

Friedel Oscillations and Charge-Density Waves Pinning in Quasi-one-dimensional Conductors: An X-ray Access.

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We present an x-ray diffraction study of the vanadium-doped blue bronze $\text{K}_{0.3}(\text{Mo}_{0.972}\text{V}_{0.028})\text{O}_3$. At low temperature, we have observed both an intensity asymmetry of the $\pm 2k_F$ satellite reflections relative to the pure compound, and a profile asymmetry of each satellite reflections. We show that the profile asymmetry is due to Friedel oscillation around the V substituant and that the intensity asymmetry is related to the charge density wave (CDW) pinning. These two effects, intensity and profile asymmetries, give for the first time access to the local properties of CDW in disordered systems, including the pinning and even the phase shift of Friedel oscillations.

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The effects of impurities on the physical properties of crystals is one of the major issues of solid state physics. In metals, impurities are known to originate Friedel oscillations [1] (FOs) of the electronic density and to affect generic ones like charge-density waves (CDWs) [2]. In quasi-one dimensional (1D) metals both features occur. Due to its divergent susceptibility at twice the Fermi wave vector $2k_F$, a 1D electron gas is unstable with respect to the formation of a $2k_F$ -CDW, which, coupled to the lattice, induces a $2k_F$ -periodic lattice distortion. The $2k_F$ -satellite reflections arising from this distortion provides a rich variety of information on the CDW. While the peak intensity and its position give the amplitude and the wave length of the CDW, the satellite reflections profiles is related to the phase-phase correlation function of the CDW. In CDW materials like blue bronze $\text{K}_{0.3}\text{MoO}_3$ [3] or transition metal trichalcogenides like NbSe_3 [4], [5], diffraction experiments have clearly demonstrated the loss of the CDW long range order upon doping. But despite this recent progress in the description of the CDW structure, the microscopic nature of the pinning is still largely unknown. Recently, two new methods have been found to access the local properties of CDW in disordered systems [6] [7]. The first one is the analysis of the intensity asymmetry (IA) of the satellite reflections at $+2k_F/-2k_F$ from a Bragg reflection, which gives information of the value of the phase at an impurity position. Another method, that we describe here for the first time, consists in analysing the profile asymmetry (PA) of the individual peaks. In this letter, we shall demonstrate that both effects, intensity and profile asymmetries, can be observed simultaneously and that they provide a unique tool to access the FO's and the pinning.

Let us first consider the general case of a modulated crystal containing impurities in concentration c . The substitution disorder is characterized by $\sigma(\mathbf{r})$, which is 1 if an impurity sits in position \mathbf{r} and 0 otherwise [8]. The displacements of the atoms from their regular positions are $\mathbf{u}(\mathbf{r})$. The total diffracted intensity at the scattering

vector $\mathbf{Q} = \mathbf{G}_{hkl} + \mathbf{q}$ close to one of the reciprocal wave vector \mathbf{G}_{hkl} reads, [7]:

$$I(\mathbf{Q}) = I_L + I_d + I_a \quad (1)$$

$$= \Delta f^2 \langle \sigma_{\mathbf{q}} \sigma_{-\mathbf{q}} \rangle + \bar{f}^2 \langle |\mathbf{Q} \cdot \mathbf{u}_{\mathbf{q}}|^2 \rangle - 2\bar{f}\Delta f \text{Im} \langle \sigma_{-\mathbf{q}} \mathbf{Q} \cdot \mathbf{u}_{\mathbf{q}} \rangle$$

where $\langle \dots \rangle$ denotes an average on both disorder and thermal fluctuations. $\Delta f = f_I - f$ is the difference between the impurity and the host atom form factors, $\bar{f} = cf_I + (1-c)f$ is the average form factor and $\mathbf{u}_{\mathbf{q}}$ and $\sigma_{\mathbf{q}}$ are the Fourier transforms of $\mathbf{u}(\mathbf{r})$ and $\sigma(\mathbf{r}) - c$ respectively. \mathbf{q} , which is any wave vector of the first Brillouin zone, is close to $2\mathbf{k}_F$ in the present case.

The first term gives the scattering intensity due to disorder, usually called the "Laue scattering". The second term represents the intensity due to atomic displacements *i.e.* the usual Fourier transform of the correlation function $\langle \mathbf{u}(0)\mathbf{u}(\mathbf{r}) \rangle$. The third term arises from the coupling between the disorder and the displacements. Remarkably, I_a is *linear* in $\mathbf{u}_{\mathbf{q}}$ and *odd* in \mathbf{q} , which changes the relative intensities at $\mathbf{G}_{hkl} + \mathbf{q}$ and $\mathbf{G}_{hkl} - \mathbf{q}$ with respect to that of the pure crystal. An intensity asymmetry occurs around the \mathbf{G}_{hkl} reciprocal position. Physically, this term is due to an interference between the reference wave scattered by the impurity and the wave scattered by the atomic displacements originated by the same impurity. In that sense, this phenomenon can be seen as an *holography* of the lattice distortion around the impurity. I_a cancels out when there is no coupling between the impurity positions and the atomic displacements ($\langle \sigma_{-\mathbf{q}} \mathbf{Q} \cdot \mathbf{u}_{\mathbf{q}} \rangle = \langle \sigma_{-\mathbf{q}} \rangle \langle \mathbf{Q} \cdot \mathbf{u}_{\mathbf{q}} \rangle = 0$). However such a coupling does exist for FO's and CDW when it is pinned. In a simple model of strong pinning, where the lattice distortion has an amplitude $\mathbf{u}_{2\mathbf{k}_F}$ and a phase φ_0 at the impurity site, it has been shown that [6], [7]:

$$I_a(\mathbf{Q} = \mathbf{G}_{hkl} \pm 2\mathbf{k}_F) \sim \mp \bar{f} \Delta f (\mathbf{Q} \cdot \mathbf{u}_{2\mathbf{k}_F}) \cos \varphi_0. \quad (2)$$

This gives an intensity asymmetry of the $+2k_F/-2k_F$ satellite reflections and provides a unique way of evalu-

ating $\cos\varphi_0$. In organic materials, "white lines" due to strong intensity asymmetry have been observed and used to determine the phase φ_0 [6], [9]. With the same formalism, it can be shown that if the phase of the CDW undergoes a deformation around the defect, a profile asymmetry of each satellite is produced [7]. The same effects is produced by the notorious phase shifts of FO's. In this communication we report on how these ideas have been tested in doped blue bronzes, which can be considered, with NbSe_3 as a prototype of charge-density wave materials.

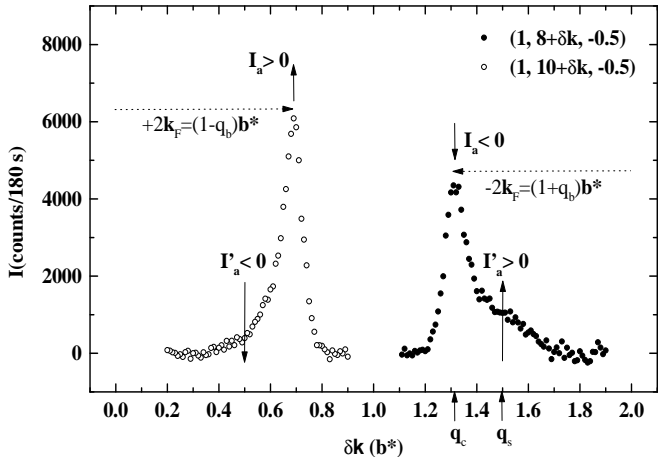


FIG. 1. High resolution profiles of the large- k $(1, 9 + q_b, 6.5)$ and $(1, 11 - q_b, 6.5)$ peaks at 60 K. The position of the \mathbf{q}_c - and \mathbf{q}_s -scattering are indicated on the x-axis. The vertical arrows indicate the intensity asymmetry of the \mathbf{q}_c - and \mathbf{q}_s -scattering.

Quasi-one-dimensional blue bronze $\text{K}_{0.3}\text{MoO}_3$ undergoes a Peierls transition at $T_p=183\text{K}$ [11]. Below T_p , satellite peaks appear at the reduced wavevector \mathbf{q}_c , with $\mathbf{q}_c = (1, 0.748, 0.5)$ at 15K [12]. In order to maximize the effect of impurities on the scattering, we have investigated heavily vanadium-doped blue bronzes (2.8 at.% V). X-ray diffraction studies were performed with a three-circle diffractometer on a 12 kW rotating anode ($\lambda_{\text{MoK}\alpha}=0.711\text{\AA}$) and with a four-circle diffractometer at the BM2 beamline in ESRF for high resolution measurements ($\lambda=0.7\text{\AA}$ and $\lambda=0.8\text{\AA}$). Previous studies had shown that at low temperature, the $2k_F$ -satellite reflections observed at the reduced position $\mathbf{q}_c=(1, 1 - q_b = 0.68, 0.5)$ were broadened, indicating the lost of the CDW long range order [3]. At last, the measured $2k_F = (1 - q_b)b^*$ ($b^* = 2\pi/b$) was in accordance with the $2k_F$ value expected from the change in band filling, due to the substitution of 2.8% V^{5+} for Mo^{6+} [3].

In order to gain evidence for an intensity asymmetry, we have measured the profiles of $2k_F/-2k_F$ scattering at different reciprocal positions and carefully compared the results obtained in doped and pure crystals. Typical high resolution scans in the chain (b) direction around two satellite reflections are shown in Fig. 1, after background subtraction. A casual inspection of Fig. 1 clearly reveals

a profile asymmetry of the satellite reflections, already noted in Ref. [3]. This asymmetric peaks can be analyzed by a sum of two components, a broad one, located at the reduced position $\mathbf{q}_s = (1, 1 - q_s, 0.5)$, where $q_s=0.5$ at 15 K, and a narrow one, corresponding to the regular \mathbf{q}_c -scattering by the CDW.

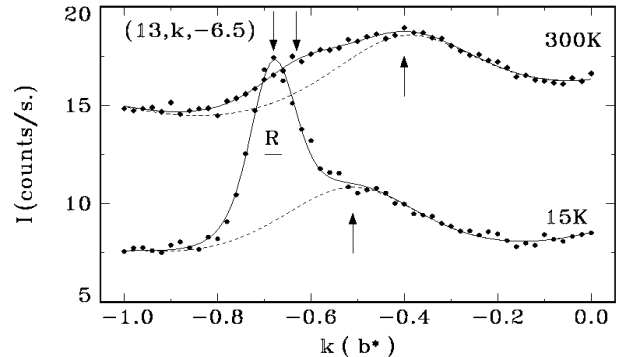


FIG. 2. Profile of the $(13, -1 + q_b, -6.5)$ diffuse scattering at 300 K and 15 K. The downwards (upwards) arrows point towards the \mathbf{q}_c -scattering (\mathbf{q}_s), respectively. The solid and dotted lines are the results of fit described in the text.

This analysis is confirmed by the temperature variation of the satellite profile. Fig. 2. shows that the \mathbf{q}_s broad component is still present at 300 K, with the same intensity. The curves in fig. 2 are the result of a fit by a sum of Lorentzian-squared functions, convoluted to the resolution function. From this analysis, the temperature dependences of $1 - q_b$ and $1 - q_s$ have been extracted and are displayed in Fig. 3.

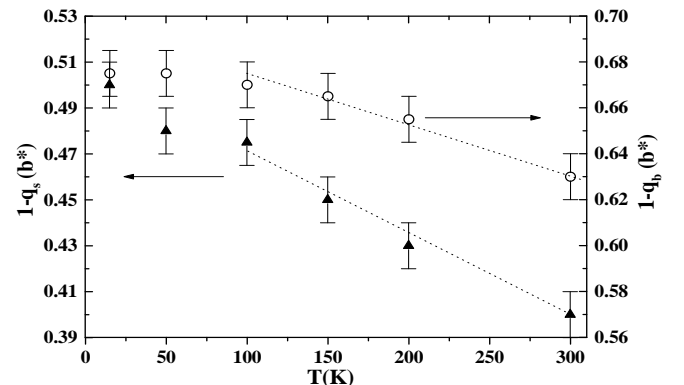


FIG. 3. Temperature dependence of $1 - q_b$ (right scale) and $1 - q_s$ (left scale).

Another striking feature of Fig. 1 is the difference between the $+2k_F$ and $-2k_F$ profiles. Consistently with the previous analysis, this has been interpreted as due to an intensity asymmetry I'_a of the \mathbf{q}_s -scattering, as indicated in Fig. 1. At last, a comparison with the satellite reflection intensities of the pure blue bronze (not shown here) reveals an intensity asymmetry of the \mathbf{q}_c -scattering [13]. This is evidenced by an intensity ratio I_{-2k_F}/I_{2k_F} 20%

lower than that of the pure compound at low temperature [13]. This effect is indicated by I_a in fig. 1.

As far as the low temperature CDW correlation lengths are concerned, they can be estimated from the inverse of the Half Widths at Half Maximum (HWHM) of the \mathbf{q}_c -scattering. Along the chains, one finds $\ell_{b^*} = 28.7 \text{ \AA}$ at 15 K [14]. The ordered domains are quasi-one-dimensional and they contain on average one V substituant [14].

Let us now present a simple model, which indicates that the \mathbf{q}_s -scattering is due to Friedel oscillations. At $T = 0 \text{ K}$, the oscillating part of the electronic density of a metal at large distance r from an impurity of charge $-Z$ located at $r = 0$ reads [15] :

$$\delta\rho(r) \sim \frac{\cos(2k_F r + \eta)}{r^D}, \quad (3)$$

where D is the space dimension and η is the phase shift of the electronic wave functions at the Fermi level. With these definitions, η is related to Z through the Friedel sum rule $Z = \frac{2}{\pi}\eta$.

Physically, this relation means that the additional charge $-Z$ has to be screened by the conduction electrons, by bringing an opposite charge Z in the vicinity of the impurity. In 1D, the lattice distortion associated to the FO reads :

$$\mathbf{u}(x) = \mathbf{u}_0 \frac{\exp(-|x|/\xi)}{|x|} \sin(2k_F x + \chi(x)). \quad (4)$$

where $r = |x|$. In this expression we have introduced a damping length ξ , due to the temperature and/or the disorder, and the phase function $\chi(x)$, whose limits are $\chi(\pm\infty) = \pm\eta$, consistently with equation (3). $\chi(x)$ jumps between these values on a distance roughly equal to the extension of the potential of the impurity, *i.e.* less than the lattice spacing. At last, let us remark that a decrease of the distance between neighbors corresponds to a decrease (increase) of the hole (electron) density. The two modulations are thus in quadrature, in agreement with expressions (3) and (4).

For the sake of simplicity, we shall model the x-ray scattering by taking the 1D lattice Fourier transform \mathbf{u}_q of $\mathbf{u}(x)$, which can be calculated exactly [10]. This 1D approximation is justified by the small transverse correlation lengths of the \mathbf{q}_s -scattering. The intensity diffracted by the FO, given by the $I_d \sim |\mathbf{u}_q \mathbf{u}_{-q}|$ term, mainly depends on ξ and η . Solid lines in fig. 4 represent the calculated intensity, for $\eta = \pm\pi/2$ and the blue bronze low temperature value of $2k_F = 0.75b^*$. Indeed, this value of η corresponds to the screening of a single charge impurity, which is the case here as discussed below. For large values of ξ , the intensity exhibits a sharp discontinuity at $\pm 2k_F$ and a long tail in the small- q direction. These discontinuities are smoothed for smaller values of ξ , which slightly shifts the maxima from the $\pm 2k_F$ positions. As expected from the general analysis [7], the phase distortion due to the FO phase shift gives rise to a profile asymmetry of the satellite reflections.

In fact, the total intensity diffracted by the FOs in the real crystal is given by (1). As the Laue scattering is weak here, the only additional term is the third one : I'_a . The dashed line of the lower part of Fig. 4 gives the total scattering intensity in the $\Delta f \sin \eta < 0$ case. As expected, an IA of the $+\mathbf{q}/-\mathbf{q}$ is obtained, which gives the possibility of measuring $\sin \eta$. Indeed, using (1), the IA term can be written:

$$I'_a(\mathbf{Q} = \mathbf{G}_{hkl} \pm \mathbf{q}) \sim \pm \bar{f} \Delta f (\mathbf{Q} \cdot \mathbf{u}_0) \sin \eta. \quad (5)$$

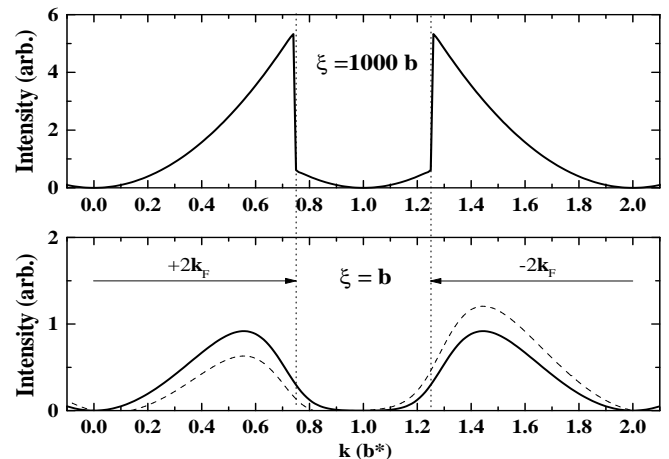


FIG. 4. Intensity of the diffraction by a Friedel oscillation for $\xi = 1000 b$ (top) and $\xi = b$ (bottom). The dashed curve is obtained by adding the linear term I'_a for $\Delta f \sin \eta < 0$.

A comparison of Figs. 1 and 4 strongly suggests the \mathbf{q}_s -scattering to be due to FOs around the single charged V impurities. From the position of the \mathbf{q}_s -scattering with respect to $2k_F$, the damping length can be estimated as $\xi \simeq 8 \text{ \AA}$. The FOs are present at ambient temperature, as shown in Fig. 2, and still exist in the CDW phase with the same characteristics. Concerning the \mathbf{q}_c -scattering, it corresponds to the regular scattering by the $2k_F$ lattice distortion at larger distance from the impurity. The correlated variation of the \mathbf{q}_c - and the \mathbf{q}_s -scattering maxima (Fig. 3), both related to the thermal variation of $2k_F$ [3], supports this interpretation.

The observation of intensity asymmetries on both \mathbf{q}_c - and \mathbf{q}_s -scattering gives evidence of a coherence between the position of an impurity, and respectively the FO and the CDW. Using eq. (2) and (5) and the signs of I_a and I'_a obtained from the experiment, one can readily calculate the signs of $\cos \varphi_0$ and $\sin \eta$. Considering that $\Delta f = f_V - f_{Mo} < 0$ and $\mathbf{Q} \cdot \mathbf{u}_{2k_F} > 0$ for positive k -values, one gets $\cos \varphi_0 > 0$ and $\sin \eta > 0$, which is consistent $\varphi_0 \simeq 0$ and $\eta \simeq \frac{\pi}{2}$. Both values correspond to a local increase of the hole density around the impurity, which is natural for the V substituant. Indeed, the V^{5+} atom provide a negative charge ($Z=1$) with respect to the molybdenum Mo^{6+} background. This charge has to be screened by a positive charge, which induces a local increase of the hole density as found experimentally. The $\eta \simeq \frac{\pi}{2}$ value is that

expected from the Friedel sum rule with $Z=1$

Fig. 5 displays a tentative representation of the CDW/FO structure around a V atom according to the present experimental results. FO's dominate the charge modulation in a tiny $2\xi \simeq 16 \text{ \AA}$ region around the impurity. Consistently with this result, this damping length can be estimated at $\xi \simeq 9 \text{ \AA}$ from $\xi^{-1} \simeq \ell^{-1} + \xi_0^{-1}$, where $\xi_0 = \hbar v_F / \Delta \simeq 13 \text{ \AA}$ is the electronic coherence length [11], and $\ell = 27 \text{ \AA}$ is the average distance between V substituents along the chains. At larger distances, the CDW dominates the charge oscillation. However, the CDW-phase extrapolated at the impurity site is $\varphi_0 \sim 0$, as indicated by the dotted line. This description is consistent with the strong pinning picture as proposed in refs. [16]. In addition, the region of mismatch between the CDW and the FO corresponds to the $q \simeq \xi^{-1}$ wave vectors, which indicates that the whole $\pm 2\mathbf{k}_F$ profiles contain also information on this important crossover region. Finally, let us point out that these $\pm 2\mathbf{k}_F$ - asymmetric profiles, which clearly depends on FOs, CDWs and their interferences, are of great importance for the understanding of the sliding of CDWs and open a unique access to the properties of CDW at both microscopic (FO) and mesoscopic pinning) scales.

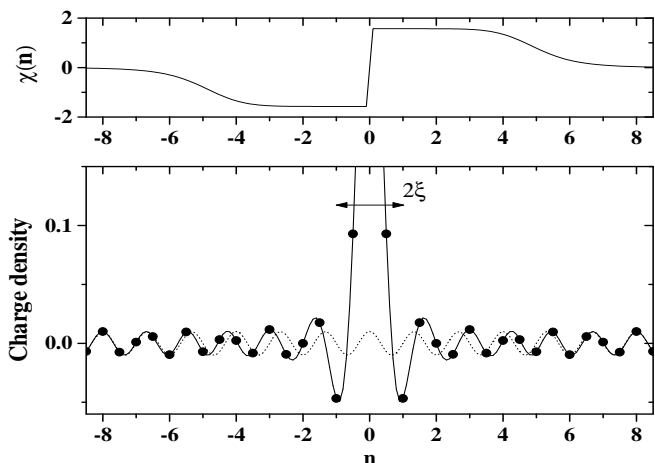


FIG. 5. Bottom : sketch of the oscillating part of the hole charge density around an impurity placed at the origin, as a function of the cell index n . Circles represent the Mo atoms. Top : Phase $\chi(x = nb)$ of this charge density, in radian.

The conclusion of this study is the evidence of Friedel oscillations in the vicinity of vanadium atoms in V-doped blue bronze. The observation of intensity asymmetries provides evidence of a coherence between the impurity position and the CDW/FO. Moreover, the observation of the profile asymmetry clearly indicates the presence of phase distortions, corresponding to a local decrease of the electronic density. Additional experiments on crystal with different doping levels are planned in order to elucidate more quantitatively the microscopic features of the pinning of CDWs in low-dimensional materials. More generally, we have demonstrated how methods of

asymmetry analyses of the x-ray scattering allows one to study the subtle interplay between structural and electronic properties in disordered systems.

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