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Energy dispersive x-ray diffraction of charge density waves via chemical filtering

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Pressure tuning of phase transitions is a powerful tool in condensed matter physics, permitting high-resolution studies while preserving fundamental symmetries. At the highest pressures, energy dispersive x-ray diffraction (EDXD) has been a critical method for geometrically confined diamond anvil cell experiments. We develop a chemical filter technique complementary to EDXD that permits the study of satellite peaks as weak as 10^{-4} of the crystal Bragg diffraction. In particular, we map out the temperature dependence of the incommensurate charge density wave diffraction from single-crystal, elemental chromium. This technique provides the potential for future GPa pressure studies of many-body effects in a broad range of solid state systems. © 2005 American Institute of Physics. [DOI: 10.1063/1.1938954]

I. INTRODUCTION

Charge density waves (CDW) emerge from Fermi-surface effects and the interaction of electrons with the crystal lattice. They can coexist with other collective ground states in solids such as spin density waves (SDW) and superconductivity.¹⁻⁶ The dependence of CDW ordering on variables such as temperature, doping,^{6,7} and pressure⁸⁻¹⁰ can provide key insights into the Fermiology of a metal or superconductor, the nature of its low-energy excitation spectrum, and the interplay of spin and charge degrees of freedom in correlated systems.

In general, pressure suppresses CDW ordering and, if pursued to sufficiently high pressures and low temperatures, can reveal underlying quantum phase transitions.⁹ Hydrostatic pressure serves as a cleaner method than doping to study such phase transitions because it retains a constant chemical environment and, unlike a magnetic field, does not break any symmetries. However, for most solids of interest, the required pressure is in the Gigapascal (GPa) range. Traditional hydrostatic cells are typically limited to pressures

below 5 GPa, whereas a diamond anvil cell (DAC) is the ideal choice for a wide range of pressures up to 200 GPa.¹¹ Since x rays directly couple to the charge modulations of a CDW, it is naturally desirable to study the pressure dependence of an incommensurate CDW state inside a DAC using x-ray diffraction.

Diffraction from a CDW is usually very weak and not readily observable compared to normal Bragg diffraction from core electrons. For example, the ratio between the CDW and Bragg diffraction peaks from chromium is about 10^{-4} at the CDW's full strength.¹² Indeed, background scattering from the environment such as the anvils and the pressure medium inside a DAC (typical total length of 5 mm compared to the sample thickness of 50 μm) easily can overwhelm the CDW signal.

In order to reduce the background levels, a collimation system is required for the detector system to focus mainly on the sample, and wide-area detectors such as an image plate will not be particularly useful. Given this confinement that collimation places on the transferred \mathbf{q} direction, one can either use a monochromatic incident x ray in combination with an energy insensitive detector such as an ion chamber to

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probe the momentum space point by point¹² or, alternatively, use a wide-spectrum incident x-ray beam with an energy-resolved detector to expedite the measurement by collecting a range of q values simultaneously. The latter approach is referred to as energy dispersive x-ray diffraction (EDXD). In this paper, we present a chemical filter technique that augments the current EDXD method and enables one to measure incommensurate CDW states from samples inside diamond anvil cells.

EDXD has been widely used for powder diffraction studies in DACs, with a typical Bragg peak to background ratio of 10^2 to 10^3 (e.g., for gold polycrystals). This ratio is much higher for a single crystal since all the intensity around the Laue circle is integrated into a single point limited only by the sample's Darwin width. In addition, the domain size of a CDW state in a perfect crystal might be comparable with the typical sample size ($\sim 100 \mu\text{m}$) for a DAC experiment.¹³ Thus, a single crystal sample is often required. From here on, we will focus on single-crystal EDXD.

When an incommensurate CDW peak lies near a Bragg peak along a crystallographic axis, the difference of 10^4 in magnitude cannot be resolved easily with current detectors, independent of the true Bragg intensity to background ratio. This is due to the fact that the simultaneously recorded EDXD spectra are typically measured with an energy-resolved solid-state Ge detector (e.g., Canberra GL0110), which has non-Gaussian-limited long- and short-term tails rising from multiple physical effects inside the detector.¹⁴ The weaker signal is then overwhelmed because of the strong tails of the detector response function.

In order to observe nearby signals with huge dynamic range, we introduce a chemical filter technique for the general EDXD setup. The core-electron absorption K -edges for many common elements are usually very sharp and foils of these elements have been widely served as well-defined low-pass filters.¹⁵⁻¹⁷ It is then possible to set the diffraction angle such that the Bragg peak and the CDW diffraction peak are located at the high and low energy sides of the absorption edge, respectively. By varying the thickness of the chemical filter, one is able to change the relative intensity between the CDW and Bragg diffraction without significantly degrading the counting statistics at the CDW peak.

The current filter idea is similar to the early balanced filters by Ross,¹⁵ but only one low-pass filter is needed here. It also draws upon one of the early monochromatizing techniques for x-ray anode tube sources that used a Ni filter to suppress the Cu $K\beta$ emission line from the closely spaced $K\alpha$ line.¹⁷ Other techniques also exist with differing abilities to suppress high-energy diffraction peaks. A low- Z mirror can reduce the intensity, but the roll-off is not sharp and there will not be a controllable reduction factor when the ratio between a CDW peak and a Bragg peak becomes quantitatively important. A graphite crystal also can be used as a notch filter at the Bragg peak position. However, such an approach would require constant adjustments whenever the sample's Bragg peak moves due to varying pressure and/or temperature. Hence, the K -edge filter provides both the sharpest roll-off in reducing the dynamical range and the most convenience.

II. EXPERIMENT

The current work was carried out at the bending magnets beamline 16-BM (HPCAT) of the Advanced Photon Source (APS) with preliminary testing at beamline X17C of the National Synchrotron Light Source (NSLS). 16-BM provides a wide spectrum x-ray beam with an on-axis peak brilliance about 3×10^{15} ph/(sec mrad² mm² 0.1% bw) at 16 keV. The incident x-ray beam of size $75 \times 75 \mu\text{m}^2$ was focused to $10 \times 10 \mu\text{m}^2$ at the sample position by two 10-cm K - B mirrors. The EDXD setup is a general type with three translational (x, y, z) and two rotational (χ, ω) degrees of freedom for the sample stage, and two motorized double slits defining the collimation at the detector side within the horizontal plane. A tin filter was chosen and inserted in the incident x-ray path because the relatively high K -edge energy of Sn gives a smaller 2θ angle, important in the DAC geometry. Other materials such as silver also can be used as chemical filters, but with a larger 2θ angle.

We examine pure chromium to illustrate this technique. Chromium is the archetypal example of incommensurate SDW/CDW ordering in three dimensions.^{4,18} At ambient pressure, Cr has a bcc lattice and a weakly first-order paramagnetic to antiferromagnetic phase transition at a Néel temperature of 311 K. The CDW state is incommensurate with the lattice constant a and its primary diffraction pattern is a set of six satellite peaks surrounding the (2 0 0) Bragg peak with a separation $2\delta/2\pi/a$ in momentum space of 0.35 \AA^{-1} .¹² Cr plates of $400 \mu\text{m}$ size and $50 \sim 60 \mu\text{m}$ thickness were cut and ground from a single crystal wafer (Alfa Aesar, 99.996+%, #13547) with a final polish to an optical finish (below $1 \mu\text{m}$ roughness). These plates were then diced with a pulsed laser into miniature squares of roughly $100 \mu\text{m}$ size and etched (Cr etchant, Type 1020, Transene Co. Inc.) to remove about $10 \mu\text{m}$ from each side, relieving the surface stress caused by polishing and laser dicing. In order to simulate a high-pressure DAC environment, a miniature Cr crystal was affixed by silicone grease onto one of the culets of a symmetric DAC, and measured without pressurization. The DAC was mounted on the cold plate of a helium-flow cryostat with its sapphire windows defining a total 2θ -angle allowance of approximately 20° , and the cryostat was mounted on the sample stage of the EDXD diffractometer.

III. RESULTS AND DISCUSSION

We plot in Fig. 1 two EDXD spectra taken with and without a $330\text{-}\mu\text{m}$ Sn filter, respectively. The 2θ angle of 16.51° was chosen such that the Sn K -edge (29.200 keV) was below the Cr (2 0 0) Bragg peak (30.019 keV). The spectrum without the filter was taken with a reduced incident slit size to protect the detector from saturation, and converted to the same incident slit size of the filtered spectrum by multiplying by a geometric factor. The comparison clearly indicates a CDW peak ($2-2\delta, 0, 0$) at 28.562 keV, after the overwhelming long-term tail of the Bragg peak was attenuated.

In order to probe the effects of the chemical filter, we show in Fig. 2 three spectra taken with different filter thickness with varying CDW to Bragg intensity ratios. The dis-

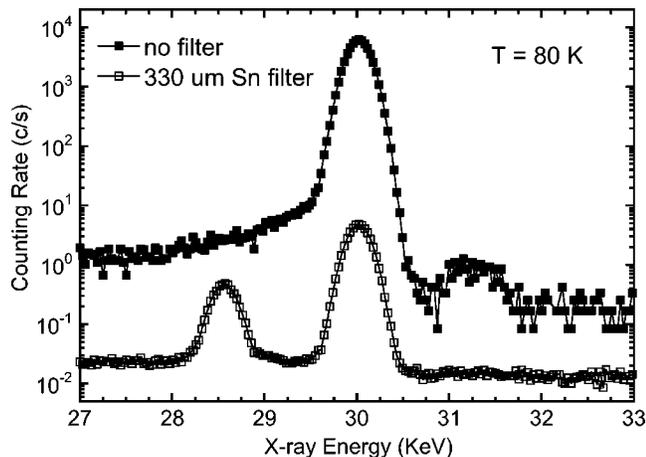


FIG. 1. Single-crystal Chromium EDXD spectra about the (200) Bragg peak taken with (open square) and without (solid square) a 330- μm Sn filter. The CDW peak, at 10^{-4} the intensity, only emerges after chemical filtering.

continuity at the Sn K -edge (29.200 keV) is apparent with the thicker filter, which also sacrifices the counting statistics. Comparing Fig. 1 and 2 indicates a decrease in momentum space separation between the CDW and Bragg peaks as temperature is increased from 80 to 295 K, a consequence of the temperature-dependent incommensurability of the CDW. Many samples were tested as a check for sample consistency, and the data in Figs. 1 and 2 are taken on different crystal pieces. Hence the CDW intensities in Figs. 1 and 2 cannot be compared directly due to different antiferromagnetic domain configurations in different samples, although the incommensurate $Q=1-\delta$ is consistent over all tested samples. Measuring CDW diffraction along different cubic directions while samples were outside the cryostat established the existence of multi- Q states in our miniature samples. However, we are not able to estimate individual domain size from the line shape and sharpness of the CDW peak;¹² our q -space resolution is mainly limited by the energy resolution of the solid-state detector, which has a full width at half maximum

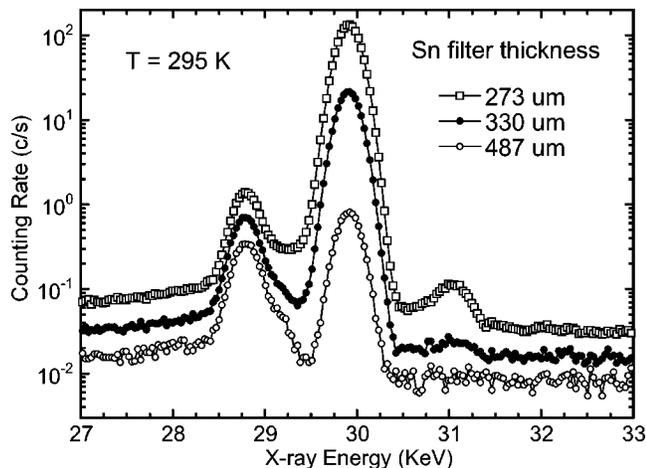


FIG. 2. The effect of different filter thicknesses (open square, 273 μm ; solid circle, 330 μm ; open circle, 487 μm) in changing the relative intensities of the CDW and Bragg peaks.

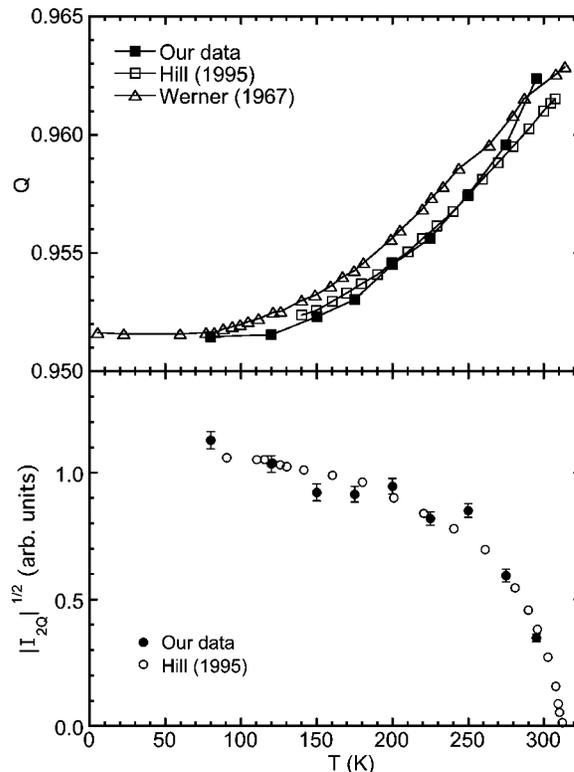


FIG. 3. (Top): EDXD results in a DAC for the temperature dependence of the incommensurate CDW wave vector Q (solid square), in agreement with two previous measurements using monochromatic incident x rays in atmosphere [open square (Ref. 12); open triangle (Ref. 19)]. All lines are guides to the eye. (Bottom): Temperature dependence of the normalized CDW intensity following the general scaling form of Hill *et al.* (Ref. 12).

(FWHM) of approximately 280 eV at 30 keV, or 1% of the reciprocal space distance. This is a limitation intrinsic to the EDXD technique.

An examination of the satellite peak as a function of temperature T is necessary in order to prove the true nature of the claimed CDW. We plot in Fig. 3 both the temperature dependence of the CDW wave vector Q and its intensity normalized by the Bragg peak. Q was calculated simply by taking a ratio between the energies of the CDW and Bragg peaks on the same EDXD spectrum, thereby avoiding any systematic error of the 2θ value. Our data show good consistency with two previous measurements^{12,19} using monochromatic x rays. Their use of the room temperature lattice constant a_0 to normalize all temperature data gives a slightly flatter slope in $Q(T)$. The temperature dependence of the CDW intensity also is consistent with previous data with $|I_{2Q}|^{1/2}$ vs T following the universal scaling of Hill *et al.*¹²

The plotted error bars represent a combined 2~6% counting statistical uncertainty and a 5% systematic uncertainty due to a 1% variation of the filter thickness. This thickness variation is deduced from the data consistency over spectra in Fig. 2. The measurement time for each spectrum averages 3000 s with collection times up to 11 000 s close to the Néel temperature where the signal is small. The efficiency is physically limited by the incident slit size because the (4 0 0) Bragg peak at a higher energy saturates the detector as well as a limited focusing K - B mirror length.

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