Observability of Charge-Density Waves by Neutron Diffraction

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It is shown that atomic displacements $\vec{A}\sin\vec{Q}\cdot\vec{L}$ associated with a charge-density wave (CDW) modulation of a metal crystal cause several changes in the anticipated diffraction properties. Very weak satellite reflections should occur at locations $\pm\vec{Q}$ from the ordinary (cubic) reflections. However it is found that vibrational excitations, corresponding to phase modulation of the CDW, may weaken the satellite intensities below the level of observation. The structure factors of the cubic reflections are reduced from unity to (the Bessel function) $J_0(\vec{K}\cdot\vec{A})$, where $\vec{K}$ is the scattering vector. Measurements of structure factors are difficult to interpret in the alkali metals because of severe primary extinction (mosaic block size ~ 0.5 mm) and unknown anharmonic contributions to the Debye-Waller factor. Nevertheless, an unambiguous test for CDW structure is possible since $\vec{Q}$ (and $\vec{A}$) must be orientable by a large magnetic field at 4 °K. Consequently high-index Bragg reflections should be turned off or on by a magnetic field rotated parallel or perpendicular to $\vec{K}$. Motivation for such an experiment is suggested by a survey of electronic anomalies which have been reported in the alkali metals and which can be explained with the CDW model.

I. INTRODUCTION

The alkali metals are generally considered to have a body-centered cubic (bcc) crystal structure. In recent years, however, a variety of electronic properties have been found anomalous. In Sec. VII, we present a brief survey and commentary on these anomalies. Many of these can be explained quantitatively if one assumes that the conduction electrons have experienced a charge-density wave (CDW) instability.[1] Such a phenomenon, if it exists, would result from exchange and correlation interactions among electrons.

The purpose of this study is to show how the presence *or absence* of a CDW in potassium, say, can be determined decisively. We adopt the view that evidence from electronic properties, no matter how extensive, is inconclusive.

Electric fields caused by a CDW will displace the positive ions from their ideal bcc equilibrium sites $\{\vec{L}\}$. The displacements $\vec{u}(\vec{L})$ are

$$\vec{u}(\vec{L}) = \vec{A}\sin(\vec{Q}\cdot\vec{L}+\varphi), \tag{1}$$

and can be regarded as a static modulation of the lattice. The wave vector $\vec{Q}$ of the CDW has a magnitude slightly larger than $2k_F$, the diameter of the Fermi surface.[1] Its direction is unknown. The amplitude $\vec{A}$ is (approximately) parallel to $\vec{Q}$; and its magnitude can be estimated by requiring the fractional modulation in positive-ion density to equal the fractional modulation ($p \sim 0.2$) of the CDW. Accordingly, div $\vec{u} \sim AQ \sim 0.2$, so

$$A \sim 0.1\ \text{Å}. \tag{2}$$

This estimate neglects effects arising from pseudo-atom form factors which, if included, would lead to a larger A. Nevertheless the value (2) is so large that it constitutes a severe modification of the crystal structure. If a CDW exists, it must be directly visible in a diffraction experiment.

We confine our attention to neutron diffraction, which can easily be carried out with large specimens. (Alkali metals are so chemically reactive that x-ray experiments cannot easily be proven to exhibit bulk properties.)

II. CDW SATELLITES

The diffraction pattern expected from a monatomic crystal is obtained by Fourier analysis of the positive-ion density $\rho(\vec{r})$

$$\rho(\vec{r}) = \sum_{\vec{L}} \delta(\vec{r} - \vec{L} - \vec{A}\sin\vec{Q}\cdot\vec{L}), \tag{3}$$

where $\delta(\vec{r})$ is the Dirac δ function. We neglect the phase angle φ appearing in (1). The Fourier amplitude associated with a scattering vector $\vec{K}$ is

$$\rho(\vec{K}) \equiv \int \rho(\vec{r})\, e^{i\vec{K}\cdot\vec{r}}\, d\vec{r}\ . \tag{4}$$

After substituting (3) into (4) and performing the integration, we find

$$\rho(\vec{K}) = \sum_{\vec{L}} e^{i\vec{K}\cdot(\vec{L}+\vec{A}\sin\vec{Q}\cdot\vec{L})}. \tag{5}$$

The factor involving $\sin\vec{Q}\cdot\vec{L}$ in (5) can be transformed with the help of the Jacobi-Anger generating function for Bessel functions:

$$e^{iz\sin\varphi} = \sum_{n=-\infty}^{\infty} e^{in\varphi} J_n(z). \tag{6}$$

Accordingly, we obtain

$$\rho(\vec{K}) = \sum_{\vec{L},n} J_n(\vec{K}\cdot\vec{A})\, e^{i(\vec{K}+n\vec{Q})\cdot\vec{L}}\ . \tag{7}$$

The sum over $\{\vec{L}\}$ yields zero unless $\vec{K}+n\vec{Q}$ is 2π times a reciprocal-lattice vector $\vec{G}$. Therefore, the allowed Bragg reflections are those with scattering vector

$$\vec{K} = 2\pi\vec{G} - n\vec{Q} . \tag{8}$$

For these reflections the sum (7) is the number of atoms times $F(\vec{K})$

$$F(\vec{K}) = J_n(\vec{K}\cdot\vec{A}) . \tag{9}$$

This is the structure factor of the reflection $\vec{K}$.

The ordinary bcc Bragg reflections are those given by (8) with $n=0$. The (first-order) CDW satellites are those with $n=\pm 1$. The intensity (for $\vec{K}=\vec{Q}$) *relative* to an ordinary Bragg reflection is

$$F^2 = J_1^2(\vec{Q}\cdot\vec{A}) \sim \tfrac{1}{4}(\vec{Q}\cdot\vec{A})^2 \sim 10^{-2} . \tag{10}$$

However, a macroscopic single crystal will probably subdivide into "$\vec{Q}$ domains," each domain having a different orientation of $\vec{Q}$. Depending on the symmetry of the favored $\vec{Q}$ direction, the expected intensity will be reduced by a factor between 3 and 24.

In Sec. VI, we shall show that low-frequency phononlike excitations of the CDW will contribute an enormous Debye-Waller factor to the CDW satellites (but not to the bcc reflections). Consequently, CDW satellites will likely be too weak to be seen directly, although in principle they must be present (if the metal has a CDW structure). A careful search[2] for CDW satellites in potassium revealed no reflections that could be so identified.

III. STRUCTURE FACTORS OF CUBIC REFLECTIONS

Every Bragg reflection of a monatomic bcc lattice will have a structure factor $F=1$. However, if the crystal is modulated by a CDW, these cubic reflections will remain, but will be reduced in intensity. From (9), with $n=0$, their structure factor will be

$$F(\vec{K}) = J_0(\vec{K}\cdot\vec{A}) \tag{11}$$

instead of unity. If θ is the angle between the scattering vector $\vec{K}$ and the amplitude $\vec{A}$ of the CDW, the integrated intensity of a bcc reflection will be proportional to $J_0^2(KA\cos\theta)$. The observed intensity will be proportional to the average of this function over all discrete (or continuous) values of θ obtaining in the sample

$$F^2 = \langle J_0^2(KA\cos\theta)\rangle_{\theta\ \mathrm{av}} . \tag{12}$$

The solid curve in Fig. 1 shows the decrease in F^2 with KA for an isotropic average over θ. It is clear that the existence of a CDW state could be determined by quantitative measurement of the structure factors of (observable) bcc reflections. Experimental deviations from $F^2=1$ for high-index

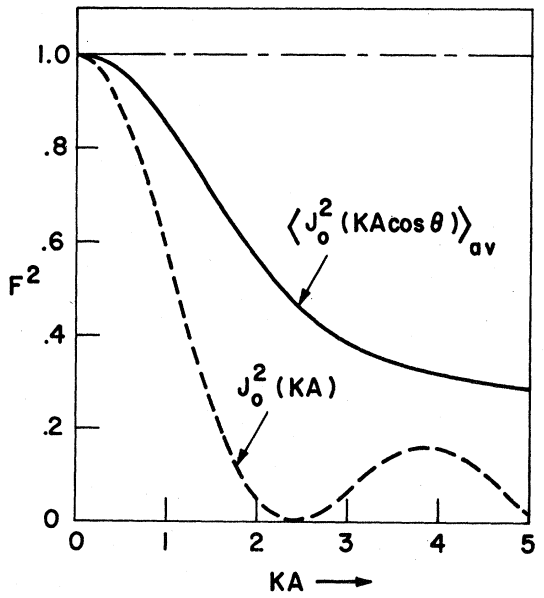

FIG. 1. Structure factor F^2 vs scattering vector $\vec{K}$ for Bragg reflections of a metal modulated by a CDW of amplitude $\vec{A}$. Dashed curve applies if $\vec{K}$ is parallel to $\vec{A}$, and the broken curve (at unity) applies if $\vec{K}$ is perpendicular to $\vec{A}$. Solid curve is an isotropic average of F^2 over the angle θ between $\vec{K}$ and $\vec{A}$.

bcc reflections would indicate that a structure is not really cubic.

Measurements of this type can be rather difficult in alkali metals. The observed integrated intensity I_{obs} of a Bragg reflection is

$$I_{\mathrm{obs}} \sim (y+\alpha)F^2 e^{-2W}/\sin 2\theta_B . \tag{13}$$

y is the primary extinction factor, α the contribution of thermal-diffuse (phonon) scattering to a Bragg peak, e^{-2W} the Debye-Waller factor, and θ_B the Bragg angle. We include no correction for secondary extinction in (13), since we have found that it is negligible ($<2\%$) in potassium by transmission experiments through 3 cm of a single crystal rocked through a [110] reflection. (The width of the rocking curve, in the parallel position, was $\sim 0.25°$.)

Primary extinction is severe. We have determined the mosaic block size in potassium by fitting measurements of (13) to Zachariasen's theory[3] for y. We found the mosaic block size to be ~ 0.05 cm. Extinction of the [110] reflection was a factor $1/y = 5$. By slight thermal stress we were able to reduce the extinction by a factor of 2; however, it completely recovered in less than an hour at room temperature. This suggests that large mosaic-block size is a characteristic of such material. Ideally one would prefer to measure (13) at 4 °K to minimize corrections for thermal diffuse scattering and the Debye-Waller factor. However, even the

high-index reflections (in neutron diffraction) will be highly extinguished at 4 °K. Since the Zachariasen theory does not make proper allowance for the dependence of y on θ_B,[4] interpretation of high-index intensities would be suspect.

Unfortunately, interpretation of room-temperature measurements of (13) is also uncertain. The Debye-Waller factor is then an extreme correction since the appropriate characteristic temperature $\Theta^M = 84$ °K is so small. This is known accurately from the lattice-entropy analysis due to Martin,[5] which leads to $\Theta^M = 89 \pm 1$ °K at 0 °K. A correction for thermal expansion[6]

$$\Theta^M(T)/\Theta^M(0) = (V_0/V_T)^{\alpha}, \tag{14}$$

where V is the molar volume and $\alpha (\approx 1.30)$ the Grüneisen constant, yields the first value given. The Debye-Waller factor for potassium (at 292 °K) in the quasiharmonic approximation is then found to be

$$e^{-2W} = e^{-0.213(h^2+k^2+l^2)}, \tag{15}$$

where h, k, l are the Miller indices of the reflection. This factor reduces the [330] by a factor 30 relative to the [110]. We have attempted to find F^2 from I_{obs}, corrected for primary extinction,[3] thermal diffuse scattering,[7] and the foregoing temperature factor (15). We found $F^2 \sim 0.5$ for the [330]. This result cannot be taken seriously since Maradudin and Flinn[8] and Willis[9] have shown that there can be anharmonic contributions to the Debye-Waller effect, not included in (15), which introduce an extra factor $\exp[-\beta(h^2+k^2+l^2)^2]$. Since little is known about the magnitude (or sign) of β, we are unable to set error limits on our measurements[10] of F^2.

IV. MAGNETIC FIELD MODULATION OF $F(\vec{K})$

In Secs. I–III, we have shown that it is difficult to prove from nonobservance of CDW satellites or from structure-factor measurements that potassium (for example) does not have a CDW. There remains, however, a diffraction effect required by the CDW model that is necessarily observable and spectacular.

The apparent isotropy of the Fermi surface (to one part per thousand in Na and K) as seen in de Haas–van Alphen measurements[11] rules out the CDW model unless $\vec{Q}$ can be oriented by a magnetic field. Otherwise a large Fermi-surface distortion (~ 7%) caused by CDW energy gaps would be immediately evident. Consequently, the CDW model is viable only if it can be taken as axiomatic that the direction of $\vec{Q}$ is (approximately) parallel to that of a sufficiently large magnetic field in a stress-free crystal at 4 °K. Interpretations of spin- and cyclotron-resonance anomalies (Sec. VII) also require this postulate. It is difficult to say how large the field $\vec{H}$ must be, but 15 kG should suffice.

The experiment we propose requires a large stress-free single crystal at 4 °K in a neutron diffractometer and an orientable magnetic field. Since the CDW amplitude $\vec{A}$ is approximately parallel to $\vec{Q}$, and therefore to $\vec{H}$, the structure factors $J_0(\vec{K}\cdot\vec{A})$ of the bcc reflections, Eq. (11), could be varied at will between $J_0(KA)$ and $J_0(0) = 1$. This would be accomplished merely by rotating $\vec{H}$ from parallel to $\vec{K}$ to perpendicular. If a high-index reflection is chosen, so that $KA \sim 2.4$ (near the root of J_0) the reflection could be virtually turned off and on with the field. Observance of such an effect would obviously establish the existence of a CDW beyond doubt. What is perhaps more important, absence of field modulation would rule out the CDW model unambiguously.

An advantage of this experiment is that no analysis or interpretation of data is required. The Bragg intensities either change or they do not. If they do, the maximum intensity ratio would not be $J_0^2(KA)$, however. When primary extinction is large, $y \sim 1/|F|$, so the intensity ratio would more nearly be $|J_0(KA)|$.

This experiment should be attempted in potassium. (The partial martensitic transformation of sodium below 36 °K may introduce elastic stresses that could hinder alignment of $\vec{Q}$ with $\vec{H}$.) Short-wavelength (~ 0.5 Å) neutrons should be employed so that high-index reflections, i.e., [10, 10, 0], can be reached at angles compatible with pole geometry of the magnet. We also emphasize that the crystal should be free standing, so as to avoid thermal stress (during cooling to 4 °K), which could inhibit alignment of $\vec{Q}$.

V. PHASE MODULATION OF CDW

In this section we shall study the low-lying phononlike excitations of a CDW ground state. This is necessary in order to understand the Debye-Waller temperature factor for CDW satellites, which we treat in Sec. VI.

We must begin by estimating the energy difference between a CDW state and the normal ground state of a simple metal. This is most easily done by analogy with the condensation energy of a superconductor,[12]

$$E_s \approx -\tfrac{1}{2}\rho_F \Delta^2 = -3n\Delta^2/4E_F, \tag{16}$$

where ρ_F is the electronic density of states at the Fermi surface (energy E_F), Δ is one-half the superconducting energy gap, and n is the electron density. The last equality in (16) results if we assume a parabolic band, so $\rho_F = 3n/2E_F$. A simplified interpretation of Eq. (16) is that the condensation energy can be attributed to the $\rho_F \Delta$ electrons near the Fermi surface which have their energy lowered an average amount $\frac{1}{2}\Delta$ relative to their nonsuper-

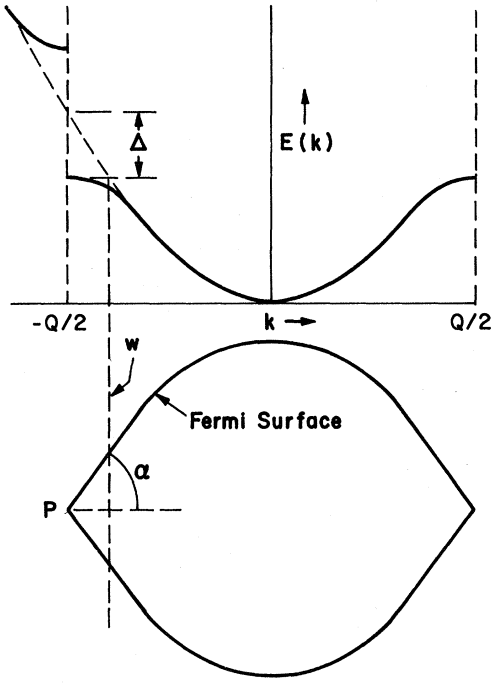

FIG. 2. One-electron energy spectrum and Fermi surface of a metal with a CDW of wavevector $\vec{Q}$. Energy gap caused by the CDW periodic potential is 2Δ. Distortion of the Fermi surface at the conical point P is exaggerated. Half-angle α of the cone would be $\sim 75°$. Electron wave functions most severely deformed are those between the conical point P and the plane w.

conducting energy spectrum.

We shall assume that an analogous relation also applies to a CDW condensation energy. The major difference is that the CDW energy gap 2Δ touches the Fermi surface only at a point.[1] This is shown by the energy spectrum and Fermi surface in Fig. 2. The number of electron states contained within the circular cone bounded by the conical point P and the plane w (an energy depth Δ below P) is

$$N_\Delta = n\Delta^2/16E_F^2 . \tag{17}$$

We have used a relation, derived earlier,[13] that the half-angle α of the cone is given by $\tan\alpha \approx (2E_F/\Delta)^{1/2}$. Because of the conical shape the average energy shift is $\sim \frac{1}{4}\Delta$ instead of $\frac{1}{2}\Delta$. Accordingly, the condensation energy (including both conical points) is

$$E_0 \approx -n\Delta^3/32E_F^2 . \tag{18}$$

The difference in form between (16) and (18) may be verbalized by saying that (for a CDW) only a fraction $\approx \Delta/24E_F$ of the Fermi surface is affected by the CDW energy gaps. With $\Delta \sim 0.3$ eV, the condensation energy (18) for potassium is $\sim 2\times10^{-4}$ eV per electron. This very small energy indicates the delicate nature of the instability.

The (supposed) CDW ground state is the minimum point in a four-dimensional potential valley, whose coordinates are the magnitudes of $\vec{Q}$ and $\vec{A}$ and two parameters needed to specify the direction of $\vec{Q}$. If we omit the dependence on $|\vec{A}|$, the CDW energy can be approximated,

$$E \approx E_0[1 - \lambda L(x,y,z) - \mu(\delta Q/Q)^2] . \tag{19}$$

$\delta Q/Q$ is the fractional deviation of $|\vec{Q}|$ from its equilibrium value, and $L(x,y,z)$ is a function of x,y,z, the direction cosines of $\vec{Q}$. The dimensionless parameters λ and μ are unknown. On account of the isotropy of the Fermi surface we expect $\lambda < 1$, whereas we expect $\mu \gg 1$, since CDW instabilities can arise only for $|\vec{Q}|$ very near $2k_F$. We expect[14] that the easy direction for $\vec{Q}$ is [110]. The simplest function having this property and full cubic symmetry is

$$L(x,y,z) = 2(x^4+y^4+z^4) + 24x^2y^2z^2 - 1 . \tag{20}$$

This form was chosen so that $L = 0$ at the minima ([110] directions) and is isotropic for small deviations in direction; also, $L = 1$ at the maxima ([100] directions).

We are now in a position to discuss dynamical modes of excitation that arise from a CDW structure. Since $\vec{Q}/2\pi$ is incommensurate with the (reciprocal) lattice, there is, strictly speaking, no Brillouin zone. The lattice-vibration dynamical matrix will be $3N\times3N$ in size rather than 3×3. Nevertheless, we should be able to treat long-wavelength phase modulation of the CDW in a manner similar to the quasicontinuum approximation for long-wavelength phonons. The physical model is that the direction (and magnitude) of $\vec{Q}$ can vary from its equilibrium value. We suppose that the phase φ in Eq. (1) can be expanded,

$$\varphi(\vec{L},t) = \textstyle\sum_{\vec{q}} \varphi_{\vec{q}} \sin(\vec{q}\cdot\vec{L} - \omega t). \tag{21}$$

$\vec{q}$ is the wave vector of a phase-modulation phonon, or "phason," and $\omega(\vec{q})$ its frequency. For simplicity, consider a single-phason mode to be excited. Then the atomic displacements relative to their bcc sites are

$$\vec{u}(\vec{L}) = \vec{A}\sin[\vec{Q}\cdot\vec{L} + \varphi_{\vec{q}}\sin(\vec{q}\cdot\vec{L} - \omega t)] . \tag{22}$$

It is easy to see that phase modulation corresponds to a local change in direction and magnitude of $\vec{Q}$: Consider a point in the lattice where $\vec{q}\cdot\vec{L} \sim 0$. Then (22) can be written, for $t = 0$,

$$\vec{u}(\vec{L}) \approx \vec{A}\sin[(\vec{Q} + \varphi_{\vec{q}}\vec{q})\cdot\vec{L}] . \tag{23}$$

We define $q_\perp$ and $q_\parallel$ as the components of $\vec{q}$ perpendicular and parallel to $\vec{Q}$. Then, from (19) and (20) the potential-energy increase $U_{\vec{q}}$ caused by the phase modulation is, for small $\vec{q}$,

$$U_{\vec{q}} = \tfrac{1}{2}|E_0|\varphi_{\vec{q}}^2[6\lambda(q_\perp/Q)^2 + \mu(q_\parallel/Q)^2]. \quad (24)$$

The factor $\frac{1}{2}$ arises from averaging (19) over a full wavelength of the phason.

The kinetic energy $T_{\vec{q}}$ of a phason can also be derived easily. For each ion the kinetic energy is $\frac{1}{2}M(\partial\vec{u}/\partial t)^2$. Accordingly, from (22), the energy density is

$$T_{\vec{q}} = \tfrac{1}{8}nMA^2\omega^2\varphi_{\vec{q}}^2, \quad (25)$$

where a factor $\frac{1}{4}$ has entered from averaging over all lattice sites. The phason frequency spectrum (in the small q limit) is found by recalling that for harmonic oscillators $T_{\vec{q}}$ and $U_{\vec{q}}$ are equal. By equating (24) and (25), we obtain

$$\omega^2 = (4|E_0|/nMA^2)[6\lambda(q_\perp/Q)^2 + \mu(q_\parallel/Q)^2]. \quad (26)$$

The phase velocity of the phasons cannot be calculated until λ and μ are known. However, if we estimate $\lambda \sim 1$, $\mu \sim 10$, $A \sim 0.1$ Å, and use (18) for E_0, we find that phason and phonon velocities are of the same magnitude.

Finally, it is relevant to find the relationship between phasons and phonon modes of the undistorted lattice. This is easily done using (22) and standard trigonometric relations. For small amplitudes $\varphi_{\vec{q}} \ll 1$, we find

$$\vec{u}(\vec{L}) \cong \vec{A}\sin\vec{Q}\cdot\vec{L} + \vec{A}\varphi_{\vec{q}}(\cos\vec{Q}\cdot\vec{L})\sin(\vec{q}\cdot\vec{L} - \omega t). \quad (27)$$

Transforming the last term, we obtain

$$\vec{u}(\vec{L}) \cong \vec{A}\sin\vec{Q}\cdot\vec{L} + \tfrac{1}{2}\vec{A}\varphi_{\vec{q}}\sin[(\vec{q}+\vec{Q})\cdot\vec{L} - \omega t] + \tfrac{1}{2}\vec{A}\varphi_{\vec{q}}\sin[(\vec{q}-\vec{Q})\cdot\vec{L} - \omega t]\ . \quad (28)$$

The last two terms, which represent the phason deviations from the equilibrium CDW state, constitute a coherent superposition of phonon modes having wave vectors $\vec{q}+\vec{Q}$ and $\vec{q}-\vec{Q}$. This means that (in wave-vector space) long-wavelength phason modes are located near the CDW satellite positions, as shown in Fig. 3.

That the phason frequency $\omega(\vec{q}) \to 0$ as $\vec{q} \to 0$ is related to the fact that $\vec{Q}/2\pi$ is incommensurate with the (reciprocal) lattice. If $\vec{Q}/2\pi$ were commensurate, the phason branch would be a soft optical-phonon branch, with $\omega(0)$ finite, analogous to the soft modes in a ferroelectric near the transformation temperature.

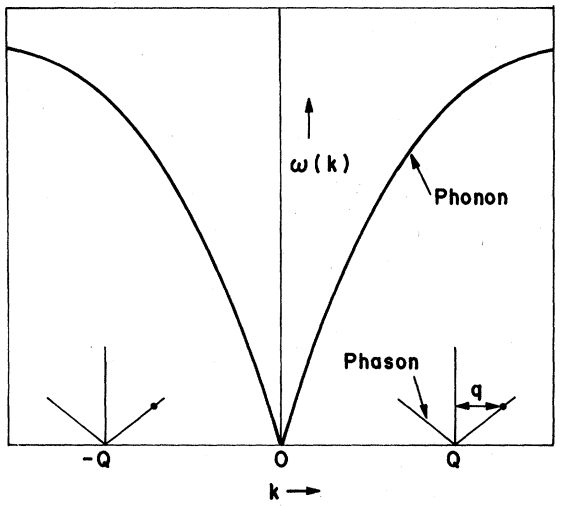

FIG. 3. Schematic illustration of the vibrational modes in a metal having a CDW. Frequency of the phason branch goes to zero at $\vec{Q}$, the location of the CDW satellite reflections. Such a diagram has only an approximate meaning since, strictly, an incommensurate CDW structure does not have a Brillouin zone.

VI. DEBYE-WALLER FACTORS FOR PHASONS

In Sec. V, we have shown that phason modes constitute a separate branch of the phonon spectrum, and that their frequency spectrum goes to zero at the CDW satellite locations, e.g., Fig. 3. Here we shall investigate the relative contribution of phason and phonon modes to the Debye-Waller temperature factor.

Consider first the effect of phonons on an ordinary Bragg reflection of a bcc crystal. The ionic displacements caused by all the phonons $\{i\}$ having amplitudes and frequencies $\{\vec{a}_i, \omega_i\}$ can be written

$$\vec{u}(\vec{L}) = \sum_i \vec{a}_i \sin(\vec{k}_i\cdot\vec{L} - \omega_i t). \quad (29)$$

One repeats the steps from Eqs. (3) to (9) and obtains the structure factor for the bcc reflection $\vec{K}$:

$$F(\vec{K}) = \prod_i J_0(\vec{K}\cdot\vec{a}_i). \quad (30)$$

Since all amplitudes $\vec{a}_i$ are infinitesimal, the product in (30) can be evaluated by taking the logarithm of each side and expanding, $J_0(x) \cong 1 - \frac{1}{4}x^2$. One then obtains,

$$F(\vec{K}) = \exp(-\textstyle\sum_i K^2a_i^2/12)\ . \quad (31)$$

We have used the fact that $\langle\cos^2\theta\rangle_{av} = \frac{1}{3}$ for the angles between $\vec{K}$ and the phonon amplitudes $\vec{a}_i$. The square of (31) is just the Debye-Waller factor e^{-2W}.

The kinetic energy of each phonon mode for a sample containing N atoms is

$$T_i = \tfrac{1}{4}NM\omega_i^2a_i^2 = \tfrac{1}{2}k_BT, \quad (32)$$

where k_B is the Boltzmann constant and T the temperature. From (31) and (32), the contribution w_i of each phonon to the exponent in the Debye-Waller factor e^{-2W} is

$$w_i = -K^2k_BT/3NM\omega_i^2. \quad (33)$$

This is the standard result, appropriate for sufficiently high temperature. (Our definition is $-2W = \sum_i w_i$.)

We next consider the ionic displacements of a phase-modulated CDW, Eq. (22). Repeating the steps from Eqs. (3) to (7), we obtain

$$\rho(\vec{K}) = \sum_{\vec{L},n} J_n(\vec{K}\cdot\vec{A}) e^{i(\vec{K}+n\vec{Q})\cdot\vec{L}}\, e^{in\varphi_{\vec{q}}\sin(\vec{q}\cdot\vec{L}-\omega t)}. \quad (34)$$

Now we apply the Jacobi-Anger generating function (6) to the last factor in (34),

$$\rho(\vec{K}) = \sum_{\vec{L},n,m} J_n(\vec{K}\cdot\vec{A}) J_m(n\varphi_{\vec{q}}) e^{i(\vec{K}+n\vec{Q}+m\vec{q})\cdot\vec{L} - im\omega t}. \quad (35)$$

The bcc reflections correspond to $n = m = 0$, for which (35) leads again to Eq. (11) for $F(\vec{K})$. In other words, we have shown that phason excitations do not contribute to the Debye-Waller factor of the bcc reflections.

The (first-order) CDW satellites correspond to $n = 1$, $m = 0$. From (35) their intensity will be proportional to

$$F^2 = J_1^2(\vec{K}\cdot\vec{A})\, J_0^2(\varphi_{\vec{q}}) \quad (36)$$

instead of (10). We see that the phason $\vec{q}$ contributes a factor $J_0^2(\varphi_{\vec{q}})$. If we included all phason modes, there would be a similar factor for each one, as in the (infinite) product in (30). An exponential Debye-Waller factor would result, analogous to (31), with each phason contributing a term to the exponent (in e^{-2W}) of

$$W_{\vec{q}} = -\tfrac{1}{2}\varphi_{\vec{q}}^2. \quad (37)$$

Furthermore, the mean kinetic energy (25) of a phason is also $\frac{1}{2}k_BT$. Accordingly, for a sample having N atoms,

$$w_{\vec{q}} = -2k_BT/NMA^2\omega^2. \quad (38)$$

Comparing this result with (33), we find the relative contribution of phasons and phonons to the exponent of the Debye-Waller factor to be

$$w_{\vec{q}}/w_i = 6\omega_i^2/K^2A^2\omega^2. \quad (39)$$

This is an extremely large ratio: For a CDW satellite, $K \sim 1.6\times10^8$ cm^{-1}, so that with $A \sim 10^{-9}$ cm and $\omega \sim \omega_i$ the ratio (39) is ~200.

The foregoing results may be summarized: Phasons do not contribute to the Debye-Waller factor of the cubic reflections. For a CDW satellite, however, each phason contributes to the *exponent* of the temperature factor an amount ~200 times larger than that of a phonon having the same frequency. Of course, the complete Debye-Waller factor for satellites will include contributions from all $3N$ modes (ordinary phonons and phasons). Phasons can be regarded as the analog of spin-wave excitations of a magnetic structure. However, they do not represent new degrees of freedom. They are merely a subset of the vibrational degrees of freedom. Their unique properties, derived in this and Sec. V, justify their separation into a distinct category.

A likely consequence of phason excitations is that intensities of CDW satellites may be reduced below the limits of observability. Furthermore, static deviations in the direction of $\vec{Q}$, caused by imperfections, dislocations, residual stress, etc., may supplement the (dynamic) contribution of phasons to e^{-2W}.

VII. SURVEY OF ELECTRONIC ANOMALIES

The purpose of this section is to summarize *briefly* the experimental evidence relevant to CDW structure in the alkali metals. We intend this to provide motivation for the field-modulation experiment proposed in Sec. IV. A number of electronic anomalies will be discussed, most of which are major. A unified and quantitative interpretation of these phenomena can be made using the CDW model. However, three additional postulates are required: (i) The direction of $\vec{Q}$ can be oriented approximately parallel to a (sufficiently strong) magnetic field $\vec{H}$ at 4°K in a stress-free specimen. (ii) The direction of $\vec{Q}$ is subject to elastic stress which, if sufficiently severe, can impede the action of a magnetic field. (iii) The direction of $\vec{Q}$ near a metal surface may orient perpendicular to the surface, especially if the surface is in contact with an oxide layer or substrate to which the metal adheres.

These postulates are reasonable *a priori* in view of the symmetry of the Fermi surface in alkali metals and the small condensation energy (Sec. V) of a CDW. There has been no attempt to justify them theoretically. However, similar postulates are known to be valid for the spin-density wave state of chromium; so they are neither novel nor speculative.

A. Optical Anomalies

The existence of the Mayer-El Naby[15] optical-absorption anomaly in K (with a threshold at $\hbar\omega \approx 0.6$ eV) has been called into question by the work of Smith,[16] who found no evidence for such absorption. Postulate (iii) allows both sets of data to be consistent with the CDW model: Mayer and El Naby measured the reflectivity at a bulk-metal vacuum interface, whereas Smith measured the reflectivity on evaporated films. The theory[13] of the anomalous absorption predicts the observed intensity (oscillator strength ~0.1) and spectral shape of the Mayer-El Naby absorption if $\vec{Q}$ is oriented at random. But if $\vec{Q}$ is perpendicular to the surface, as seems possible in evaporated films, the matrix element (for electronic transitions across a CDW energy gap) becomes zero. This follows from the fact that the electric vector of the light (within the metal) is always parallel to the surface. Similar anomalies have been reported[17]

in Na, Rb, and Cs (with thresholds at 1.2, 0.8, and 0.8 eV).

B. Conduction-Electron Spin Resonances

In ultrapure potassium, Walsh *et al.*[18] found conduction-electron spin resonance (CESR) linewidths as narrow as 0.13 G. They also observed this narrow resonance to split into two well-resolved components when the magnetic field direction was tilted from an initial orientation parallel to the metal surface. The maximum splitting was about 0.5 G. This is a large effect since the resonance shift (caused by the spin-orbit interaction) is only 5 G. This behavior was explained quantitatively[19] by the CDW model. It results from the fact that the conduction-electron g shift depends on the angle between $\vec{Q}$ and $\vec{H}$. The separation into two components is attributed to the highly stressed character of the specimens which, with the help of the three postulates given above, allows a specimen to subdivide into regions having either $\vec{Q}$ parallel to $\vec{H}$ or $\vec{Q}$ (nearly) perpendicular to $\vec{H}$. (The splitting should not occur in a stress-free specimen.) The reported behavior was reproduced in many specimens.[20] Serious attempts[21] to explain it in more conventional ways were unsuccessful.

C. Doppler-Shifted Cyclotron Resonance

CDW energy gaps which touch the Fermi surface at the conical points P, Fig. 2, cause the $\vec{Q}$ component of the electron group velocity to approach zero near P. A consequence is that the maximum velocity in the $\vec{Q}$ direction is less than the Fermi velocity $v_F=\hbar k_F/m^*$. For a free-electron-sphere model of a metal, the magnetic field H for doppler-shifted cyclotron resonance (DSCR) is given by $eH/m^*c=qv_F$, where q is the wave vector of a helicon or acoustic wave. (Note that m^* cancels out of this relation.) For a CDW with $\vec{Q}$ aligned parallel to $\vec{H}$ [postutate (i)], DSCR will occur at a smaller field.[22] High-precision DSCR with helicons was carried out on free-standing single crystals of Na and K by Penz and Kushida.[23] In K they found the DSCR to be shifted ~1 kG below that of the free-electron model, in *quantitative* agreement with the CDW model. There was no comparable shift in Na.[24] In contrast, Libchaber and Grimes[25] have measured the DSCR edge in K, sandwiched between Mylar sheets. (The thermal contraction of K on cooling to 4 °K will introduce the maximum stress permitted by plastic yield.) They found no shift from the free-electron value. These two studies, when juxtaposed, are contradictory if the free-electron-sphere model is supposed, but are consistent with the CDW model: The DSCR shift need not occur in a maximally stressed sample where [according to postulate (ii)] $\vec{Q}$ need not align parallel to $\vec{H}$.

The apparent absence of a DSCR shift with acoustic waves[26] might also be ascribed to thermal stress caused by transducers glued to the K surfaces. Several radio-frequency size-effect studies[27] in K, which in principle could reveal CDW distortions of the Fermi surface, were all carried out on K-Mylar or K-Parafilm sandwiches. Stresses introduced on cooling to 4 °K disqualify these experiments as critical tests of the CDW model.

D. Magnetoresistance

The magnetoresistance of a metal having a simply connected Fermi surface must saturate near $\omega_c\tau\sim 1$ and thereafter become independent of H.[28] However, all workers have found a substantial linear magnetoresistance in Na and K which does not saturate up to $\omega_c\tau\sim 300$. Results obtained by four-terminal,[29] helicon-resonance,[30] and eddy-current-torque[31] techniques substantially agree. A serious attempt to explain this behavior by anisotropic relaxation[32] fell short by many orders of magnitude. The CDW model explains most of the general features without difficulty. Two mechanisms are involved:

(a) Bragg reflection and magnetic breakdown of electron orbits by heterodyne gaps,[33] which arise from ionic displacements having periodicities with wave vector $2\pi\vec{G}\pm\vec{Q}$. The size and k-space location of these gaps is very sensitive to the orientation of $\vec{Q}$ relative to the crystal axes. The mechanism leads to an approximately linear magnetoresistance (which would eventually have to saturate). It explains the observed[30] dependence of the transverse magnetoresistance on orientation of $\vec{H}$ relative to the crystal axes, the wide variation of the linear slope from sample to sample, and the sensitivity to elastic stress;

(b) anisotropy of the resistivity tensor relative to the axis $\vec{Q}$ of the deformed Fermi surface (see Sec. VII G). The resistivity parallel to $\vec{Q}$ is larger than that perpendicular to $\vec{Q}$. Accordingly, with increasing $\vec{H}$, the longitudinal resistivity should be enhanced (as $\vec{Q}$ domains align parallel to $\vec{H}$) and the transverse resistivity should be reduced (relative to the increase caused by the first mechanism, above). This would explain why the longitudinal magnetoresistance exceeds the transverse.[31] Furthermore, since this mechanism is suppressed by elastic stress, it explains why the longitudinal effect is reduced by stress,[34] whereas the transverse is enhanced.[30] Since the two mechanisms need not "track" together with increasing field, dominance of the second mechanism over the first at low field could sometimes occur and explain the initially negative transverse magnetoresistance found in some specimens.[29]

E. Hall Effect

The theory of Lifshitz *et al.*[28] requires that the high-field ($\omega_c\tau > 1$) Hall coefficient of a metal with a simply connected Fermi surface be $R = -1/nec$, independent of H. Penz[35] has observed, however, that $|R|$ decreases monotonically with increasing H in K. The decrease varies from sample to sample and is ~ 7% at 110 kG. Garland and Bowers[36] verified this by two different methods and found an equally large effect in Na. This behavior can be accounted for semiquantitatively with the CDW model: Bragg reflection of electrons at heterodyne gaps [mechanism (a)] causes a fraction f, say, of the electrons to behave like (positively charged) holes. Accordingly, $|R|$ is proportional to $[n(1-2f)]^{-1}$ instead of to n^{-1}. As magnetic breakdown reduces f (with increasing H), $|R|$ must decrease. The magnitude of the decrease is correctly predicted when f is chosen to fit the observed magnetoresistance.[35]

F. de Haas-van Alphen Effect

The extremely small variation of the de Haas-van Alphen frequency as $\vec{H}$ is rotated relative to the crystal axes of Na[37] and K[11] precludes the CDW model unless postulate (i) is assumed. (The Fermi surface appears spherical to ~ 0.1%.) If $\vec{Q}$ is always parallel to $\vec{H}$ in a 50-kG field, then the observed de Haas-van Alphen frequency F corresponds to the extremal area perpendicular to $\vec{Q}$ of the lemon-shaped Fermi surface, Fig. 2. Variations of this belly area with $\vec{H}$ orientation should manifest the Fermi-surface anisotropy that would be present without a CDW. However, one might anticipate deviations from perfect alignment when $\vec{H}$ is in a "hard-$\vec{Q}$" direction, cf. Eq. (19). In such a case, detailed interpretation[38] of anisotropy data in terms of crystalline pseudopotentials would have to be revised.

Since the volume (in k space) enclosed by the Fermi surface must correspond to one electron per atom, any extra volume associated with the conical-point distortion must be compensated for by a decrease in belly area. Shoenberg and Stiles[11] attempted to compare the observed frequency F with F_0, calculated for a free-electron sphere. They found $(F-F_0)/F_0$ to be 0.6, −0.2, −0.7, and −1.4% for Na, K, Rb, and Cs. The relative accuracy of these numbers was 0.2%, although the absolute error (of magnet calibration) was much larger. Thomas and Turner[39] have measured F precisely in K, which provides a magnet calibration for the prior work. The revised values for $(F-F_0)/F_0$ are 0.4, −0.4, −0.9, and −1.6%. $\{F_0\}$ here are based on the lattice parameters of Barrett,[40] and observed anisotropies in F were averaged so that F is the frequency for a Fermi sphere of equal volume.[41] A more precise value for K can be obtained from the Thomas and Turner F together with a new value[42] for the K lattice constant, $(F-F_0)/F_0 = -0.20 \pm 0.04\%$.

We conclude that the (mean) de Haas-van Alphen frequencies in K, Rb, and Cs deviate from the free-electron-sphere model by about five times the experimental uncertainties. If the periodic potential of a CDW is treated as a local potential, the predicted belly-area defects for these three metals can be shown to be −0.8, −1.5, and −1.8%. However, a CDW is caused by exchange and correlation effects,[1] and exchange and correlation potentials are known[43] to be *highly* nonlocal. Consequently, Fermi-surface distortions caused by such phenomena cannot be accurately predicted. The CDW model allows discrepancies between F and F_0 of the observed magnitudes, whereas the usual model allows no deviation whatsoever.[44]

G. Electron-Phonon Interaction

In a recent study, Rice and Sham[45] found significant disagreement between theory and experiment in the angular dependence of electron-phonon scattering at low temperature (~ 10 °K) in K. This could be studied because the electrical-resistivity relaxation time τ_1 differs from the ultrasonic-attenuation relaxation time τ_2. If $\sigma(\theta)$ is the cross section for electron scattering through an angle θ, then $1/\tau_1$ is proportional to the solid-angle average of $\sigma(\theta)$ with a $1-\cos\theta$ weighting function. On the other hand, $1/\tau_2$ depends on the average of $\sigma(\theta)$ with a $\frac{3}{2}\sin^2\theta$ weighting function. Using four different electron-phonon interaction models, Rice and Sham found that τ_2/τ_1 should be ~ 0.9, whereas experimentally this ratio is ~ 2.7. This indicates there is a large unexpected contribution to the electrical resistivity from large-angle scattering. Such a contribution is expected with the CDW model: Electrons near one conical point can be easily scattered to the other conical point by small-q phonons (umklapp scattering caused by CDW energy gaps). Small-q phasons will also contribute since, from Eq. (28), they have the same $\vec{k}$-conservation rules as umklapp processes. These mechanisms have not been studied quantitatively. It is obvious that the resistivity tensor will be highly anisotropic, with a much larger resistivity parallel to $\vec{Q}$ compared to perpendicular. The degree of anisotropy will be sensitive to both temperature and purity. It is not clear, however, that solution of the transport equation, which would be very complex, would still lead to a low-temperature phonon resistivity ~ T^5, as is observed.[46] A realistic calculation of bulk resistivity (or magnetoresistivity) must take account of large-scale heterogeneities caused by $\vec{Q}$ domains.

H. Positron Annihilation

The CDW periodic potential introduces anisotropy into the conduction-electron momentum distribution. In principle, this can be measured by angular correlation of γ rays arising from positron annihilation. Such an experiment requires a magnetic field orientation of $\vec{Q}$, so that momentum components parallel and perpendicular to $\vec{Q}$ can be compared. The predicted effect is small, 2.4%; the observed[47] effect was $2.3 \pm 0.8\%$.

J. Other Properties

If CDW's exist, they will influence in some way almost any physical property of the metal. The phenomena we have discussed above are ones which are profoundly affected. Others will be only slightly modified. For example, the electronic specific-heat coefficient should be enhanced ~10%. It would be difficult to measure this experimentally since band-structure, many-body, and phonon-interaction contributions are not known with sufficient accuracy. However, the electron density of states should rise abruptly to its enhanced value near E_F.[48] Such a rise has been seen[49] in the soft x-ray emission of Na, but this may have another explanation.[50] Nuclear magnetic resonance could be broadened by quadrupole interaction with CDW electric fields or by variations in the Knight shift from crest to trough. (Both of these effects may be diminished by phason excitation.) Anomalous NMR broadening has been reported in Rb and Cs,[51] and attributed to pseudodipolar interactions. However, a theoretical study of this latter mechanism[52] indicates that the observed broadening is much too large.

VIII. CONCLUSION

We have shown that CDW modulation of a cubic metal modifies the diffraction properties of the crystal in three ways: (i) The structure factors of the cubic reflections are reduced to $J_0(\vec{K} \cdot \vec{A})$ from unity; (ii) satellite reflections, at $\vec{K} = 2\pi\vec{G} \pm \vec{Q}$, are introduced; (iii) intensities of the cubic reflections can be modulated with a magnetic field.

We have carried out structure-factor measurements on K and have found that quantitative interpretation is made difficult either by large primary extinction corrections (mosaic-block size ~0.5 mm) or by unknown anharmonic contributions to the Debye-Waller factor.

Satellite reflections, very small to begin with, are reduced further in intensity by phase-modulation excitations of the CDW. The low-energy frequency spectrum of these modes was calculated. They were shown to have no effect on the intensity of cubic reflections, but contribute extremely to the Debye-Waller factor of CDW satellites. Accordingly, nonobservance of satellites can (perhaps) be rationalized.

Finally, we have emphasized that field modulation of high-index cubic reflections is a decisive experiment. The CDW model requires a spectacularly large effect. Failure to observe it would vitiate the model.

Motivation for carrying out the aforementioned experiment was summarized in a survey of reported alkali-metal anomalies. Published experiments, if all are accepted at face value, provide a spectacle of theoretical failure. None have been explained within the conventional framework—a nearly spherical simply-connected Fermi surface. In contrast, the CDW model provides a unified (and for the most part quantitative) explanation of all of them. But this is entirely circumstantial. If the atoms are displaced from their cubic sites, those displacements must be seen. The field-modulation experiment should successfully separate myth from reality.

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