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Search for charge-density waves in a single crystal of potassium

Hoydoo You and J. D. Axe
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

Dietmar Hohlwein* and J. B. Hastings
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973
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We have searched for charge-density-wave (CDW) satellites in a single crystal of potassium at 10 K using synchrotron x rays. The satellite positions reported by Giebultowicz, Overhauser, and Werner were studied at a sensitivity of 10^{-7} of the (110) Bragg peak. No CDW satellites were observed, thereby setting an upper limit on the combination of width and intensity within the reciprocal space probed in this study.

There is great interest in the description of the conduction electrons in the alkali metals. While the nearly-free-electron (NFE) description is generally accepted,[1] Overhauser and his co-workers[2] suggest an alternative charge-density-wave (CDW) description. A direct consequence of the CDW model is a periodic incommensurate distortion of the ion-core lattice not present in the NFE description. Diffraction experiments showing weak CDW satellites[3-5] around a Bragg reflection would be strong evidence of a CDW. Since Overhauser's initial suggestion,[3] several experiments[6,7] have been performed to search for the satellites based on these predictions with no success. Recently, however, Giebultowicz, Overhauser, and Werner[8] reported the observation of CDW satellites in a neutron-diffraction study of single-crystal potassium. Since the discovery would have a profound effect on the fundamental description of simple metals, we sought, using the increased resolution possible in a synchrotron x-ray diffraction study, to explore satellites not accessible to neutron scattering experiments.

The observed CDW wave vectors from the neutron studies are (0.995, 0.975, ± 0.015) and (0.975, 0.995, ± 0.015) in the units of $a^* = b^* = c^* = 1.2$ Å^{-1}. Based on this observation, Overhauser calculated[9] 48 expected satellite positions corresponding to the 24 possible CDW domains. He also calculated the relative intensities based on the known elastic constants for potassium. Figure 1(a) shows the entire pattern of all 24 Q domains near (110) projected onto the $hk0$ plane. The calculated intensities show that due to the polarization of the CDW modulation some satellites (open circles) are zero or weaker by an order of magnitude than others (circled letters).[9] Because of the relatively low resolution of the neutron-diffraction study[8] only satellites marked by A–D, among the strong ones, could be studied. The satellite intensity, 1.5×10^{-5} of (110) Bragg peak,[8] was reported to be in good agreement with the predicted intensity[4] and the widths of the satellites and the (110) Bragg peak were resolution limited.

The potassium crystals, used in the present study, were grown as droplets from commercially available 99.95% pure molten potassium[10] in dry, warm mineral oil.[11] The sample crystal, a 2-mm sphere with a mosaic of 0.05°, was selected by Laue photographs. It was etched with diluted alcohol in a helium-filled dry box. It was then supported by gravity on a thin, dry mylar cone inside a Be can and mounted on a closed-cycle helium refrigerator (Displex). The present experiments were performed on a triple-axis, four-circle spectrometer with horizontal diffraction geometry at Beam line $X22$, at the National Synchrotron Light Source. A Ge(220) monochromator crystal was used, providing unfocused radiation of 1.05 Å. The penetration depth of this radiation in the sample was ~0.3 mm.

Instrumental resolutions referred to in the text as high resolution (HR), medium resolution (MR), and low resolution (LR), were achieved using Ge(111), LiF(200), or no analyzer crystal, respectively. The half maximum intensity contours for (110) reflection of the sample measured with the three resolutions are schematically shown in Fig. 1(b). The resolution of the neutron study (NR)[8] is also shown for comparison. The vertical components for HR, MR, and LR contours were mainly determined by vertical slits of the instrument and were all $\sim 1.2 \times 10^{-2}$ Å^{-1}. The vertical NR is unknown. The HR scans and some of the LR scans were made in an approximate (111) zone, while the MR scans and some of the LR scans were made in a (001) zone.

HR scans, whose direction and coverage are shown by vertical arrows in Fig. 1(b) for a given satellite position, provided a sensitivity, defined as the square root of the background divided by the (110) intensity, of better than 10^{-7}. Since it was not possible to cover a large volume of reciprocal space due to the small size of HR contours [Fig. 1(b)], the HR scans were made around the reported[8] and calculated[9] satellite positions only. The reciprocal volume covered by HR scans at each satellite position is $0.7 \times 0.7 \times 1.2$ ($\times 10^{-6}$ Å^{-3}), which is substantially larger than the uncertainty of the satellite positions reported in the neutron study.[8] Scans were made around all 12 CDW domain positions [marked by letters in Fig. 1(a)] at one (110) Bragg peak. Additional scans were made at several CDW domains around (220), and a few domain positions at another (110) peak. In spite of the high sensitivity, no satellites were observed at these positions. In Fig. 2, one of the typical HR scans at a reported

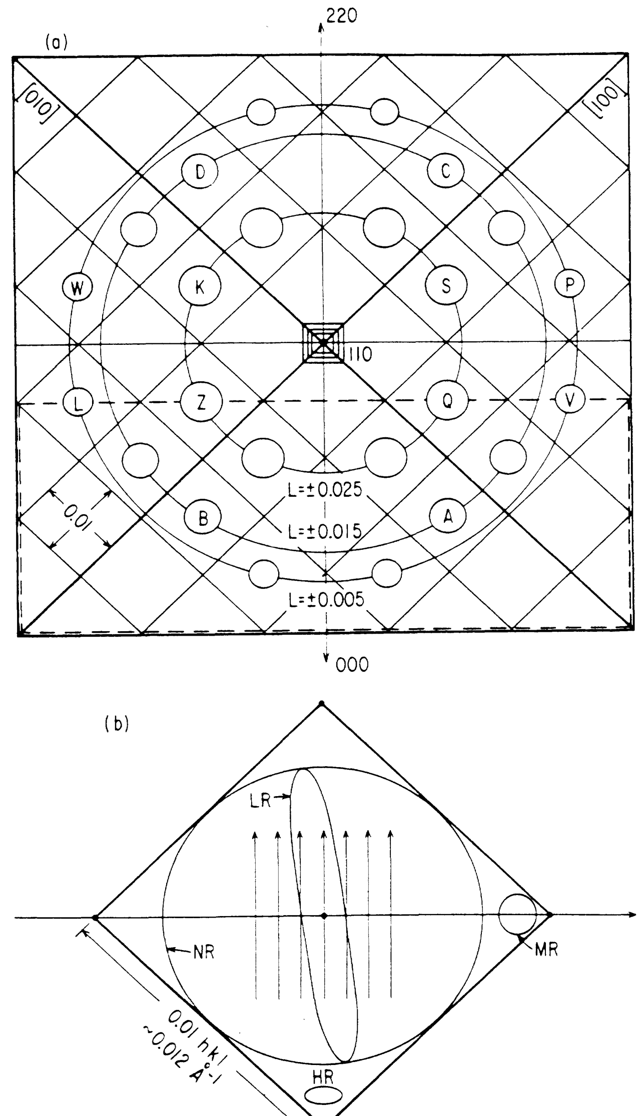

FIG. 1. (a) $(hk0)$ plane around (110). All the CDW satellites (small circles) are located on the surface of a sphere (big circles) around (110). The satellites on a same large circle have the same L value as specified. The MR mesh-scan area is shown by a large dashed rectangle. (b) One of the divisions in (a) is enlarged. The half-maximum contours of (110) reflection measured with HR, MR, LR, and NR are displayed for easy comparison. The vertical arrows indicate the HR scan coverage, and the horizontal arrow represents the LR scan direction.

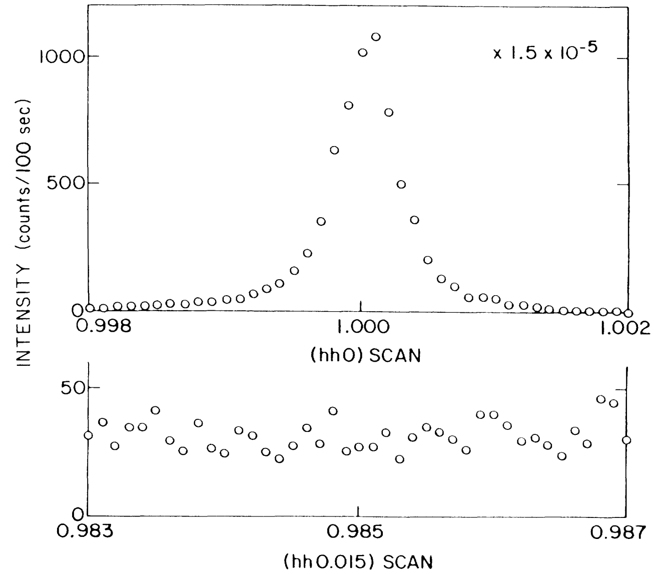

FIG. 2. One of the HR scans is compared with (110) reflection reduced by the factor of 1.5×10^{-5}.

satellite position[8] is compared with the HR scan of a (110) reflection reduced by a factor of 1.5×10^{-5} (the reported intensity ratio from the neutron study), which visually demonstrates the sensitivity of the HR scans.

In order to investigate the possibility of CDW satellites with widths broader than the (110) Bragg peak but comparable to the observed neutron results,[8] LR scans, providing higher sensitivity, were performed. The longitudinal (∥ to **Q**) size of the LR was adjusted by horizontal slits after the sample to be almost identical to the NR. The path of the LR scans, shown by a horizontal arrow in Fig. 1(b), results in a reciprocal volume coverage of $\sim 2.4\times1.2\times1.2$ ($\times10^{-6}$ Å^{-3}). LR scans for satellites $A-D$ and for others farther from the mosaic scattering of the nearby (110) Bragg peak provided sensitivities better than 10^{-6} even for satellites with the maximum width allowed by the neutron observations. The LR scans nearer to the mosaic line than the $A-D$ satellites suffered from very high background due to thermal diffuse scattering (TDS) and sometimes showed spurious peaks. One critical test made for the spurious features was searching for its inversion symmetric mate. None of the spurious features passed this test. One of the LR scans is presented in Fig. 3(a) with the best-fit Lorentzian curve. The Lorentzian tail was an excellent fit for the data as expected for TDS background.

To determine the detectability limits for the combination of integrated intensity (~CDW strength) and FWHM (~inverse CDW correlation length), 99.5% significance tests with a generalized R-factor (GRF) ratio[12] were made on the HR and LR data. The ratio of the GRF for a fit including a test satellite of the required intensity over that without it was tested against a 99.5%-significance F distribution.[12] The intrinsic three-dimensional widths of the test satellites (hence the correlation lengths) were assumed to be isotropic. When the width of a test satellite is larger than that of the resolution envelope, the integrated intensity was divided by the factor satellite volume divided by resolution volume before testing. The test results for various combinations of integrated intensity and width are summarized by solid curves HR X-RAY and LR X-RAY in Fig. 4. The horizontal width of the NEUTRON region is determined by the NR, the vertical width by a reasonable estimate of the random uncertainties in the satellite intensities reported.[8] The test for HR scans provides the lowest limit, 10^{-7} of the integrated (110) intensity, for the satellites with a full

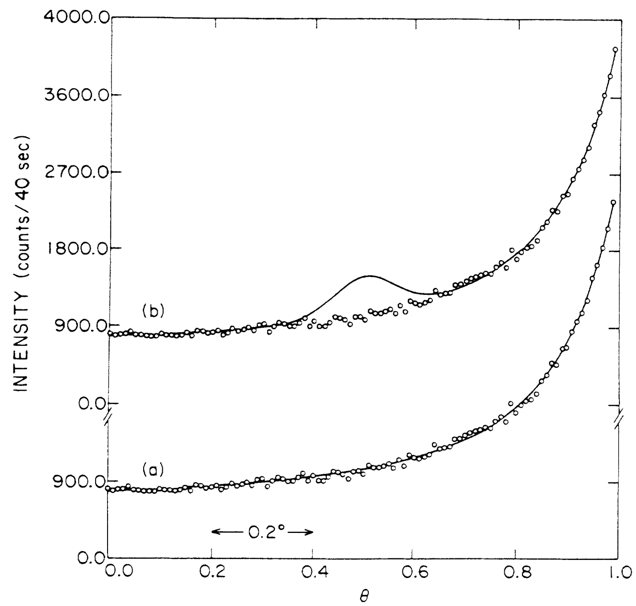

FIG. 3. (a) One of the LR scans is shown with the best Lorentzian fit. (b) A test satellite with the maximum width allowed by the neutron scattering study (marked by "+" in Fig. 4) plus the Lorentzian fit. The intensity of the test satellite is reduced by the ratio of satellite volume divided by resolution volume.

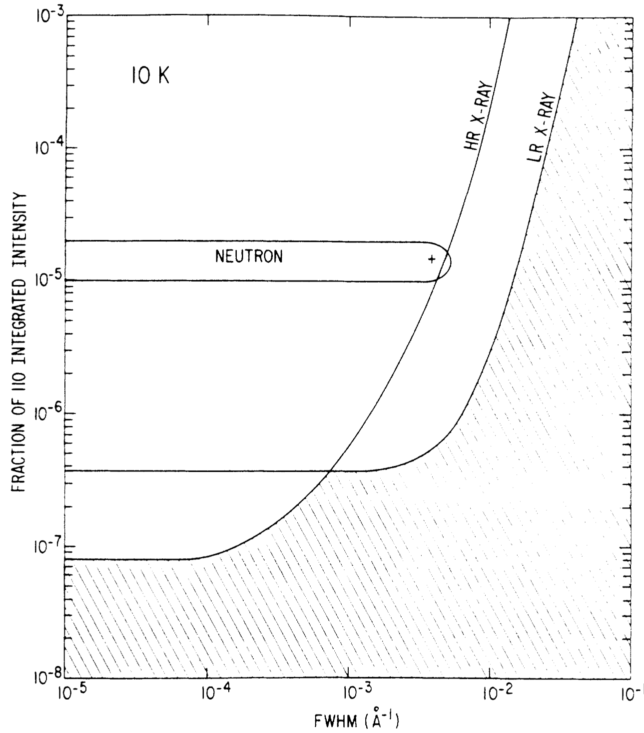

FIG. 4. Detectability diagram of our measurements. The area NEUTRON is the assumed confidence region of the neutron scattering study. The unshadowed region is rejected with the 99.5% significance test (see text for details).

width at half maximum (FWHM) smaller than 10^{-4} Å^{-1}. The test on LR scans rejects satellites as intense as the reported[8] satellites even when the width of the satellite is as broad as 1.2×10^{-2} Å^{-1}. [To see this, a Gaussian peak of $1\times10^{-5}\times(110)$ integrated intensity with a NR limited width of 4×10^{-3} Å^{-1} is superposed on the best fit of the LR scan in Fig. 3(b).] These tests show that the unshadowed area (Fig. 4) which includes the NEUTRON region is rejected with 99.5% significance by the HR and LR scans.

The region of reciprocal space was extended with MR scans that provided a relatively low background. The contour plot of the mesh-scan data over the range marked by the dashed rectangle of Fig. 1 [covered volume of $8.5\times3.4\times1.2$ ($\times10^{-6}$ Å^{-3}) at $L=0.015$] also showed no satellites. Smooth contours of the mesh-scan elongated along the mosaic line were similar to calculated[13] x-ray TDS contours. Aside from these, no contours higher than 1×10^{-6} of (110) intensity could be seen. The mesh-scan data were numerically convoluted with various assumed resolution envelopes to maximize the visibility of any possible broad satellites. No visible features with an intensity and FWHM within the unshadowed region of Fig. 4 were found.

In the above analysis only equally populated multiple-Q domains were considered. However, the chance production of single-Q-domain samples cannot be ruled out. To search for a possible single-Q domain, MR scans were used to cover all 24 CDW domains of the strongest intensity satellites, using two mutually perpendicular (110) reflections. Since the satellite intensity should be ~24 times larger than that of a multiple-Q-domain sample, long transverse MR scans passing through all the expected positions of the 24 domains should be able to detect them. None of these scans showed any feature that could be accounted for as a satellite.

One possible explanation for the discrepancy between the neutron and x-ray observations lies in extinction effects. Since extinction reduces the intensity of the strong Bragg reflections but not the weak satellites, the observed satellite-to-Bragg intensity ratio, given in Ref. 8, is an upper limit. If extinction effects were much more severe ($\times10$ or more) in the neutron scattering experiment than in the present x-ray experiment, the observed satellite would be weaker than originally claimed and might escape detection with x rays. However, estimates for extinction[14] for neutron and x rays on samples with comparable mosaic structure (as is observed) differ by a factor of only 2–3, which makes such an explanation unlikely.

In conclusion, the present study finds no evidence for CDW satellites at the reported positions of the neutron scattering study and sets upper limits at 10 K on the combination of integrated intensity and width at these and the other satellite positions predicted by Overhauser.[9]

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*Permanent address: Institute of Crystallography, University Tubingen, 74 Tubingen, West Germany.

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