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子計畫四：金屬氧化物的結構與晶格形變的 X 光散射研究

(1/3)

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過度金屬及硫屬化合物之物性研究與應用

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共同主持人：

計畫參與人員：

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一、 摘要

本計畫的主要目的是要建立一座具有高解析度(high-resolution)及高輝度(brilliance)的三軸四環 X-光繞射儀來研究金屬氧化物中由電子及晶格擾動所產生的有序調制結構(modulated structure)，及其他金屬氧化物塊材、薄膜之結構分析，並配合使用同步輻射X-光共振散射(resonant x-ray scattering)，來進一步了解這些調制結構的電子及磁結構在外加電場及磁場下的物理特性．此計畫的另一目的則在於訓練及教導學生使用三軸四環繞射儀的相關技術及研究．

關鍵詞：X-光散射，過度金屬氧化物，硫化物，調制結構，晶格形變

Abstract

The objective of this proposal is twofold. The first is to build a triple-axes and 4-circle diffractometer for the studies of x-ray scattering on single crystals and thin films. With a special designed cryostat, we will be able to directly probe the charge modulations of materials and their coupling to the lattice at very low temperature (7 K) and very high electric field (about 1000 V). In addition, this study will also use the synchrotron X-ray scattering with the application of magnetic fields to further study the modulations related electronic and the magnetic structures. The second goal is to educate students using the triple-axes diffractometer and the related knowledge.

Key words: transition metal oxides, static modulation, dynamic modulation, x-ray diffraction

二、 緣由與目的

There exist many condensed materials in which the charge degrees of freedom form regular spatial patterns commonly known as “stripes”. These stripe-like modulated structures typically result from the competition between the short-range attractive forces, which give rise to a condensed phase, and the largely unscreened, the long-range Coulomb interactions. Specifically, in the condensed phase and in the absence of long-range repulsive forces between charges, the charge degrees of freedom tend to form clumps that are to phase separate. This tendency to phase separation is frustrated by the long-range repulsive Coulomb interactions, and results in the spontaneous organization of the charge degrees of freedom in low-dimensional structures. Such stripe-like modulations have been recently observed experimentally in a large class of strongly correlated electrons systems, i.e., doped Mott insulators such as the copper oxides, the nickelates, and the manganates, and demonstrated to play an important role on the transport behaviour. For instance, in the cuprate family, the holes doped into the CuO_2 planes can order in an array of periodically

spaced stripes which separate antiferromagnetic domains, which has been observed using inelastic neutron scattering and been interpreted as dynamic stripes [9]. The transport measurements also evidence that the electronic state of high-T_C superconductors possesses the anisotropic characteristic.

Based on the experimental findings, anisotropic and static/dynamic charge inhomogeneity, Kivension and Emery further proposed that there should exist electronic quantum liquid-crystal phases in those highly correlated electron systems, namely the stripe liquid phases [10], and these electronic liquid phases can be superconducting or insulating at low temperatures. Since then, there are many theoretical models devoting to the studies of the correlations of the spin and charge liquid states and the superconductivity [10, 11], but the experimental evidences are of lack because of the difficulties in probing the stripe liquid phases using high-resolution neutron or x-ray scattering.

Analogous to the classical liquid crystals which break spontaneously the rotation and/or translation symmetries of free space, and resulting in the nematic, smectic, and isotropic phases, the proposed electronic liquid crystals are quantum analogous of these phases, i.e., the nematic stripes, the smectic stripes, and the isotropic stripes phases. Both x-ray and neutron scattering are the ideal probes for directly studying the modulations. Neutron scattering is sensitive to the dynamic or static magnetic structures, but it loses the sensitivity to the charge and the spatial resolution. Contrast to neutron scattering, x-ray is more sensitive to the charge modulation and with a higher spatial resolution (typically it can be as high as 10^{-4} $Å^{-1}$), so x-ray scattering is suitable for probing the static nematic, smectic and isotropic charge liquid phases, and the coupling of the modulations and the lattice. In order to study the fields effects on the stripes liquid phases and the coupling interactions of the lattice and the modulations, two strongly correlated electron systems, nickelites, $La_{2-x}Sr_xNiO_4$, and ruthenate, $BaRuO_3$, will be used as the studying materials.

This proposal aims at studying the dynamic behaviour of the electronic liquid phases as that observed in $La_{2-x}Sr_xNiO_4$ under the application of electric and magnetic fields and the lattice distortions in the ruthenate $BaRuO_3$ using x-ray scattering. As the modulated structures and the lattice distortions are the common characteristics in many transition metal oxides, therefore, the studies and the characterization of the structures of the newly synthesized metal oxides by other sub-groups are also the target of this proposal.

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 electron-electron [1]. Among many other interesting aspects of CDW, transport property has attracted lots of attentions from both experimental and theoretical sides. 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].

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. In this report, we address this issue by applying the techniques of multiple (three-wave) X-ray diffraction and x-ray scattering to measure the changes in the CDW lattice and its internal structure with respect to the applied electric fields. From the extracted phase $\delta_3(V)$ of the three-wave diffraction and the peak profile of the CDW satellite reflection, we demonstrate that the occurrence of nonlinear conductivity caused by the periodic media is through the internal deformation of the CDW lattice, i.e., a phase jump of 2π, as the applied voltage exceeding the threshold. From the evolution of the measured peak width of satellite reflections as a function of the field strength, we also report that the CDW lattice can be driven to move and undergo a dynamic phase transition from the disordered pinning state to ordered moving solid state and then to disordered moving liquid.

A good quality single crystal $K_{0.3}MoO_3$ was first characterized and oriented at room temperature. The non-linear conductivity [4] was confirmed by measuring the *I*-*V* curve at 70 K as shown in figure 1*a*, indicating the dynamic transition from the pinned CDWs to sliding motions at the threshold filed $V_C \approx 0.165$ V. It is noteworthy that the nonlinearity is not as robust as at low temperature due mainly to the thermal fluctuations smearing out the switching behavior.

The *in-situ* measurements were carried out on the Taiwan Beamline BL12B2 of Spring-8 synchrotron facility. The incident x-ray wavelength was selected to be 1Å. The satellite reflections signal the formation of CDW, located at the Bragg position G = (13 q 6.5), where $q \approx 0.748$. Scans were performed through the longitudinal direction of [2 0 -1], and the data was convoluted with the resolution function obtained from the nearby Bragg peak (12 0 -6). Figure 1*b* shows the evolution of the peak width of CDW reflection as a function of applied

voltage at T = 70 K.

As shown in figure 1*b*, the FWHM of the satellite reflection, (13 *q* -6.5), remains more or less unchanged below the critical voltage *Vc* ≈ 0.165 V determined from the transport measurement. Above the critical voltage, where the CDW enters the sliding phase, the FWHM width decreases as predicted by previous theoretical investigations. As the voltage exceeding 0.18 V, the lattice shows a long-range ordered state; namely a moving solid phase [5]. This interesting dynamical narrowing of half width is a strong indication that the pinning forces due to random potentials become irrelevant (or less efficient) when the CDW starts to slide. When the voltage goes beyond 0.22 V, non-equilibrium effects, amplitude fluctuations and others become important and the Bragg peaks disappear. This is clearly evidenced by the sharp increase of FWHM.

The other key quantity we studied is the triplet phase δ_3 of a 3-wave multiple diffraction at different biased voltages. To set up a 3-wave (O,G_1,G_2) multiple diffraction experiment, the crystal is first aligned for a primary reflection G_1. It is then rotated around the reciprocal lattice vector G_1 with an azimuthal angle ψ to bring in the secondary reflection G_2 which also satisfies Bragg's law. Namely, both G_1 and G_2 reflections take place simultaneously. O stands for the incident reflection. The interaction of the multiply diffracted waves modifies the intensity of the primary reflection. Intensity variation showing asymmetric distribution versus ψ gives the information about δ_3, which is the triplet phase of $F_{G2}F_{G3}/F_{G1}$ involved in the 3-wave diffraction. Previously [6], we demonstrated that the triplet phase δ_3 due to the coupling between the CDW lattice and its host lattice can be probed using multiple diffraction. Here we further demonstrate that measuring the relative change in δ_3, $\Delta\delta_3$, caused by a driving force, makes the study of the internal deformation of the CDW lattice possible.

Through the azimuthal scan around the primary reflection G_1 = (13 q -6.5) at T = 70 K, we obtained the three-wave diffraction pattern containing lots of multiple diffraction peaks. We concentrated, here, only on the particular three-wave diffraction, (0 0 0), (13 q -6.5) and (4 -8 4) at ψ=108.53^o, where the primary reflection is (13 q -6.5) and the coupling reflection is (9 8+q 10.5). The profile asymmetry of the diffraction intensity of (13 q -6.5) versus ψ at V= 0 is typical for δ_3 =0. The phase variation $\Delta\delta_3$ due to non-zero applied voltages was analyzed based on the dynamical theory for multiple diffractions [7]. In Fig. 2, the profile develops different asymmetry at different finite voltages. In the static CDW state, the crystal lattice possesses a centrosymmetric structure, and a change in the peak profile means that this centrosymmetry is broken due to the relative motion of ions by a driving force. This results in a non-zero of $\Delta\delta_3$, suggesting the internal deformation of the original charge density distribution by the driving force. As shown in figure 1*c*, The estimated $\Delta\delta_3$ from curve fitting at 0.1, 0.12 0.13, 0.14, 0.15, and 0.16 V are about 6^o, 10^o, 18^o, 17^o, 17^o, and 10^o respectively,

and then back to 0^o for $V > 0.18$ V. This evidences experimentally that the occurrence of non-linear transport behavior is through a phase jump of 2π at the sliding threshold, i.e., from the pinned to sliding states [8].

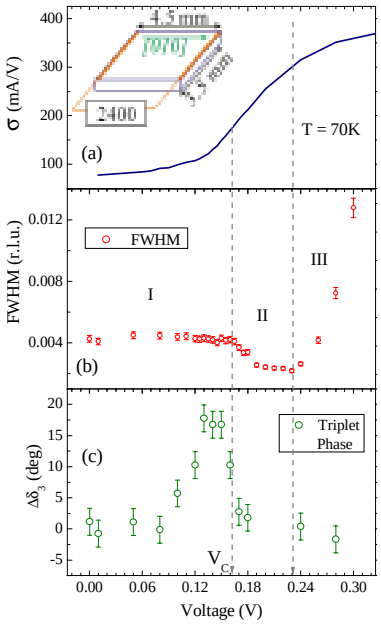

Figure 1: (a) Resistance versus voltage at 70 K. It shows the nonlinear behavior with a threshold voltage $V_C \approx 0.165$ V. The inset shows the dimension of the sample and the experimental setup. (b) Evolution of the FWHM of the CDW satellite reflects as a function of applied voltage. One can classify CDW into three phases: (I) the creeping CDW state, (II) the moving solid and (III) the moving liquid. (c) The triplet phase $\Delta\delta_3$ at different voltages. Note that, in the sliding phase, $\Delta\delta_3 = 0$ is a direct evidence that the pinning forces become irrelevant.

四、 計畫成果自評

We have, so far, demonstrated that the nonlinear conductivity due to the formation of density wave modulation is correspondent to the phase jump of 2π at the boundary of the nonlinearity, and the modulated lattice can be driven to move as the applied field exceeding the threshold. In addition, an in-house x-ray source and a 4-circle diffractometer have also been set up for the x-ray scattering study of single crystals and highly orientated thin films in my laboratory, and testing-works are currently under going. Stepping into the second year of this project, the studies of dynamic and static phase transitions of the modulations in transition metal oxides will be still carried out using synchrotron radiation source. The in-house facility will be open to other research groups soon.

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