Charge-density-wave satellite intensity in potassium

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The intensity of a charge-density-wave diffraction satellite in potassium is calculated. Velocity dependence of the exchange and correlation potential, which is responsible for the conduction-electron charge modulation, significantly affects the deduced value of the charge-density-wave amplitude. The amplitude of the periodic lattice displacement, which screens the electronic modulation, is reduced to a very small value, 0.03 Å, when the real charge distribution of a positive ion is recognized. A random $\vec{Q}$-domain structure can lead to a reduction by a factor of 24, compared to a single-$\vec{Q}$ specimen, of the satellite intensity. In such a case it is only 1.4×10^{-5} that of a crystallographic Bragg reflection. At temperatures above liquid helium, satellite intensity may be reduced further by phason excitations.

I. INTRODUCTION

The alkali metals, and in particular potassium, display a wide range of anomalous properties[1,2] which a normal electron-gas picture cannot account for. In order to find a comprehensive theoretical interpretation of experimental data it has been suggested[3] that the conduction electrons suffer a charge-density-wave (CDW) instability. Exchange and correlation potentials play a role of primary importance in the theory of such an instability. In this paper we will show that the nonlocal velocity dependence of exchange and correlation reduces significantly the observability of a CDW in a diffraction experiment.

The translational invariance of a crystal is broken by a CDW. In order to maintain microscopic charge neutrality the positive-ion lattice undergoes a small sinusoidal displacement. This can be observed directly. Two small diffraction satellites will appear[1,3] in reciprocal space for each reciprocal-lattice vector. Detection of these is the unequivocal signature of a CDW.

An early estimate of the intensity ratio of a CDW satellite to a Bragg reflection was about 1%.[3] This was based on a jellium model with a charge modulation of 17%, which corresponds to the suggested CDW energy gap of 0.6 eV for potassium. A unique orientation of the CDW wave vector $\vec{Q}$ throughout the sample was assumed.

Atoji and Werner[4] carried out a neutron scattering experiment on potassium at low temperature with a sensitivity of two parts in 10^4. They scanned high-symmetry directions with particular emphasis on the [110], which was expected to be the preferred orientation of the CDW.[1] No satellites were found.

In a recent paper[5] the authors developed a theory for the preferred orientation of the wave vector $\vec{Q}$. In the alkali metals anisotropy of the elastic stiffness is the determining factor. For potassium the optimum direction of $\vec{Q}$ is tilted about 4° away from a [110] direction. Although small, this tilt must be allowed for in a search for the satellites. Furthermore, the possibility of 24 different, but equivalent, orientations of $\vec{Q}$ would cut down the intensity of each satellite to 4×10^{-4}.

Motivated by the new information regarding the direction of $\vec{Q}$, Werner, Eckert, and Shirane[6] conducted a new search by neutron diffraction. Their experiment was sufficiently sensitive to detect satellites having an intensity 2×10^{-5} that of an ordinary Bragg reflection. None were found that could be attributed to a CDW.

The aim of this paper is to present an improved estimate for the intensity of a CDW peak in potassium. The result, Eq. (22), is unfortunately about a factor of 2 smaller than the minimum detectability of the Werner, Eckert, and Shirane experiment.

The satellite intensity depends on the amplitude of the charge-density modulation of the electron gas,[3] on the interaction between the electronic CDW and the lattice,[7] and also on the excitation spectrum[1] of the system. All of these factors contribute to the revised estimate.

The structure of the paper is as follows. In Sec. II the theory of the scattering intensity in a CDW system[1] is reviewed with particular emphasis on the role of CDW collective excitations. In Sec. III the ionic lattice distortion is examined. Section IV is devoted to the theory of the CDW

fractional amplitude; and a new evaluation of this quantity is reported. Finally, in Sec. V the CDW satellite intensity is calculated.

II. NEUTRON-SCATTERING ELASTIC INTENSITY

In a neutron experiment the wave-vector- and frequency-dependent diffracted intensity $I_{\vec{k},\omega}$ is proportional to the following dynamic structure factor[8]:

$$S_{\vec{k},\omega}=\frac{1}{N}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\sum_{ij}\langle e^{i\vec{k}\cdot\vec{R}_i(t)}e^{-i\vec{k}\cdot\vec{R}_j(0)}\rangle_T . \tag{1}$$

The indices i and j label the N atoms of the system, $\vec{R}_i(t)$ represents the position of the atom i at the time t, and an equilibrium thermal average is taken of the right-hand side.

In a CDW state the tendency towards microscopic charge neutrality causes the ionic lattice to undergo a distortion with respect to the ideal crystal. The new equilibrium positions of the ions of a single CDW state are given by

$$\vec{R}_i=\vec{R}_i^0+\delta\vec{R}_0\cos(\vec{Q}\cdot\vec{R}_i^0+\phi), \tag{2}$$

where $\vec{R}_i^0$ are the atomic sites of the original undistorted lattice, $\delta\vec{R}_0$ is the ground-state amplitude, $\vec{Q}$ the wave vector, and ϕ the phase of the distortion. Furthermore, the dynamics of $\vec{R}_i(t)$, the actual ionic positions, are related to the dynamics of the amplitude and the phase of the CDW.

A. Static CDW

We assume for the moment that both phase and amplitude degrees of freedom are frozen. In this case the dynamic structure factor reduces to a simple form:

$$S^{\mathrm{CDW}}_{\vec{k},\omega}=\frac{2\pi\delta(\omega)}{N}\left(\sum_i \exp[i\vec{k}\cdot(\vec{R}_i^0+\delta\vec{R}_0\cos\vec{Q}\cdot\vec{R}^0{}_i)]\right)^2 , \tag{3}$$

where for convenience ϕ has been set equal to zero. In the limit of zero amplitude the usual result for the undistorted lattice is readily recovered:

$$S^0_{\vec{k},\omega}=2\pi N\delta(\omega)\sum_{\vec{G}}\delta(\vec{k}-\vec{G}). \tag{4}$$

The allowed Bragg reflections are those with scattering vector equal to a reciprocal-lattice vector $\vec{G}$. For finite $\delta\vec{R}_0$ we can use in (3) the following formula[1]:

$$e^{iz\sin\alpha}=\sum_{n=-\infty}^{+\infty}e^{in\alpha}J_n(z), \tag{5}$$

where n is an integer and $J_n(z)$ a Bessel function of the first kind. $S_{\vec{k},\omega}$ can be rewritten now as

$$S^{\mathrm{CDW}}_{\vec{k},\omega}=2\pi N\delta(\omega)\sum_{n=-\infty}^{+\infty}\sum_{\vec{G}}\delta(\vec{k}-(\vec{G}+n\vec{Q}))\,J_n^2(\vec{k}\cdot\delta\vec{R}_0). \tag{6}$$

Notice that the new relevant feature of the diffraction pattern is that satellite spots appear at $\vec{k}=\vec{G}+n\vec{Q}$. As the amplitude $\delta\vec{R}_0$ of the distortion is expected to be small compared to the lattice spacing, and because the limiting behavior of Bessel functions is $J_n(x)\approx(\frac{1}{2}x)^n/n!$ for small x, each Bragg reflection will be surrounded by a sequence of weak satellite spots. Although in principle all the satellites are present, usually only the set with $n=1$ has sufficient intensity to be easily observed. Even though the magnitude of $\vec{Q}$ may be known[9] from the diameter of the Fermi surface, these first-order satellites may be hard to find if the direction of $\vec{Q}$ is unknown.

B. Dynamic excitations

For an incommensurate CDW, in the absence of any source of pinning, the phase ϕ is free to assume all possible values. This infinite degeneracy of the ground state results in the existence of a new branch of acoustic, collective modes called phasons.[1] These modes are associated with space and time variations of the variable ϕ of Eq. (2). Together with phase modulation the CDW may also experience amplitude modulation. Amplitude and phase modes occupy only a small portion of the wave-vector space associated with vibrational excitations of the system. The remaining degrees of freedom are the normal phonons. In the following discussion we will disregard these as they reduce the intensity of all diffraction peaks according to the ordinary Debye-Waller factor.

The inclusion of amplitude modes and phasons in the theory[1,10] gives for $S^{\mathrm{CDW}}_{\vec{k},\omega}$:

$$S^{\mathrm{CDW}}_{\vec{k},\omega}=2\pi N\delta(\omega)\sum_{n=-\infty}^{+\infty}\sum_{\vec{G}}\delta(\vec{k}-(\vec{G}+n\vec{Q}))\,J_n^2(\vec{k}\cdot\delta\vec{R}_0)\exp[-2n^2w_\phi+2|n|(|n|-1)w_A]+\cdots , \tag{7}$$

where the ellipsis represents inelastic terms, which contain the contribution associated with emission and absorption of phasons and amplitude modes. The factors containing w_A and w_ϕ are the amplitude and the phason temperature factors.[1,10,11] They are the analogue of the Debye-

Waller factor for an ordinary Bragg reflection. w_A and w_ϕ are proportional to the mean-square fluctuation of the amplitude $|\delta\vec{R}|$ and the phase ϕ of the CDW.

We notice here that the normal Bragg reflection ($n=0$) are unaffected by phase and amplitude fluctuations. Furthermore the latter do not alter the intensity of the first satellite spots ($n=\pm1$).

C. Domain structure

In a recent paper[5] the authors have derived the preferred orientation of the wave vector $\vec{Q}$ of a CDW in alkali metals. Since $\vec{Q}$ is not along a symmetry axis or in a symmetry plane, all 24 cubically equivalent axes will be equally favored. In the absence of uniaxial stress, which could split this 24-fold degeneracy, a single-crystal sample will, in general, be divided into $\vec{Q}$ domains[1,2] having $\vec{Q}$'s aligned without preference along all allowed directions. This will reduce the intensity of a specific satellite spot by a factor of 24 compared to the intensity it would have if the sample were single $\vec{Q}$.

However, a compensating advantage is that each crystallographic Bragg reflection will be surrounded by 48 CDW satellites. One need not scan along all 24 axes to be sure of finding a satellite.

III. LATTICE DISTORTION

The electronic charge of a CDW can be written as[3]

$$\rho(\vec{r}) = -en(1 + p\cos\vec{Q}\cdot\vec{r}), \tag{8}$$

where n is the average electron density, and p is the fractional amplitude of the modulation. Such an electronic state can be energetically more favorable than the usual undistorted homogeneous state provided the underlying positive background is sufficiently deformable to allow microscopic cancellation of the charge modulation. Otherwise a positive electrostatic energy would dominate the energy.[3]

An analysis[7] of this phenomenon was carried out. It was found that for the alkali metals the screening of the CDW is about 99.9%. The theoretical amplitude $|\delta\vec{R}_0|$ of the periodic lattice distortion is $\simeq$0.03 Å. A particularly relevant quantity is $\delta\vec{R}_0\cdot\vec{Q}$. Equations (3.6), (3.16), and (3.17) of Ref. 7 lead to

$$|\delta\vec{R}_0\cdot\vec{Q}| = p/\rho_{\vec{Q}}, \tag{9}$$

where p is the CDW fractional amplitude defined above. $\rho_{\vec{Q}}$ is the $\vec{Q}$ component of the ionic charge distribution.[12,5] Since the wavelength of the CDW is small ($\simeq$4 Å in potassium), an assumption of pointlike ions is unjustified. Incorporation of the ionic form factor takes account of the finite size. For potassium $\rho_{\vec{Q}}$ is easily estimated from available values of the x-ray form factor, $\rho_{el}(\vec{p})$,[13] for a single K^+ ion. We have found

$$\rho_{\vec{Q}} = 19 - \rho_{el}(\vec{Q}) \simeq 2.92\,. \tag{10}$$

This result will be employed with Eqs. (6) and (9) when the satellite intensity is estimated in Sec. V.

IV. CDW FRACTIONAL AMPLITUDE IN POTASSIUM

An *a priori* theory of the CDW fractional amplitude p could only come from an exact solution of the electronic many-body problem, which is not at hand. So we will rely on a semiempirical calculation to obtain an estimate of this important parameter.[3,14]

Consider an electron gas embedded in a neutralizing, perfectly deformable jelly and modulated by a single-CDW ground state of wave vector $\vec{Q}$. Each electron is acted upon by a periodic potential which self-consistently sustains the charge modulation. Since any electrostatic (Hartree) field is assumed to be exactly cancelled by an equal modulation of the positive background,[15] this periodic potential originates from exchange and correlation effects.[3]

The periodic potential is proportional to $\cos\vec{Q}\cdot\vec{r}$, so each one-electron state $\vec{k}$ is mixed with $\vec{k}\pm\vec{Q}$. This causes the charge modulation, and produces a gap Δ (in the single-particle spectrum) on planes perpendicular to $\vec{Q}$ through the points $\pm\vec{Q}/2$. Furthermore, when Δ is small compared to the Fermi energy ϵ_F, the periodic potential can be treated as a perturbation. The free-electron plane waves, which we take as our basis functions, become amplitude modulated. The fractional amplitude p of the CDW is just the Fermi-sea average of this modulation.

A. Local theory

The simplest choice for the exchange and correlation potential is:

$$V^{xc}(\vec{r}) = -\Delta\cos\vec{Q}\cdot\vec{r}\,, \tag{11}$$

where Δ is independent of $\vec{k}$. The perturbed wave functions are to first order,[17]

$$\Psi_{\vec{k}} \simeq e^{i\vec{k}\cdot\vec{r}}\left(1 - \frac{\Delta}{2\omega_+}e^{i\vec{Q}\cdot\vec{r}} - \frac{\Delta}{2\omega_-}e^{-i\vec{Q}\cdot\vec{r}}\right), \tag{12}$$

where the denominators are defined in terms of the free-electron energies, $\vec{E}_k = h^2k^2/2m$.

$$\omega_\pm \equiv E_{\vec{k}} - E_{\vec{k}\pm\vec{Q}}\,. \tag{13}$$

We average $|\Psi_{\vec{k}}|^2$ over the occupied states of the Fermi sphere to obtain the charge modulation amplitude defined by Eq. (8) (Ref. 3):

$$p_L = \left(\frac{3\Delta}{4\epsilon_F}\right)\left(1+\frac{1-u^2}{2u}\,lu\left|\frac{1+u}{1-u}\right|\right), \tag{14}$$

where $u = |\vec{Q}|/2k_F$.

The typical values for potassium are $\Delta/4\epsilon_F \simeq 0.07$ and $|\vec{Q}|/k_F \simeq 1+\Delta/4\epsilon_F \simeq 1.07$.[9,3] In this case Eq. (14) gives[3]

$$p_L \simeq 0.17. \tag{15}$$

B. Nonlocal theory

As already pointed out by one of the authors,[14] in a nonuniform electron gas the periodic part of the exchange operator connecting the electronic states $\vec{k}$ and $\vec{k}+\vec{Q}$, is extremely nonlocal; i.e., it has, for fixed $\vec{Q}$, a dramatic dependence upon $\vec{k}$. When correlation effects are accounted for,[16] this dependence is reduced but still remains pronounced. A correct theory of the exchange and correlation periodic potential for a CDW must allow for this nonlocality. A straightforward generalization of the exchange and correlation potential $V^{xc}(\vec{r})$ which allows for this is,

$$V^{xc}_{CDW}(\vec{r}) = -\tfrac{1}{2}\left[\Delta^{+}(\vec{k})e^{i\vec{Q}\cdot\vec{r}} + \Delta^{-}(\vec{k})e^{-i\vec{Q}\cdot\vec{r}}\right]. \tag{16}$$

$\Delta^{\pm}(\vec{k})$ is a function of the electronic state. These functions have been calculated by Duff and Overhauser[16] using the "plasmon" model.[18]

For the case $|\vec{Q}| \simeq 2k_F$, their results can be summarized as follows: $\Delta(\vec{k})$ is a smooth function of $\vec{k}$; furthermore if $\Delta(\vec{k})$ is equal to Δ at $\vec{k} = -\frac{1}{2}\vec{Q}$, then $\Delta(0) \simeq 0.5\Delta$, $\Delta(\frac{1}{2}\vec{Q}) \simeq 0.36\Delta$. Furthermore $\Delta(\vec{k})$ is practically independent of the component of $\vec{k}$ perpendicular to $\vec{Q}$.

A simple, smooth function with these properties is

$$\Delta^{+}(\vec{k}) = \Delta\left[1+0.55\left(\frac{k_z}{Q}+\frac{1}{2}\right)-0.03\left(\frac{k_z}{Q}+\frac{1}{2}\right)^2\right]^{-1},$$
$$\Delta^{-}(\vec{k}) = \Delta^{+}(-\vec{k}), \tag{17}$$

where k_z is measured along $\vec{Q}$. Then the perturbed wave functions are given as before by Eq. (12), but now Δ is dependent on $\vec{k}$. A numerical calculation gives for the nonlocal value of p, using again a spherical Fermi surface,

$$p_{NL} \simeq 0.10. \tag{18}$$

In order to take into account the effect of Fermi-surface distortion caused by the CDW we have repeated the calculation with the distorted Fermi surface given by Bishop and Overhauser,[19] where it is assumed that the Fermi surface touches the gap plane in a single point.[9] The fractional modulation is increased slightly by this improvement. Our final value is

$$p_{NL} \simeq 0.11. \tag{19}$$

V. RESULTS

In a neutron-diffraction experiment on a CDW system a quantity of interest is the intensity ratio of a satellite spot to a normal Bragg reflection. With the use of Eq. (7) we obtain the following result:

$$\frac{I_{\vec{G}+n\vec{Q}}}{I_{\vec{G}}} = \frac{1}{D}\left(\frac{J_n(\delta\vec{R}_0\cdot(\vec{G}+n\vec{Q}))}{J_0(\delta(\vec{R}_0))}\right)^2 \times \exp[-2n^2w_\phi + 2|n|(|n|-1)w_A]. \tag{20}$$

D is the $\vec{Q}$-domain degeneracy (unity for a single-domain sample).

The most intense satellite spots have $n = \pm 1$. The scattering vectors are then $\vec{G}\pm\vec{Q}$. For small CDW amplitude we can use in (20) the limiting behavior of the Bessel functions, i.e., $J_1(x) \simeq x/2$ and $J_0(x) \simeq 1$. It follows that a satellite's intensity is proportional to $|\vec{G}\pm\vec{Q}|^2$. This suggests that satellites of large reciprocal-lattice vectors, $\vec{G}$, will be easier to observe. The problem, however, is to find a small satellite in a thermal diffuse background, which also increases in intensity as the square of the scattering vector. For potassium the CDW satellites are expected to be very close (in $\vec{k}$ space) to reciprocal-lattice vectors. The requirements on angular resolution to separate them become severe if satellites of large $\vec{G}\pm\vec{Q}$ are selected for study. The optimum satellite to search for will depend on experimental resolution and available flux.

For purposes of illustration we shall evaluate Eq. (20) for the CDW satellite at $\vec{k} = \vec{Q}$ for potassium. Equations (9) and (20) imply:

$$\frac{I_{\vec{G}}}{I_{\vec{G}(110)}} \simeq \frac{1}{24}\left(\frac{p}{2\rho_{\vec{Q}}}\right)^2 e^{-2w_\phi}, \tag{21}$$

where p is the fractional modulation given by (19). The factor D has been taken to be 24 on account of the degeneracy of equivalent $\vec{Q}$-domain orientations.[5] If we disregard the phason temperature factor as seems justified in a 4 K experiment and use the values (10) and (19) to obtain $I_{\vec{Q}}$, we find

$$I_{\vec{Q}} \simeq 1.4\times10^{-5} I_{\vec{G}(110)}. \tag{22}$$

We believe that any future experimental search for CDW satellites in potassium should have a sensitivity consistent with this result.

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