X-RAY DIFFRACTION FROM PINNED CHARGE DENSITY WAVES

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Abstract. We present an x-ray study of doped charge density waves systems. When a $2k_f$-charge density wave is strongly pinned to impurities, an interference effect gives rise to an asymmetry between the intensities of the $+2k_f$ and $-2k_f$ satellite reflections. Moreover, profile asymmetry of the satellite reflections indicates the existence of Friedel oscillations (FOs) around the defects. We have studied these effects in V- and W-doped blue bronzes. A syncrotron radiation study of the V-doped blue bronze clearly reveals the presence of FO around the V atoms.

1. INTRODUCTION

The pinning of charge density waves (CDW) on impurities has a crucial influence on the collective properties of quasi-one-dimensional (1D) metals [1]. Although the interaction between CDW and impurities has been studied for more than two decades in quasi-1D systems, it is far from being correctly understood. In particular, the presence of Friedel oscillations (FOs) around the defect and their influence on the CDW order, though suggested theoretically [2], has not received experimental confirmation so far. Recently, a new x-ray diffraction effect resulting from the interference between the CDW displacive contribution and the disorder contribution has been able to bring some valuable information and a thorough insight into the local description of the CDW-defect interaction [3]. With this technique, the phase of the CDW at the impurity position together with local distortions of the CDW phase around the impurity become measurable.

The theory of the scattering of CDW pinned on impurity has already been presented [3] and the main results can be summarized as followed. The $2k_f$-periodic lattice distortion (PLD) in quadrature with the $2k_f$-CDW, gives rise to satellite reflections at the reciprocal positions $\pm 2k_f$ around each Bragg reflection. The main point is that the spatial coherence between the impurity position and the phase of the PLD (the strong pinning case) can result in interferences between the satellite reflections and the diffuse scattering due to the chemical disorder. At first-order, this effect gives rise to a $+2k_f/-2k_f$ intensity asymmetry (IA) of the satellite reflection. The direction of this asymmetry depends on the pinning value of the phase (Φ_0) of the PLD on each impurity site. It allows to determine whether the first-neighbor atoms are displaced away ($\Phi_0 = 0$) or towards ($\Phi_0 = \pi$) the impurity. Moreover, in presence of a change of the wave length of the modulation around the impurity, a profile asymmetry (PA) of each satellite reflection is expected. This is the case of FOs which will be discussed later. These asymmetry effects have been first discovered in the organic charge transfer salts of the TTF-TCNQ family [3,4], giving rise to "white lines" on the diffuse scattering patterns. Here, we report an X-ray study of vanadium-(2.8%) and tungsten-(2%) doped blue bronzes.

Blue bronze $K_{0.3}MoO_3$ crystallizes in the monoclinic $C2/m$ spatial group with the cell parameters a=18.25Å, b=7.56Å, c=9.885Å and β=117.5^o. MoO_6 octahedra stack along the **b** direction and form layers along the [102] direction. Below the Peierls transition at T_p=183K [5], the PLD associated to the charge density wave gives rise to satellite reflections located at the reciprocal reduced wavevector $\mathbf{q}_c = (1, 2k_F, 0.5)$. The value of the Fermi vector at 15K was accurately measured by x-ray scattering experiments [5] and found to be equal to the incommensurate value $2k_F$=0.748b^* at 15K. In the vanadium-doped crystals, previous studies [6] had shown that the low temperature satellite reflection reduced position $\mathbf{q}_c$=(1, $2k_F = 0.685, 0.5$) was slightly changed with respect to the pure compound. This value is in accordance with the $2k_F$ value expected from the change in band filling due to the substitution of Mo^{6+} by 2.8% V^{5+}. In the W-doped crystal, where the tungsten atom is isoelectronic to the molybdenum, no significant change of the Fermi wave vector was observed.

2. EXPERIMENTAL

The measurements have been performed with a three circles diffractometer on a 12kW-rotating anode x-ray source. High resolution experiment have been performed with a four circles diffractometer on the D2AM beamline at ESRF, with $\lambda = 0.7$ Å. In order to investigate the interference effect on the $+2k_f/-2k_f$ satellite reflections, careful measurements were carried out in the pure, the V-
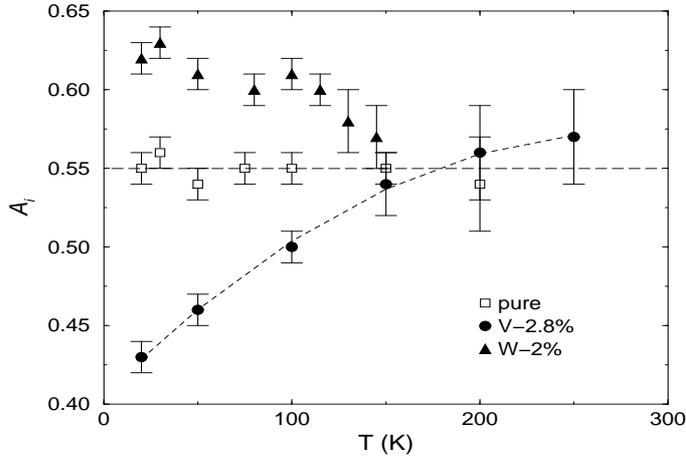
Figure 1: Temperature dependence of the asymmetry ratio A_i in the pure (squares), V-doped (circles) and W-doped (triangles) crystals.

doped and the W-doped crystals on the same satellite pairs. These pairs were chosen around the $(\overline{1}, 7, 0.5)$ and $(\overline{1}, \overline{11}, 0.5)$ reciprocal position. The ratio $A_i = I_{-2k_F}/I_{+2k_F}$ between the $(\overline{1}, \overline{11} - 2k_F, 0.5)$ and $(\overline{1}, \overline{11} + 2k_F, 0.5)$ peak intensity was measured as a function of temperature in the three compounds. The temperature dependence of the ratio A_i is shown in Figure 1. In the pure compound, $A_i = .55$ remains essentially constant in the temperature range studied (10 K- 300 K). In the doped crystals however, a clear deviation from $A_i = .55$ is observed below $T \sim 150K$. This temperature, close to T_p, is the temperature below which the intensity of the satellite reflection starts to increase in both compounds. In the V-doped crystals, the value A_i is about 20% lower than in the pure compound while in the W-doped crystal the value A_i is about 10% larger than in the pure compound. It is worth noting that the IA occur in opposite directions in the two types of doped crystals.

In addition, a strong PA has been observed at low temperature in the V-doped case. Fig. 2 shows the profile of the $(\overline{1}, \overline{10.685}, 0.5)$ satellite reflection in the b^* direction at T=60 K. The intensity at small wave vector $(k \leq 2k_f)$ is stronger than the intensity at high wave vector $(k \geq 2k_f)$. Since the peak is much broader than the experimental resolution, the profile is not affected by spurious resolution effects. This type of profile was also observed on different satellite reflections. Due to its unusual shape, we have not attempted to fit the profile by a special function. In the W-doped crystal, a very slight PA was observed at low temperature but the profile can be essentially fitted by a squared Lorentzian lineshape (see fig. 2). At T=15 K, the CDW coherence lengths ℓ_{b*}, ℓ_{2a*+c*} and ℓ_{2a*-c*} at 15K are equal respectively to 18.5Å, 7Å and 3.8Å for the V-doped
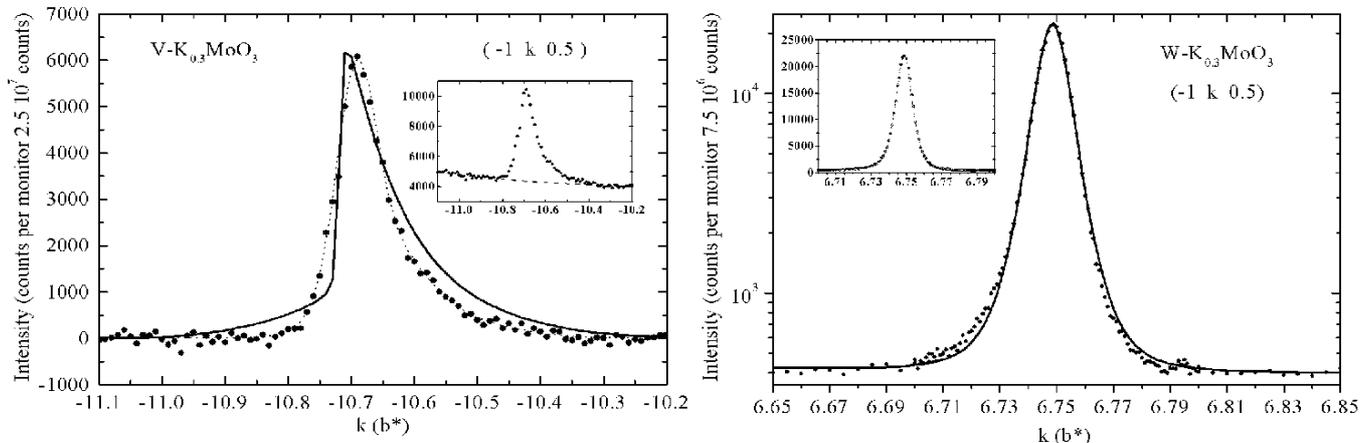
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Figure 2: Left : Profile of the $(\overline{1}, \overline{10.685}, 0.5)$ satellite reflection in the V-doped blue bronze at 60 K. Solid line is the intensity obtained from a Friedel oscillation as described in the text. Right : Profile of the $(\overline{1}, 6.748, 0.5)$ satellite reflection in the W-doped blue bronze at T=10 K. Solid line is the best fit by a lorentzian-squared form. Note the logarithmic scale and the normal scale in the insert.

compound [7a] and 70Å, 28Å and 7.5Å for the W-doped compound. This shows that the CDW domain of coherence is 2D for the W-2% crystal whereas it is only 1D for the V-2.8% one. There is only one impurity per correlated domain in the V-doped crystal and about 10 impurities per correlated domain in the W-doped crystal.

3. RESULTS AND DISCUSSION

Let us first consider the V-doped bronze previously considered in ref. [7]. Due to the small number of impurities in a coherence domain, one can conclude that the CDW is strongly pinned to each V-impurity. Using the calculation of ref. [3], one deduces from the decrease of the $-2k_F$ satellite intensity with respect to the $+2k_F$ one, that the neighboring Mo atoms are displaced away from the vanadium impurity. It is worth noting that this result is opposite to elastic effects for which molybdenum atoms will move towards the vanadium atoms of smaller size. Thus this effect clearly originates from an electronic process. As far as the PA is concerned, its direction indicates that the $2k_F-$CDW expands around the impurity. This corresponds to a local decrease of the electronic density, needed to screen the supplementary electron provided by the V^{5+} atom, with respect to the Mo^{6+} atoms [7b]. The case of the W-doped crystals is more subtle. The

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correlated domains contain 10 impurities on average, which is more consistent with a weak pinning scenario. Nevertheless, the observed IA indicates that the phase of the CDW adjusts as a whole on the impurities positions in a coherence domain. This global adjustment is expected in a weak pinning case. Furthermore, the Lorentzian squared profile of the satellite reflection is also expected in the weak pinning situation.

Let us now discuss in more detail the microscopic interactions between the CDW and the impurity potentials and the consequence of such interactions on the x-ray scattering intensity. At low temperature, when the CDW is well developed the Hamiltonian $\mathcal{H}$ describing the interaction of the CDW phase with the impurity reads :

$$\mathcal{H} = \frac{1}{s} \int d\vec{r} \{ C_\parallel/2 \, (\partial_x \varphi)^2 + C_\perp/2 \, (\partial_\perp \varphi)^2 + \sum_m V(\vec{r} - \vec{r}_m) \partial_x \varphi / \pi \tag{1}$$

$$-U \cos[q_c \vec{r} + \varphi(\vec{r})] \, \delta(\vec{r} - \vec{r}_m) \}, \tag{2}$$

where s is an area per chain and $C_\parallel$ and $C_\perp$ are the elastic moduli of the CDW in the chain direction and normal to the chains respectively. $\varphi = \varphi(\vec{r})$ is the CDW phase and $\vec{r}_m$ are the positions of the impurities. The impurity potential has been separated into a long range part V, leading to the forward scattering of the electron in the metallic state, and a short range part U, leading to its backward scattering. More generally, V is the potential interacting with the non oscillating part of the charge density $\pi^{-1} \partial_x \varphi$. From the previous equation, one can see that the effect of the backward scattering potential U is to pin the phase of the CDW at the impurity position, while the effect of V is to stretch/compress the phase of the CDW. As a general result, the x-ray IA comes from the backward scattering potential U, while the PA originates from the forward scattering potential V.

Let us now consider the effect of Friedel oscillations. It is well known that in a metal, the screening of an impurity charge occurs via the phase shift η of the electronic wave function scattered by its potential [8]. In 1D, the resulting charge oscillation $\delta\rho$ is coupled to the distortion $u(x)$, which thus reads at large $|x|$

$$u(x) \simeq \frac{1}{|x|} \sin(2k_F x + \varphi(x)), \tag{3}$$

where $\varphi(x)$ is the FO phase so that $\varphi(\infty) = \eta$ and $\varphi(-\infty) = -\eta$. The phase shift η is related to the charge Z of the impurity by the Friedel sum rule :

$$Z = \frac{2}{\pi} \eta. \tag{4}$$

In the case of a single charged vanadium impurity one has $\eta = \pi/2$. This means that the complete screening is achieved by stretching the CDW exactly by π.

The total phase shift $\delta\varphi = \pi$ of the CDW has to be accumulated on a very short distance d. Figure 2a presents the experimental results together with the computed intensity of the scattering by a FO described by the equation (2) and $d \sim 1$ Å. As expected from more general considerations on the x-ray scattering [3], this computed profile is essentially asymmetric and bears a striking resemblance with the experimental results. A complete discussion of the scattering by a FO, taken into account the damping of the FO by the microscopic coherence length ξ_0 of the electrons will be presented elsewhere The main conclusion of this study is the evidence of FO in the vicinity of the vanadium atoms in 2.8% V-doped blue bronze. IA have also been observed, which provides evidence of a coherence between the impurity position and the CDW/FO. The W-doped crystals are more likely described by a weak pinning scenario, in which the phase of a correlated domain adjusts as a whole. Nevertheless, the observation of a PA for all the satellite reflections studied clearly indicates the presence of phase distortions, corresponding to a local decrease of the electronic density. Additional experiments on crystals with different doping levels are planned in order to elucidate more quantitatively the microscopic features of the pinning of CDWs in low dimensional materials.

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