere respectively. The interferences among the diffracted waves give rise to intensity variations of the primary reflection $I_G(\psi)$ as a function of the azimuthal angle[6]. The asymmetry of the intensity profile can be used to extract the phase δ_3 of the structure-factor triplet $F_L F_{G-L}/F_G$ [6-8], provided that the effect of anomalous dispersion is negligibly small.

To measure the triplet phase, a good quality single crystal $K_{0.3}MoO_3$ was first characterized and oriented at room temperature. The crystal structure belongs to the monoclinic system with a space group *C2/m*. The lattice parameters of $K_{0.3}MoO_3$ are a =18.162 Å, b = 7.554 Å, c = 9.816 Å, and $\beta = 117.393^o$ [9]. The sample showed a mosaic spread of 0.009^o (FWHM) on the Bragg peak (8 0 -4), using an X-ray rotating anode source with Cu $K\alpha_1$. The single-crystal sample was prepared in rectangular shape of the size 2.5×3.5 mm^2. The *b*-axis of the crystal was aligned with the longer sides of the rectangle. Two gold wires were attached onto the sample surface with silver pastes. A Keithely 2400 source meter was used to generate the driving electric field, and the current-voltage characteristics were measured in the two-probe setup. The X-ray source is provided by the beamline BL12B2 at SPring-8. The sample was glued on the cold head of a cryostat mounted on a 6-circle diffractometer, and the incident energy was selected to be 1 Å by a pair of Si (1 1 1) crystals. The higher order contaminations were rejected by both collimating and focusing mirrors. The beam divergences were about 0.0033^o (vertical) and 0.0025^o (horizontal) at the center of the diffractometer and the σ-polarization was chosen for the incident beam. The beam size was set by slits to be 0.5×1 mm^2 at the sample position. The use of multi-axis diffractometer allows us to perform azimuthal scans around any reciprocal lattice vector. At room temperature, the crystal was first aligned so that the scattering plane coincided with the $a^* \times c^*$ reciprocal plane. The origin of azimuthal angle ($\psi = 0$) was chosen to be the direction where [100] lies in the scattering plane. This can be verified by finding a mirror position in the multiple diffraction pattern of the primary reflection (6 0 -3). Since the formation of density modulations occurs at $Tc \approx 180$ K, the sample was cooled down to 100 K. The satellite reflections signal the formation of CDW, located at the Bragg position $G = (13\ q\ 6.5)$, where $q \sim 0.748$ [10]. The intensities of the satellite peaks are about 1300 counts/sec. The azimuthal angular scan of peak intensity around G was monitored by the scintillation counter to measure multiple diffractions.

A portion of the multiple diffraction pattern of G is shown in Fig. 1. Note that the azimuthal angle was measured counterclockwise from the [0 1 0] direction. The horizontal background is due to the primary G reflection. Relative intensity peaks and dips are marked with the Miller indices of the secondary reflection L. Thereafter, a multiple-wave diffraction is denoted as $L/(G-L)$ and the IN and OUT positions are indicated by " + " and " - " signs respectively.

The seemingly noisy background is caused by the presence of many weak fractional reflections. We would concentrate on the particular three-wave diffraction, (4 -8 4)/(9 8.75 10.5) at $\psi = 108.53^o$, as shown in Fig. 2. The profile asymmetry at $V = 0$ is typical for a triplet phase δ_3 equal to zero. The profile develops different asymmetry at different finite voltages, readily seen at V = 7.1, 7.5 V as shown in Fig. 2(a). At these voltages, the Darwin width of the primary peak (13 q 6.5), as well as other integer reflections, remained the same. This indicates that the mosaicity of the host lattice and the internal structure of the CDW do not change. Triplet phase δ_3 was analyzed based on the dynamical theory for multiple diffractions [6]. Since the primary and the coupling reflections are the fractional reflections, their structure factor amplitude are much smaller than that of the secondary (4 -8 4) reflection. Under this condition, the modification of profile asymmetry is dominated by the phase, rather than the amplitude of the structure-factor triplet. The estimated triplet phases from curve fitting at 7.1, 7.2, 7.3, 7.4 and 7.5 V are about 15^o, 20^o, 26^o, 31^o, and 41^o respectively. The error bar is about 10^o. Note, in the present case, that triplet phase δ_3 is directly related to the ion positions in the crystal unit cells. Therefore, the shift in the triplet phase δ_3 is ascribed to the ionic displacements being induced by the internal deformation of charge density in the presence of the applied electric field.

Because of the centrosymmetry of the crystal, the resultant phase $\delta_3 = 0$ (up to sign ambiguity) in the absence of the electric field. The symmetry is broken by the applied electric field along the b^*-axis, which causes the internal deformation of the original charge density distribution. In general, the distortion of CDW is rather complicated and we only focus on the triplet phase of the structure factor here.

The main results of this Letter are summarized in Fig. 3. We measured the current, the triplet phase and the intensity of the primary Bragg peak simultaneously at different bias voltages. Before we present the details of the experimental data, it is quite helpful to briefly review previous theoretical investigations [5, 3, 11]. Note that the formation of charge-density modulations creates a finite gap in the quasi-particle spectrum and the low-energy physics is dominated by collective excitations from fluctuations in the amplitude and the phase of CDW. Since the amplitude fluctuations are also gapped, it can be safely ignored in most cases [12]. On the other hand, the phase fluctuations in the presence of impurity potential are more complicated to tackle.

If the randomness of impurity potential is weak, the spatial fluctuations are negligible and the dynamics of the phase fluctuations can be described by the single impurity model [12]. The current-voltage characteristic exhibits a sliding threshold at some voltage $V = Vs$. Below the threshold, the CDW is pinned and the transmitted current is suppressed. The pinning potential due to impurities is overcome above the threshold and the whole CDW starts to slide. It can be easily calculated that the internal structure of the CDW does not change significantly near the sliding transition. The robustness of charge distribution was verified in previous experiments.

However, when the strength of the random potential is strong, the spatial variations can not be ignored anymore. A more sophisticated theory to address this issue was developed by Balents and Fisher in 1995 [11]. They proposed three types of dynamical motion due to spatial fluctuations: creeping, plastic flow and moving solid, separated by two threshold voltages. The first threshold *Vs* indicates the crossover from creeping to plastic flow, which can be easily detected by a sudden jump in the *I-V* curve. The second threshold *Vc* denotes a true phase transition from the disordered plastic flow to the reformation of charge modulations. In the following, we present the first experimental evidence which verify the above theoretical predictions.

In the two-probe setup, we observed a sudden jump in the *I-V* curve at *Vs* = 7.51 V, seen clearly in Fig 3(a). In order to avoid overshooting of the current, the X-ray measurements of the multiple diffraction were taken carefully while monitoring the current reading. Since the dynamics near the plastic flow regime can be quite slow, the applied voltage was increased gradually to the next value after the current reached its stable value for a few minutes. Just below the sliding voltage $V < Vs$, the current displayed an exponentially increment as voltage increased. This increment has been demonstrated to be due to the creep motion of CDWs [13]. Meanwhile, the phase $\delta_3(V)$ was measured to increase from its original value $\delta_3 = 0^o$ to the maximum $\delta_3 = 41^o$ at the sliding threshold. Note that the change of the triplet phase already implies the non-zero modulation of charge densities. Furthermore, it also provides additional information about how the existing charge modulations respond to the external electric field. It is clear from Fig. 3(b) that the internal deformation of CDW increases as the voltage increased. This is expected because the competition between the pinning potential and the external electric field would change the charge distribution dramatically. The intensity measurement of the primary Bragg peak, shown in Fig. 3(c), provides further strength to the above scenario. The intensity decreases gradually upon the application of voltage, indicating the internal deformation of CDW grows stronger.

Slightly above the sliding threshold, $V > Vs$, the current increases rapidly and the CDW enters the sliding state. For voltages between 7.51 V and 7.9 V, the intensity of the primary peak *G*= (13 q 6.5) was too unstable to be measured. So was the multiple diffraction measurement. Besides, the current also shows strong fluctuations in this regime and it seems that the system is in a metastable state. In this plastic flow regime the sliding state is rough with large spatial fluctuation of the phase [4]. This implies the melting of CDW, i.e. the periodic structure of charge-density modulations is destroyed. By measuring the correlation length of the CDWs, Ringland et. al. also reported a less correlated CDW state for the driving force exceeding the sliding threshold [17]. However, our findings are consistent with the theoretical prediction of the crossover from creeping to plastic flow, where contains the mixture phase of both pinned and depinned regions and the periodic structure is smeared out by the driving force [14].

Keeping on the application of the driving force, it is surprising that the charge order is restored when the voltage is larger than the second threshold Vc = 7.9 V, as shown in Fig. 3(b)-(c). Both the triplet phase and the primary Bragg peak reappear, signaling the comeback of CDW. Furthermore, the reappeared phase assumes its original value $\delta_3(V > Vc) = 0$ as if the electric field were absent. This suggests that the depinning process involves a 2π-phase jump [15] and the phase fluctuations are suppressed in the direction the field direction [4]. The recovery of the ordering strongly evidences that the pinning potential due to random impurities has become irrelevant as the sliding velocity is larger enough. Thus, not only the charge density modulations appear again, the internal deformation of the moving CDW vanishes because the impurity pinning is no longer important. The intensity measurement, shown in Fig. 3(c), also lends hand to the above claim. While the intensity of the primary peak decreases down to about 40% of its original value near (but below) the sliding threshold, it bounces back to the original value at V = 0 when entering the moving solid phase! Such a reordering has also recently been reported in the sliding CDW state [16].

Combining all experimental evidences above, we believe that the simultaneous measurements on *I-V* curve, the triplet phase factor δ_3 and the intensity of primary Bragg peak have provided unambiguous evidences for the transitions among three types of dynamical motions of CDW. While it is already exciting to observe these transitions, it also opens up many interesting issues requiring further studies. For instance, it is important to address the issue whether the primary diffraction G would change as we vary the strength of the applied field.

Another important issue is the transition from plastic flow to the moving solid phase, which is predicted to be second-order. It implies that many physical quantities should exhibits power-law scaling near the critical regime $V \sim Vc$. Besides, in the moving solid phase, temporal long-range order develops and leads to narrow-band noises. That is to say, the power spectrum of the current noises $S(\omega)$ would develop a sharp peak around some intrinsic frequency $\omega \sim \omega_0$ with narrow half-width. Finally, crossovers between different types of dynamics can also be achieved by temperature changes. By varying temperature and the electric field together, the global phase diagram can be mapped out completely and deepen our understanding of the dynamical phenomena in CDW or even stripes in the high-T_C related perovskites.

四 計畫成果

This experiment can not be done without the grant support from NSC. The result has been written into two papers. One is titled as “Electric-Field Induced Melting and Reformation of Charge Density Waves in $K_{0.3}MoO_3$”, and has been submitted to Physical Review Letter. The second one is title as “X-ray Multiple-wave Interaction in a Quasi-two-dimensional Material 2H-$NbSe_2$”, and will be submitted to Acta Crystallographic A.

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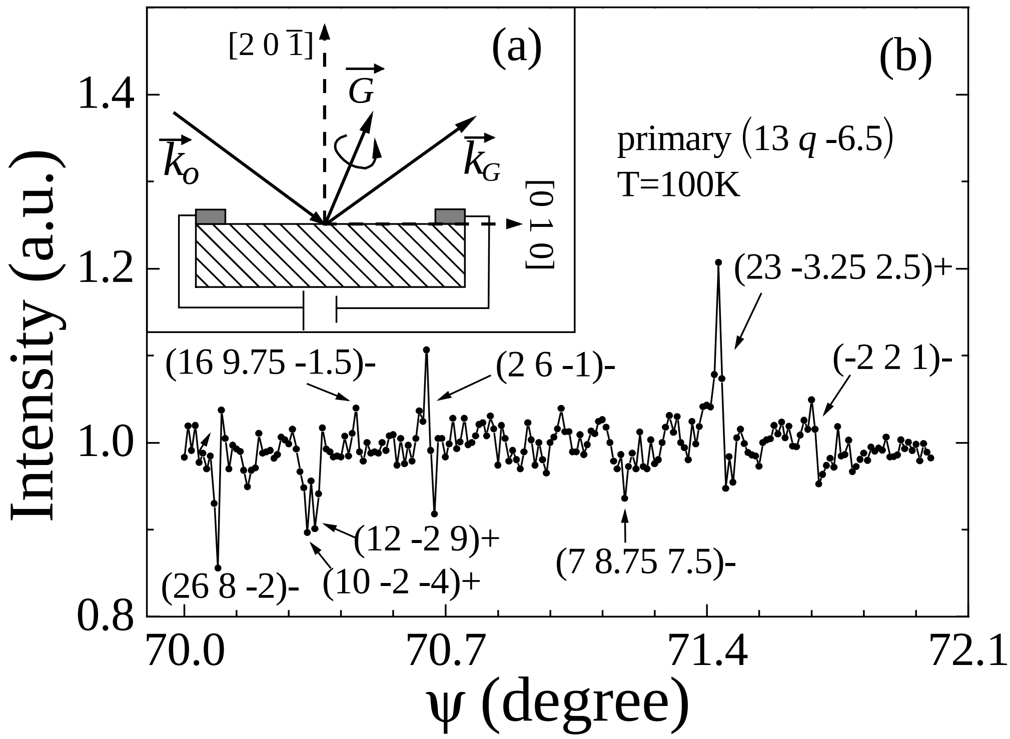
Figure captions:

Figure 1: Azimuthal scan of three-wave diffraction around the primary reflection ***G***= (13 q -6.5), where q is approximate to 0.748. For the simplicity of showing the indexes, the q is set to 0.75. Major peaks and dips are marked as explained in the text. The inset shows the experimental setup schematically.

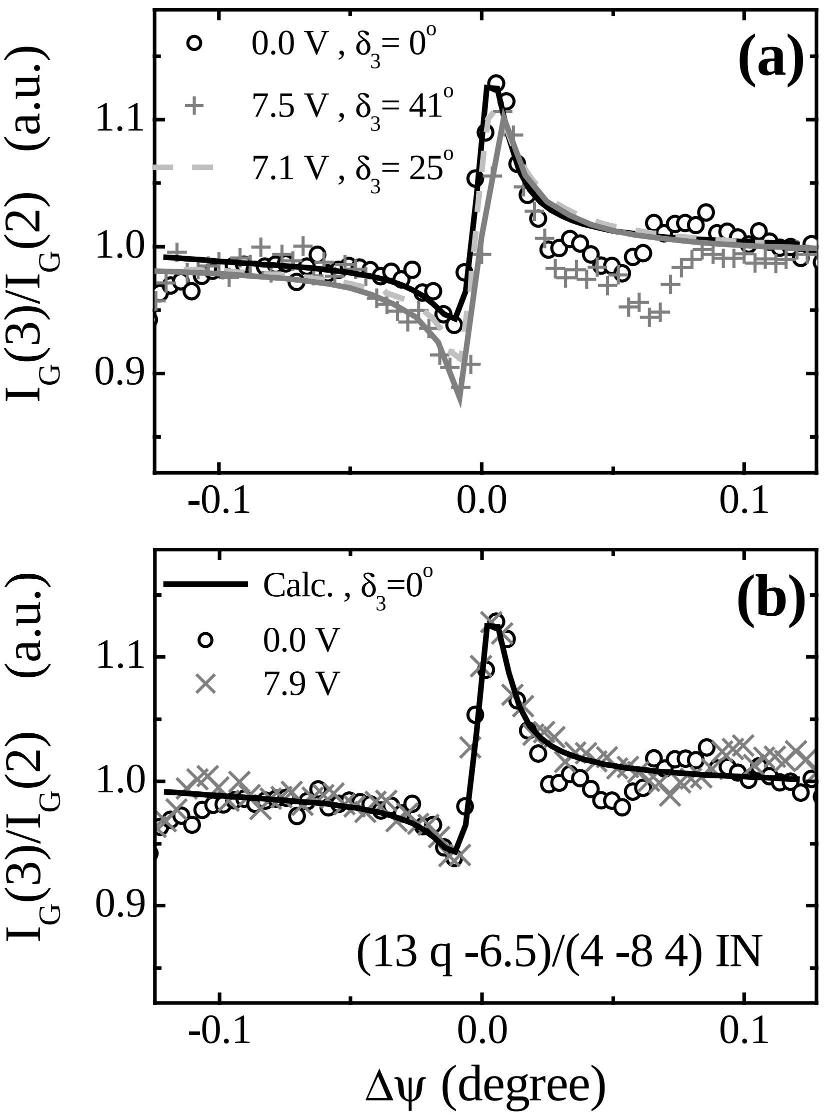
Figure 2: Curve-fitting of the triplet phase δ_3 in (a) the creeping regime and (b) the moving solid phase. In (a), for the clarity, the data plot for V=7.1 V is replaced by its fitted curve.

Figure 3: (a) Transport current, (b) triplet phase δ_3, and (c) the peak intensity of primary Bragg peak, versus applied voltage in $K_{0.3}MoO_3$ at T=100 K. The lines in (b) and (c) are only guides for the eye. In (b) I, II, and II mark the regimes of creep, plastic flow, and moving solid as proposed [11].



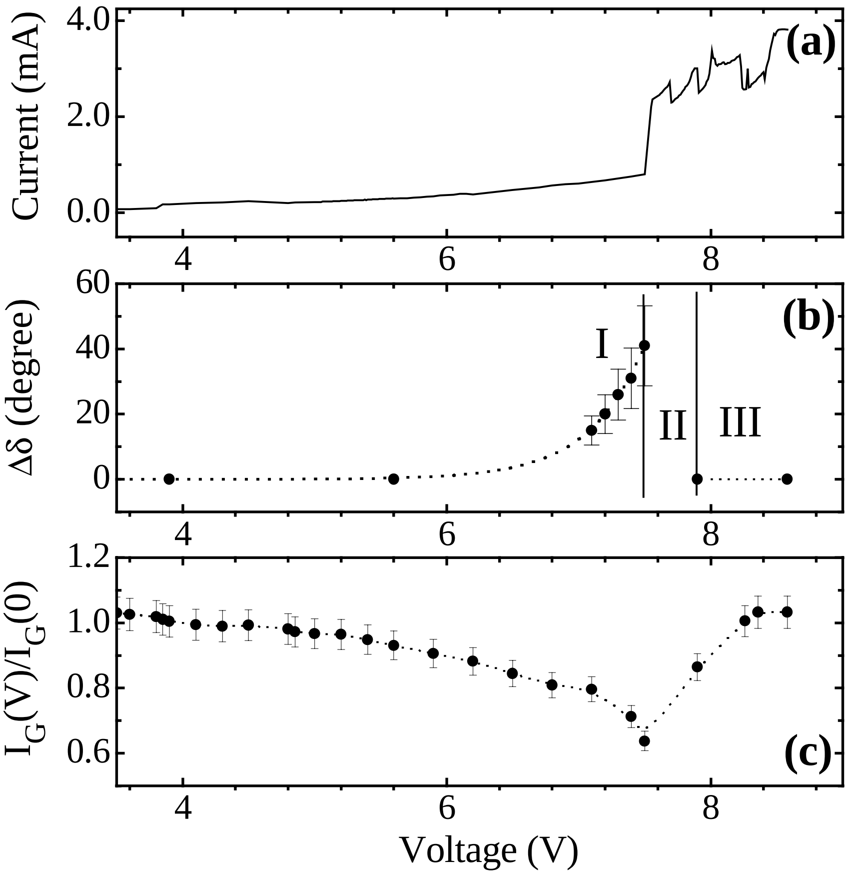
(a)
(b)
[2 0 1̄]
[0 1 0]
primary (13 q -6.5)
T=100K
(23 -3.25 2.5)+
(-2 2 1)-
(16 9.75 -1.5)-
(2 6 -1)-
(12 -2 9)+
(10 -2 -4)+
(26 8 -2)-
(7 8.75 7.5)-
Intensity (a.u.)
ψ (degree)

Figure 1



(a)
0.0 V , δ_3= 0°
7.5 V , δ_3= 41°
7.1 V , δ_3= 25°
$I_G(3)/I_G(2)$ (a.u.)
1.1
1.0
0.9
-0.1
0.0
0.1
(b)
Calc. , δ_3=0°
0.0 V
7.9 V
(13 q -6.5)/(4 -8 4) IN
Δψ (degree)

Figure 2



(a)
Current (mA)
4.0
2.0
0.0
4
6
8
(b)
Δδ (degree)
60
40
20
0
I
II
III
(c)
$I_G(V)/I_G(0)$
1.2
1.0
0.8
0.6
Voltage (V)

Figure 3