Wave-vector orientation of a charge-density wave in potassium

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(Received 23 March 1979)

A criterion for the preferred direction of the wave vector $\vec{Q}$ of a charge-density wave (CDW) is obtained by means of a simple theory. Screening of the electric field caused by the CDW is provided by a sinusoidal distortion of the positive-ion lattice. The optimum $\vec{Q}$ direction is that which minimizes the elastic energy of distortion. For potassium the $\vec{Q}$ direction is found to be tilted about 4° away from a [110] direction. The exact value of the tilt depends on the magnitude of $\vec{Q}$.

I. INTRODUCTION

The concept of a charge-density-wave (CDW) state for electronic systems was introduced many years ago by Overhauser,[1] but only recently has this kind of non-normal electronic state been observed. (Spin-density-wave states,[2] which are similar, were discovered much sooner.) In suitable quasi-two-dimensional[3] electronic systems direct observation of the typical signature of a CDW state, i.e., the superlattice structure, has been achieved by means of x-ray, electron, and neutron scattering experiments: the existence of satellite spots surrounding the usual Bragg reflections.[4,5] Very recently evidence has also been found in three-dimensional systems.[6] Furthermore, as has been extensively discussed,[7] the alkali metals, and particularly potassium, can for many reasons be expected to suffer a CDW instability. A complete clarification of this important and basic problem is needed.

Ten years ago a neutron scattering experiment on a potassium single-crystal sample was reported[8] in which no evidence for CDW satellites was found. Only high-symmetry directions, and in particular the [110] direction, were scanned. A [110] direction is expected to be the preferred orientation for the CDW wave vector $\vec{Q}$.[4] The aim of this paper is to present a simple theory of the preferred $\vec{Q}$ orientation and to provide a prediction for the particular case of potassium. Unfortunately the previous search for CDW satellites did not include scans along what we now find to be the preferred directions in reciprocal space, which are tilted 4° from [110].[9]

II. SOURCES OF ANISOTROPY

We consider an ideal jellium model for the interacting gas of conduction electrons in a metal and assume the neutralizing positive background to be deformable without any stiffness. For this sytem it has been shown[1,2] that, in Hartree-Fock approximation, the normal state (plane-wave Slater determinant) is unstable with respect to both CDW and spin-density-wave (SDW) formation. Furthermore an argument has been presented[1] showing how the correlation corrections to this Hartree-Fock result tend to stabilize the CDW with respect to both normal and SDW states.

The electronic charge density in a CDW can be written

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

where n is the density of the electron gas, and p, $\vec{Q}$, and φ are the amplitude, wave vector, and phase of the charge distortion.[10] Such a structure for $\rho(\vec{r})$ lowers the exchange and correlation energy with respect to the uniform state. However, it could lead to a macroscopic energy penalty caused by the electrostatic field $\vec{E}_{CDW}$, proportional to p, which arises from the charge inhomogeneity. If $\rho(\vec{r})$ were not neutralized, then

$$\vec{E}_{CDW}(\vec{r}) = (4\pi nep\,\vec{Q}/Q^2)\sin\vec{Q}\cdot\vec{r} \ . \tag{2}$$

In this deformable jellium model the crucial point regarding the existence of a CDW state is that this energy penalty is absent because of energetically inexpensive deformations of the positive background. Accordingly, $\vec{E}_{CDW} \sim 0$. Furthermore the spherical symmetry of the problem allows $\vec{Q}$ to have any orientation.

In more complicated situations the spatial anisotropy of exchange and correlation together with anisotropic band structure (e.g., Fermi-surface nesting) can give rise to a preferred direction of $\vec{Q}$. If we allow for a nonzero stiffness of the positive background, the energy balance will be more complicated. We must take into account the elastic energy cost associated with the screening of $\vec{E}_{CDW}$, given by Eq. (2).

At this point we recall that in order to have a CDW ground state, a metal must be as soft as possible (elastically), and that is equivalent to having small

stiffness constants c_{ij}. Alkali metals satisfy this condition extremely well.[11,12] Furthermore their practically spherical Fermi surface suggests that elastic behavior may be the principal source of anisotropy in the problem. We shall proceed on the assumption that the $\vec{Q}$ orientation is determined only by the elastic anisotropy.[13]

III. GEOMETRICAL FACTORS

Consider now the specific problem of the $\vec{Q}$ orientation in potassium. In this case $\vec{Q}$ lies outside of the Brillouin zone (BZ), and $|\vec{Q}| \approx 1.33(2\pi/a)$,[14] where a is the lattice constant. It is easy to make an approximate choice for the wave vector $\vec{Q}'$ of the acoustic-phonon mode needed to screen the electric field, Eq. (2), of the CDW. Of course $\vec{Q}'$ must lie within the BZ, so $\vec{Q}' = \vec{G}_{lmn} - \vec{Q}$, where $\vec{G}_{lmn}$ is a reciprocal-lattice vector. From the fcc geometry of the reciprocal lattice it is easy to convince oneself[4] that the most energetically favorable condition for the acoustic-mode distortion is with $\vec{Q}$ along [110]. Then

$$|\vec{Q}'| = |\vec{G}_{110} - \vec{Q}| \approx 0.08(2\pi/a) \ .$$

If $\vec{Q}$ were parallel to a cubic axis, then

$$|\vec{Q}'| = |\vec{G}_{200} - \vec{Q}| \approx 0.67(2\pi/a) \ .$$

These acoustic modes have much higher frequencies than the former ones.

In Fig. 1 we show the geometrical relations for $\vec{Q}$ and $\vec{Q}'$ when $\vec{Q}$ is near to [110]: the angles θ and θ' describe the tilt of $\vec{Q}$ and $\vec{Q}'$ from [110]. Also shown are the heterodyne gaps associated with $\vec{Q}'$, which play an important role[15,16] in the physics of the induced-torque anomalies observed in potassium.[17] The important point is the following: if for some reason $\vec{Q}$ is *slightly* tilted away from [110] (and we will show this is the case) the orientation of $\vec{Q}'$ deviates from [110] by a large angle, as is clear from Fig. 1. The small value expected for $|\vec{Q}'|$ allows us to work out the theory in the long-wavelength approximation.

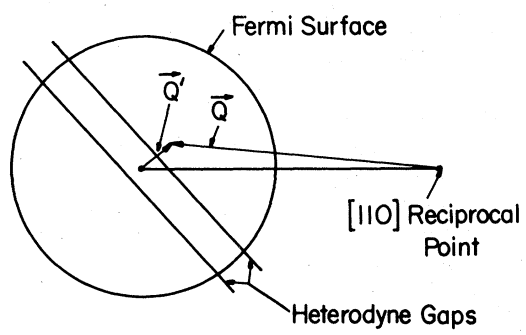

FIG. 1. Geometrical relation of $\vec{Q}, \vec{Q}'$, and $\vec{G}_{110}$. The heterodyne gaps arise from the $\vec{Q}'$ periodicity and can lead to open orbits in large magnetic fields. The main CDW energy gaps, which are perpendicular to $\vec{Q}$ and tangent to the Fermi surface, are not shown.

IV. ENERGY ANALYSIS

The elastic energy associated with the three acoustic modes of wave vector $\vec{Q}'$ is, for a monovalent metal of unit volume,

$$U_E = \tfrac{1}{4} nM \sum_{i=1}^{3} \omega_i^2 A_i^2 \ , \tag{3}$$

where M is the ionic mass, A_i is the amplitude of each (static) excitation, and ω_i is the frequency of the mode (were it allowed to oscillate). Equation (3) is the energy penalty which must be paid to screen out $\vec{E}_{\rm CDW}$. In order to determine how this is partitioned between the three polarizations we have to consider the interaction between the positive ions and the electrostatic potential $V_{\rm CDW}$ caused by the CDW. From Eq. (2),

$$V_{\rm CDW}(\vec{r}) = (4\pi nep/Q^2)\cos\vec{Q}\cdot\vec{r} \ . \tag{4}$$

Suppose $e\rho_I(\vec{r})$ is the charge density of each ion. Then the ionic charge density of the deformed lattice is

$$\rho(r) = \sum_{\vec{L}} e\rho_I\left(\vec{r} - \vec{L} - \sum_{i=1}^{3} A_i \vec{\epsilon}_i \sin\vec{Q}'\cdot\vec{L}\right) \ . \tag{5}$$

$\{\vec{L}\}$ are the lattice vectors, and $\{\vec{\epsilon}_i\}$ are the polarization vectors of the three acoustic modes of wave vector $\vec{Q}'$. The only interaction between Eqs. (4) and (5) will involve the Fourier components of wave vector $\pm\vec{Q}$. This is readily calculated from Eq. (5) if $QA_i \ll 1$,

$$\rho(\pm\vec{Q}) = \tfrac{1}{2} ne\rho_I(Q) \sum_{i=1}^{3} A_i |\vec{\epsilon}_i\cdot\vec{Q}| \ . \tag{6}$$

$\rho_I(Q)$ is the Fourier transform of $\rho_I(\vec{r})$, i.e., it is the ion (or pseudo-ion) form factor. Accordingly the interaction energy (per unit volume) is

$$U_{\rm int} = 2\pi pn^2 e^2 Q^{-2} \rho_I(Q) \sum_{i=1}^{3} A_i \vec{\epsilon}_i\cdot\vec{Q} \ . \tag{7}$$

Observe that the total energy, Eqs. (3) and (7), can be written

$$U = \sum_{i=1}^{3} (\alpha\omega_i^2 A_i^2 + 2\beta A_i \vec{\epsilon}_i\cdot\vec{Q}) \ , \tag{8}$$

where α and β are constants. Each of the three amplitudes, A_i, is obtained by minimizing U. The minimum energy is

$$U_{\rm min} = -\frac{\beta^2}{\alpha} \sum_{i=1}^{3} \left(\frac{\vec{\epsilon}_i\cdot\vec{Q}}{\omega_i}\right)^2 \ . \tag{9}$$

$\epsilon_i(\vec{Q}')$ and $\omega_i(\vec{Q}')$ are functions of the direction of $\vec{Q}$ because

$$\vec{Q}' = \vec{G}_{110} - \vec{Q} \ . \tag{10}$$

From Eq. (9) it is obvious that the optimum direction of $\vec{Q}$ is found by maximizing

$$S(\vec{Q}) \equiv \sum_{i=1}^{3} \left[\frac{\epsilon_i(\vec{Q}') \cdot \vec{Q}}{\omega_i(\vec{Q}')} \right]^2 \ . \tag{11}$$

V. RESULTS

As already mentioned in Sec. III, the smallness of $|\vec{Q}'|$ allows us to determine $\vec{\epsilon}_i$ and ω_i in the long-wavelength, acoustic limit. This means that we need to know only the three elastic (stiffness) modulii: c_{11}, c_{12}, and c_{44}. They are[12]: 4.16, 3.41, and 2.86×10^{10} dyn/cm^2 at 4 °K. $nM\omega_i^2$ and $\vec{\epsilon}_i$ are the eigenvalues and eigenvectors of the dynamical matrix

$$\begin{pmatrix} c_{11}x^2 + c_{44}(y^2+z^2) & (c_{12}+c_{44})xy & (c_{12}+c_{44})xz \\ (c_{12}+c_{44})xy & c_{11}y^2 + c_{44}(z^2+x^2) & (c_{12}+c_{44})yz \\ (c_{12}+c_{44})xz & (c_{12}+c_{44})yz & c_{11}z^2 + c_{44}(x^2+y^2) \end{pmatrix} , \tag{12}$$

where $\vec{Q}' \equiv (x,y,z)$. We have evaluated $S(\vec{Q})$ numerically for all directions of $\vec{Q}$ near [110]. Contours of $S(\theta,\varphi)/S(0,0)$ are shown in a polar plot in Fig. 2. The polar angle θ is the tilt angle of $\vec{Q}$ away from [110]. The azimuthal angle φ (rotation about the [110] polar axis) is 0 when $\vec{Q}$ lies in the (001) plane. The contours were computed from Eqs. (11) and (12) for $|\vec{Q}| = 1.33 \times (2\pi/a)$.

It is clear from Fig. 2 that the maximum value of $S(\theta,\varphi)$ is not at $\theta = \varphi = 0$. Instead, it is at $\theta = 4.1°$, $\varphi = 65.4°$. This implies that the angle between $\vec{Q}'$ and [110] is 47.3 °. It is surprising, perhaps, that the point $\theta = \varphi = 0$ is a local *minimum*, even though $|\vec{Q}'|$ here is as small as possible. The reason is that only the high-frequency longitudinal mode contributes to S for this direction. The physical reason why $\vec{Q}$ (and $\vec{Q}'$) are tilted away from [110] is that the low-frequency shear modes then contribute significantly to S, even though their polarization vectors are not closely parallel to $\vec{Q}$. For example, the pronounced "hill" along the $\varphi = 90°$ line in Fig. 2 arises from the lowest-frequency shear mode. At the absolute maximum S involves all three polarization modes and represents the best compromise between polarization and lattice stiffness.

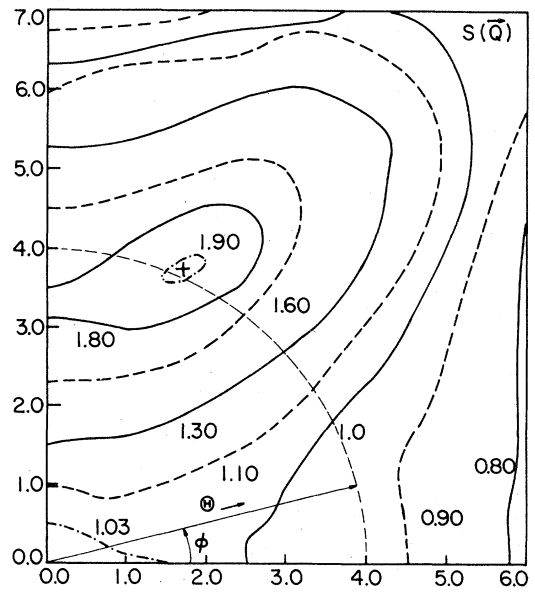

FIG. 2. Contours of $S(\theta,\varphi)$, Eq. (11), for potassium with $|\vec{Q}| = 1.33(2\pi/a)$. The contour values are normalized so that $S(0,0) \equiv 1$. The maximum S, at $\theta = 4.1°$, $\varphi = 65.4°$, is 1.91. The numbers next to the axes measure Θ in degrees.

The location of the maximum S depends on $|\vec{Q}|$, which is not yet known precisely. If $|\vec{Q}| = 1.36(2\pi/a)$, the maximum shifts to $\theta = 2.6°$ and $\varphi = 64.3°$. If $|\vec{Q}| = 1.30(2\pi/a)$, the maximum shifts to $\theta = 5.6°$, $\varphi = 66.9°$. However, as the magnitude of $\vec{Q}$ changes, the direction of $\vec{Q}'$ remains practically constant. It is always near $\theta' = 47°$, $\varphi'(=\varphi) = 65°$. In Cartesian notation the directions of $\vec{Q}'$ are the 48 (cubic) equivalents of (1.05, 1.00, 0.40). In high magnetic fields these would be the possible directions for open orbits, caused by the heterodyne gaps, shown in Fig. 1.

Although the tilt of the CDW wave vector $\vec{Q}$ from [110] is small, ~4 °, it is far enough away that a diffraction scan along a [110] direction would preclude observation of any satellites (if present). Indeed the additional $\vec{Q}$ direction degeneracy (24 instead of 6) implies that satellite intensity will be weaker than otherwise expected, since $\vec{Q}$-domain structure[7] will distribute the CDW satellite intensity among the 48 possible locations surrounding each ordinary reciprocal-lattice vector. Furthermore in a single $\vec{Q}$-domain crystal, one might have to examine all 24 equivalent $\vec{Q}$ axes in order to find a CDW satellite.

Finally, we have carried out equivalent calculations for Na and Rb, based on $T = 78$ °K elasticity data,[18,19] and with $|\vec{Q}| = 1.35(2\pi/a)$. For Na, $\theta = 3.3°$, $\varphi = 63°$; for Rb, $\theta = 3.2°$, $\varphi = 64°$.

ACKNOWLEDGMENT

We are grateful to the NSF for support of this research.

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