X-Ray Investigation of Charge-Density-Wave Pinning in Blue Bronze

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High-resolution x-ray diffraction has resolved the phase-coherence volume of the charge-density wave in electron-irradiated blue bronze. The coherence volume is 3.7×10^{8} Å^3 for defect density $n=0.034$ at.%. The coherence lengths decrease roughly as $n^{-0.4}$. Results are contrasted with various theories of pinning.

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Blue bronze ($K_{0.3}MoO_3$) undergoes a charge-density-wave (CDW) transition at 180 K.[1] Many of the unusual properties of the CDW state (most strikingly the existence of a threshold electric field for nonlinear conduction) are thought to be the result of pinning of the CDW phase by lattice imperfections.[2] The pinning is usually analyzed using the phenomenological model of Fukuyama and Lee,[3] and Lee and Rice.[4] In the limit of weak pinning, the CDW phase is determined by averaging over many pinning sites, and therefore the phase-coherence length L is much longer than the distance between pinning sites. In the strong-pinning limit, the phase is fixed by a single impurity; this is often interpreted to mean that L is equal to the distance between pinning sites.

The phase-coherence length in CDW materials has been determined primarily by indirect methods, for example, by analyzing the dependence of threshold field or dielectric constant on n.[2] Direct measurements using x-ray diffraction have been hindered by the exceedingly long coherence length along the chain direction.[5,6] The coherence length is shorter in doped or irradiated samples. Using irradiation, a complete characterization of the phase-coherence length was accomplished in the organic CDW compound TMTSF-DMTCNQ.[7] In inorganic CDW materials, direct measurements have been limited to two pinning-site densities and to two directions.[8,9] Here we report the first full determination of L in an inorganic CDW compound, including both its dependence on n and its anisotropy.

High-resolution x-ray diffraction was performed on crystals of blue bronze into which controlled densities of pinning sites were introduced by electron irradiation. Previous measurements of the electrical properties indicated that electron irradiation creates strong-pinning sites.[10] Our results are consistent with neither the standard model of strong pinning (S') nor with the standard model of weak pinning (W), but may be consistent with the modified version of strong pinning (S) by Abe[11] and further developed by Tucker and co-workers.[12]

Irradiation of the samples with 2.5-MeV electrons created pinning sites in the form of point defects with concentration proportional to dose. To inhibit annealing of the defects, the samples were stored in liquid nitrogen as much as possible between the time of the room-temperature irradiation and that of the diffraction measurements. For 2.5-MeV electrons, Mutka *et al.* determined that a dose of 1 mC/cm^2 creates 10^{-5} magnetic defects per Mo; they then argued that the fraction of Mo displacements should have the same order of magnitude.[10]

X-ray measurements were carried out at the National Synchrotron Light Source at Brookhaven National Laboratory. The wavelength was 0.9392 Å. The lattice and CDW reflections were chosen to nearly match the scattering wave vector of Si(111). The monochromator and analyzer, both Si(111), were then oriented in (nearly) nondispersive mode to realize high resolution in radial scans.[13] Using a separate silicon crystal, the radial resolution was determined to be 6×10^{-4} Å^{-1}. Each sample was cooled to 15 K in a closed-cycle helium refrigerator, and three CDW satellite peaks were examined: $(5,q_b,-2.5)$, $(1,2+q_b,-0.5)$, and $(2,q_b-1,1.5)$, where q_b is close to 0.75.[14] Radial scans through these peaks are approximately along $2\mathbf{a}^*-\mathbf{c}^*$, $\mathbf{b}^*$, and $2\mathbf{a}+\mathbf{c}$, respectively, allowing measurement of the coherence lengths along three nearly perpendicular directions.

It can be shown that the width of the CDW satellite peaks is, in principle, inversely proportional to the CDW phase-coherence length.[5] In practice, the measured peak is a convolution of the instrumental-resolution function and the intrinsic shape due to the CDW. The lattice peaks were found to be resolution limited and therefore were used as an estimate of the resolution in determining the intrinsic CDW width. The observed line shapes of both the satellite peaks and the lattice peaks were described better by Lorentzian-squared form than by Lorentzian or Gaussian forms. Therefore, the intrinsic width was determined by deconvoluting two Lorentzian-squared peaks, one having the width of the observed satellite peak and the other the width of a nearby lattice

peak.

The CDW satellite-peak width, the width of a nearby lattice peak, and the deconvoluted width, along each of the three directions, are plotted in Fig. 1 as functions of pinning-site density. Absolute errors in the widths are estimated to be on the order of 10%. The lattice widths are independent of n. The deconvoluted width is largest along $2\mathbf{a}^* - \mathbf{c}^*$ and smallest along $\mathbf{b}^*$. This makes sense physically because $2\mathbf{a}^* - \mathbf{c}^*$ is the direction between the cleavage planes and is expected to have the weakest coupling, while $\mathbf{b}^*$ is the chain direction and is expected to have the strongest coupling. Results for broadening of the CDW peak along $2\mathbf{a}^* - \mathbf{c}^*$ agree with our preliminary investigation.[15] Furthermore, the deconvoluted width increases with n along all three directions. Broadening can be discerned along $\mathbf{b}^*$ only at the highest doses; the data are inadequate to determine a functional form. For the other two directions, the relationship appears to be a power law with deconvoluted width proportional to n^{α}. Along $2\mathbf{a}^* - \mathbf{c}^*$, $\alpha = 0.44 \pm 0.04$; along $\mathbf{a} + 2\mathbf{c}$, $\alpha = 0.37 \pm 0.07$.

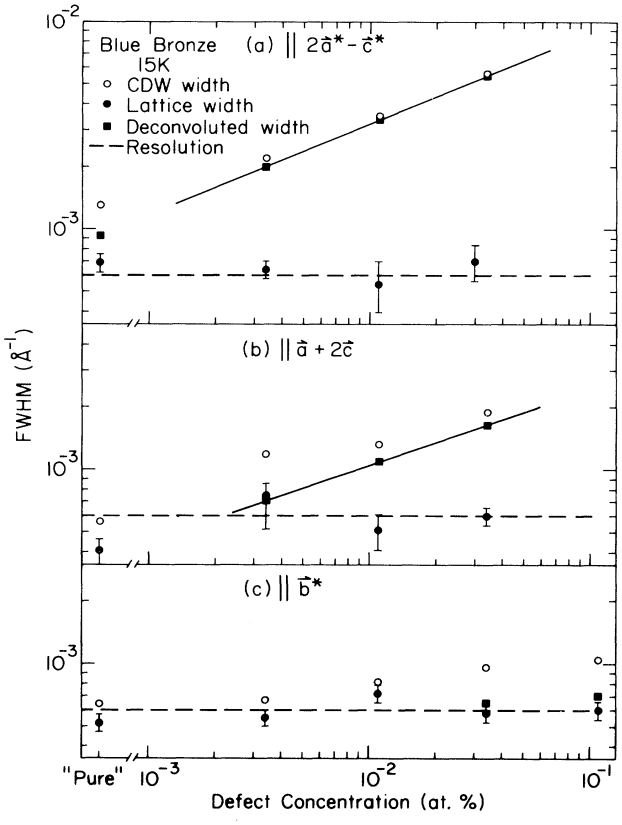

FIG. 1. CDW satellite peak widths, widths of nearby lattice peaks, and deconvoluted widths vs defect concentration. Widths are given as full widths at half maximum (FWHM). The CDW and lattice peaks are (a) (5,0.75, −2.5) and (4,0, −2), (b) (2, −0.25,1.5) and (2,0,1), and (c) (1,2.75, −0.5) and (0,2,0). The resolution is shown as a dashed line. The defect concentration was determined using the conversion factor from Ref. 10.

We take the phase-coherence length L to be 1.28/FWHM.[16,17] For $n = 0.034$ at.% Mo displacements, the coherence lengths are 240, 780, and 2000 Å along $2\mathbf{a}^* - \mathbf{c}^*$, $2\mathbf{a} + \mathbf{c}$, and $\mathbf{b}^*$, respectively. The corresponding coherence volume is $V_{\mathrm{coh}} = 3.7 \times 10^8$ Å^3, containing roughly 2100 displaced Mo atoms. Similarly, we can estimate the size of the coherence volume for the nominally pure sample. The CDW peak is broadened in the $2\mathbf{a}^* - \mathbf{c}^*$ direction even in the pure sample, with a corresponding coherence length of 1400 Å. The CDW widths in the other two directions are resolution limited so that the coherence length along $\mathbf{b}^*$ and $\mathbf{a} + 2\mathbf{c}$ is at least 2100 Å. The coherence volume then has a lower bound of 6.2×10^9 Å^3. According to Fig. 1(a), the nominally pure sample has the same width as a sample containing several ppm of displaced Mo atoms. Therefore, there are at least 500 displaced Mo atoms per coherence volume. Furthermore, if the coherence lengths fall in the same ratio in the unirradiated sample as they do for 0.034 at.%, the corresponding volume is 7.4×10^{10} Å^3 and contains 6000 displaced Mo atoms. Thus the number of defects per coherence volume appears to be large and is roughly independent of defect density.

The characteristic lengths of amplitude and phase variations in blue bronze appear to have similar degrees of anisotropy. The ratio of the amplitude-correlation lengths ξ_i in the three directions may be estimated from that of the electrical conductivities σ_i in a highly anisotropic metallic phase to be $\sigma_i/\sigma_j = (t_i a_i / t_j a_j)^2 = (\xi_i/\xi_j)^2$, where t_i is the hopping integral for the ith direction and a_i is the corresponding lattice constant.[18,19] Therefore, we estimate the ratio of the amplitude-correlation lengths to be roughly 1:4.2:24. The corresponding anisotropy of the phase-coherence lengths L_i in the three directions is 1:3.3:8.3 for $n = 0.034$ at.%.

To appreciate the significance of the results of this experiment, let us begin by making the usual assumption that each displaced Mo creates one pinning site. Whereas the correlation length is at least 10 times larger than a lattice constant, even along the transverse directions, the results should be analyzed using three-dimensional models. In the conventional picture of strong pinning, S', the phase-coherent volume contains of order one pinning site, and thus the exponent describing the dependence of L on n, $L \propto n^{-\alpha}$, is $\alpha = \frac{1}{3}$. While our results could be consistent with this exponent within our uncertainty, S' is ruled out by the enormous number of pinning sites per coherence volume. On the other hand, the number of pinning sites is consistent with weak pinning, W, but according to the standard W model, $\alpha = 1$ in three dimensions.[4] Therefore, W is also ruled out. The observed behavior seems to be a hybrid, with a power law like S', but the number of pins like W.

Thus our results are inconsistent with simple expectations. The discrepancy suggests either that the expectations are wrong (see below) or that we have incorrectly estimated the density of pinning sites. We have assumed that one pinning site is produced by each displaced Mo. One could suppose instead that only a fraction of displaced Mo atoms are effective as pinning centers. If only one in a thousand damaged sites is effective, then the number of pins per coherence volume would be of order 1 and roughly independent of dose, in accordance with expectations of S'. The problem then becomes one of explaining why some displaced Mo act differently from others. One might postulate, for example, that to be effective as a pinning site, a point defect must be associated with a dislocation.

The value of n would also be misestimated if the effective pinning sites are associated with defect clusters rather than single defects, in which case the density of pins would depend superlinearly on dose. Consequently, the number of pins per coherence volume would increase with dose, ruling out S' (except possibly at one particular dose). Moreover, the threshold field, which depends linearly (quadratically) on pin density for S' (W), should increase strongly superlinearly with dose, in disagreement with experiment.[10]

On the other hand, the discrepancy could be attributed to inadequacy of the conventional picture of strong pinning. While remaining within the Lee-Rice framework, Abe has pointed out that, because of three-dimensional coupling, phase distortions near each strong-pinning site will be confined to a small volume, of order the amplitude-correlation volume.[11] Tucker and co-workers have considered the behavior of the background phase in the regions between such strong-pin-influenced volumes, concluding that the background phase will remain coherent over many pinnning sites.[12] Therefore, the large number of pinning sites in the phase-coherence volume $V_{\rm coh}$ is consistent with this modified theory of strong pinning, S. Unfortunately, the dependence of L on n for the *static* CDW phase has not been worked out in this model. Nonetheless, we find the measured value of the exponent α surprising. Unless the pinning is infinitely strong, the energy of a pin depends on the difference between the phase at the pin and the background phase. Thus one might expect variations in the background phase to arise from random fluctuations in locations of the pins, as happens in weak pinning, giving $\alpha=1$. Our results clearly disagree with this expectation. Tucker and co-workers have considered the *dynamical* phase coherence in the modified version of strong pinning and find two length scales $\bar{L}$ and $L_{\rm min}$, which are the coherence lengths along the chain direction and transverse to the chain direction, respectively.[12] $\bar{L} \propto n^{-1}$, while $L_{\rm min} \propto n^{-1/3}$. Our results in Figs. 1(a) and 1(b) could be consistent with their prediction for $L_{\rm min}$. While Fig. 1(c) does not support the prediction for $\bar{L}$, we are reluctant to say conclusively that our results contradict their prediction on the basis of only two concentrations of pins.

The situation seems to be clearer for weak pins. Sweetland *et al.*[20] recently reported an x-ray diffraction measurement on a weakly pinned system, Ta-doped $NbSe_3$. They found a large number of pinning sites per coherence volume, and their results (deduced from two concentrations of pins) appear to be consistent with $\alpha=1$. Both results agree with the standard W model.

In conclusion, we emphasize the discrepancy between our results and CDW theory. In electron-irradiated, nominally strong-pinned blue bronze, the phase-coherence volume is quite large. Assuming that each electron-displaced Mo produces one pinning site, the phase-coherence volume contains many pinning sites, as would be expected for *weak* pins, yet the dependence of the size of the coherence volume on the pin density cannot be explained by applying simple weak-pinning arguments to the background phase. Whether the discrepancies are due to incorrect identification of the pinning entities or to inadequate analysis of the Lee-Rice theory, these results indicate a serious shortcoming in the present state of understanding of CDW pinning.

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