

Exchange and Correlation Instabilities of Simple Metals

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The influence of electron-electron correlation on exchange instabilities of a metal is examined. The employment of screened interactions does not constitute a proper treatment. Correlation effects suppress ferromagnetic instabilities, as is well known, but they need not suppress instabilities of the spin-density-wave type. On the contrary, it is shown that correlation enhances exchange instability of the charge-density-wave type. For either type, the wave vector of such a state adjusts so that the Fermi surface makes critical contact with the energy gaps introduced by the instability. This circumstance optimizes the correlation energy. The observed conjunction of the long-period-superlattice periodicity with the Fermi surface in order-disorder alloys is probably an example of this phenomenon. It is suggested that charge-density-wave ground states are likely in simple metals having weak Born-Mayer ion-ion interactions, such as the alkali metals. The intensity of Bragg reflection satellites caused by a concomitant positive-ion modulation is computed.

I. INTRODUCTION

EXCHANGE interactions among itinerant electrons tend to cause magnetic instabilities, an effect first discussed by Bloch.¹ The extensive bibliography which has accumulated on this topic is summarized and enlarged upon by Herring.² The prevailing opinion is that correlation corrections to the Hartree-Fock approximation always cancel substantially the effects of exchange. This was shown originally for ferromagnetic instabilities by Wigner.³

The influence of electron-electron correlation on the stability of a spin-density-wave (SDW) state has not been adequately investigated. The question is critical because there are always SDW states of lower Hartree-Fock energy than the normal state for all electron densities.⁴ One purpose of this paper is to show that modifications of the electronic density of states $N(E)$ by, say, SDW energy gaps augment the correlation energy and enhance the instability.

This effect is pertinent to a general exchange-instability wave, which we now define. Consider a (supposed) electronic ground state for which the spin-up and spin-down electron densities are

$$\begin{aligned}\rho^+(\mathbf{r}) &= \frac{1}{2}\rho_0[1 + p \cos(\mathbf{Q} \cdot \mathbf{r} + \varphi)], \\ \rho^-(\mathbf{r}) &= \frac{1}{2}\rho_0[1 + p \cos(\mathbf{Q} \cdot \mathbf{r} - \varphi)].\end{aligned}\quad (1)$$

The mean electron density is ρ_0 , and the fractional modulation is p . We shall refer to a state for which the phase φ is 0 as a charge-density wave (CDW). The three possible types of exchange-instability wave are

$$\begin{aligned}\varphi &= 0, & \text{pure CDW;} \\ \varphi &= \frac{1}{2}\pi, & \text{pure SDW;} \\ 0 &< \varphi < \frac{1}{2}\pi, & \text{mixed CDW-SDW.}\end{aligned}$$

At first sight, the possibility of a CDW ground state seems remote. A large Coulomb energy, the volume integral of $\mathcal{E}^2/8\pi$, is the obvious reason. However, our primary concern is not with an ideal electron gas having a rigid background of neutralizing positive charge; it is with a real metal, where the positive ions are more or less free to adjust their positions to minimize their local potential energy. For example, the Born-Mayer ion-ion interactions are known to be extremely weak in the alkali metals. Consequently, the equilibrium positions of the positive ions could be displaced from their ideal cubic sites, to cancel most of the Coulomb energy mentioned above.

The existence of an exchange-instability wave, described by (1), requires a nonconstant potential $V(\mathbf{r})$ in the one-electron Hamiltonian. It will have the form

$$V(\mathbf{r}) = A\sigma_z \sin \mathbf{Q} \cdot \mathbf{r} - C \cos \mathbf{Q} \cdot \mathbf{r}, \quad (2)$$

where A and C are the coefficients of the exchange and Coulomb contributions. Both will be proportional to the fractional modulation p . σ_z is the usual Pauli matrix. A spin-up electron will accordingly experience a potential

$$V(\mathbf{r}) = -G \cos(\mathbf{Q} \cdot \mathbf{r} + \varphi). \quad (3)$$

A spin-down electron will experience a similar potential, but with the sign of φ reversed. The relationship between (2) and (3) is

$$A = G \sin \varphi, \quad C = G \cos \varphi.$$

The periodic potential (3) will introduce energy gaps of magnitude G in the one-electron energy spectrum $E(\mathbf{k})$. These will occur on planes perpendicular to the wave vector \mathbf{Q} , a distance $\frac{1}{2}Q$ from the origin of k space.

The effect of a CDW or SDW on the correlation energy cannot be determined with precision. It is convenient to take the second-order perturbation correction to the Hartree-Fock energy E_0 as the basis for discussion. In this crude approximation, the correlation energy is

$$W_c = -\sum_i |\langle 0 | U | i \rangle|^2 / (E_i - E_0). \quad (4)$$

¹ F. Bloch, *Z. Physik* **57**, 545 (1929).

² Conyers Herring, in *Magnetism*, edited by T. Rado and H. Shul (Academic Press Inc., New York, 1966), Vol. VI.

³ E. P. Wigner, *Phys. Rev.* **46**, 1002 (1934); *Trans. Faraday Soc.* **34**, 678 (1938).

⁴ A. W. Overhauser, *Phys. Rev.* **128**, 1437 (1962).

The matrix elements are those of an electron-electron interaction. (See the Appendix for an explicit interpretation of $\langle 0|U|i\rangle$.) The excited states $\{i\}$ are those for which two electrons have been removed from below the Fermi energy and placed in states above the Fermi energy, but with no change in total momentum. A CDW or SDW changes the numerical value of W_e by altering both the matrix elements and energy denominators of (4). We shall consider first the latter effect, since this has heretofore been entirely neglected. It is obvious that electron excitations of low energy play a proportionately greater role in the sum than those of high energy. Consequently, the electronic density of states $N(E)$ near the Fermi energy E_F is of paramount interest.

$N(E)$ for electrons interacting with a CDW-SDW potential is shown in Fig. 1. There are striking deviations from the \sqrt{E} dependence appropriate to an energy spectrum without such a potential. Point A of Fig. 1 corresponds to the constant-energy surface (in k space) which makes critical contact with the energy gaps introduced by the potential (3). (We shall show below that point A will coincide with E_F , but this may be ignored for the present.) Point B of Fig. 1 corresponds to the constant-energy surface which just begins to include states on the high-energy side of the gap G . $N(E)$ is rigorously horizontal between A and B. This may be seen by considering a two-dimensional electron gas, with $E(\mathbf{k}) = \hbar^2 k^2 / 2m$. For this case, the (unit-area) density of states is

$$N_2(E) = m / 2\pi \hbar^2, \quad (5)$$

a constant. Consider now the three-dimensional electron gas to be sliced up perpendicular to \mathbf{Q} into a large number of thin circular segments. Because (5) is constant, the increase in $N(E)$ with increasing E occurs only because new segments are continually being added.

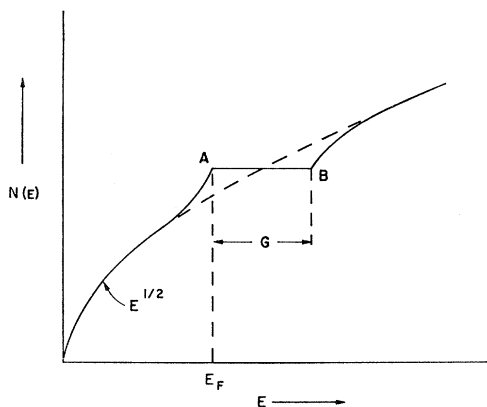


FIG. 1. Electronic density of states versus energy for a free-electron gas. The parabolic curve corresponds to the normal, paramagnetic state. The solid curve, passing through points A and B, applies to a collective-electron deformation of the CDW-SDW type, having energy gap G .

However, as soon as E reaches the value for which its surface just touches the energy-gap plane (critical contact), new segments are no longer added with increasing E . The surfaces of constant energy acquire necks at each energy gap, and $N(E)$ remains constant. Only when E exceeds its critical contact value by G , allowing further addition of new segments, does $N(E)$ resume its increase.

The location of A or B in Fig. 1 depends on the magnitude of Q . If Q is large compared to the diameter $2k_F$ of the Fermi surface, the energy at which critical contact occurs will exceed E_F , and $N(E_F)$ will not differ appreciably from its normal value $N_0(E_F)$. Consider the change of $N(E_F)$ as Q is gradually reduced (with G held constant). The variation is shown in Fig. 2. There is a cusplike maximum in $N(E_F)$ at point A, correspond-

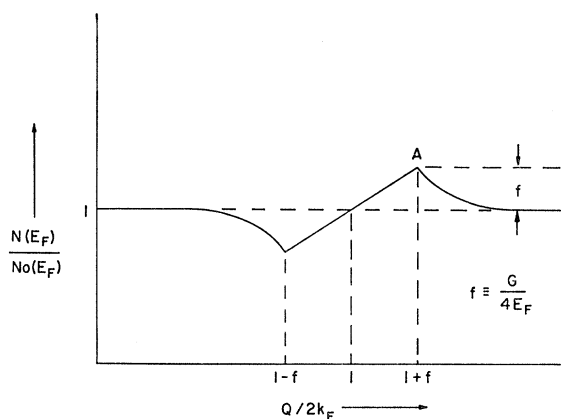


FIG. 2. Electronic density of states at the Fermi energy versus wave vector Q of an exchange-instability wave, for a given energy gap G . The optimum Q [maximum $N(E_F)$] is slightly larger than $2k_F$ and corresponds to critical contact of the Fermi surface with the energy-gap planes in k space.

ing to critical contact. At this point,

$$N(E_F) \approx N_0(E_F) [1 + (G/4E_F)]. \quad (6)$$

This incremental increase in $N(E_F)$ can be deduced from Fig. 1, to terms linear in G . It is just the slope of \sqrt{E} (at E_F) times $\frac{1}{2}G$. The value of Q corresponding to critical contact also depends on G , because the constant-energy surfaces are appreciably distorted by the potential (3). The equation of the surface in critical contact has been derived previously.⁵ It requires

$$Q \approx 2k_F [1 + (G/4E_F)]. \quad (7)$$

Consequently, the wave vector of a CDW or SDW in critical contact with the Fermi surface is slightly larger than $2k_F$.

Since the correlation energy W_e is negative, a larger magnitude for W_e is associated with greater stability. Obviously, modifications of the one-electron $E(\mathbf{k})$ which increase the proportion of low-energy virtual excitations

⁵ A. W. Overhauser, Phys. Rev. Letters 13, 190 (1964).

contributing to (4), increase this magnitude and reduce the total energy. It follows that the upward cusp at A in Fig. 2 will correspond to a downward cusp in the total energy. Therefore, if the ground state contains a CDW or SDW, the optimum Q will be that given by Eq. (7) for critical contact.

The foregoing argument assumes that the cusplike behavior of $N(E_F)$ provides the sharpest variation to the Q dependence of the total energy. In a Hartree-Fock approximation, the optimum Q will be smaller than $2k_F$, since the Hartree-Fock energy decreases smoothly with decreasing Q near $Q \sim 2k_F$. This has been called the "clamp-down" effect,⁴ which describes the tendency of SDW energy gaps to clamp down on the Fermi surface, causing neck formation. This effect is still present in a Hartree-Fock treatment using screened interactions.⁵ However, such calculations with realistically screened interactions do not show SDW-type instabilities.⁷ It follows that if a CDW or SDW were the ground state of a typical metal, the correlation-energy stabilization arising from the enhanced $N(E_F)$ has dominated, and should likewise dominate the determination of Q .

The fallacy of all calculations employing screened interactions in attempts to discuss delicate questions such as stability is apparent. The appropriate screened interaction, if such is ever possible, must certainly depend on the character of the deformation (i.e., Q) and the amplitude of the deformation p . Even for ferromagnetic deformations ($Q=0$), the remaining dependence on p must be included.⁸ To ignore the deformation parameters in U , as almost everyone does, is to beg the question. Unfortunately, it is difficult to envision how to determine U . The alternative is to compute deformed one-electron wave functions and energy spectra for employment in an expression such as (4). But the computational task seems prohibitive.

Consider the $N(E_F)$ variation for a ferromagnetic polarization of conduction electrons. This is easily derived:

$$N(E_F) = \frac{1}{2} N_0(E_F) [(1+P)^{1/3} + (1-P)^{1/3}], \quad (8)$$

where P is the fractional polarization. This variation is shown in Fig. 3, along with that derived above for a CDW-SDW state. In contrast with the latter case, a ferromagnetic polarization decreases the density of states

⁶ D. R. Penn and M. H. Cohen, Phys. Rev. **155**, 468 (1967). These authors ignored the correlation-energy contribution leading to critical contact. Consequently, their conclusions regarding neck formation are invalid. Another serious error in their work is a claim to have shown that finite-amplitude SDW instabilities could occur before differential ones. For the finite case, their calculation allowed repopulation of k space, as is required, in order that the Fermi surface be one of constant energy. This should also have been done in the differential case, since the factorized interaction employed for a fixed Q would require a nonspherical Fermi surface even in the zero-amplitude limit. Their apparent failure to do this prevents a meaningful comparison of the two cases.

⁷ D. R. Hamann and A. W. Overhauser, Phys. Rev. **143**, 183 (1966). See also Refs. 2 and 6.

⁸ S. Misawa, Phys. Rev. **140**, A1645 (1965).

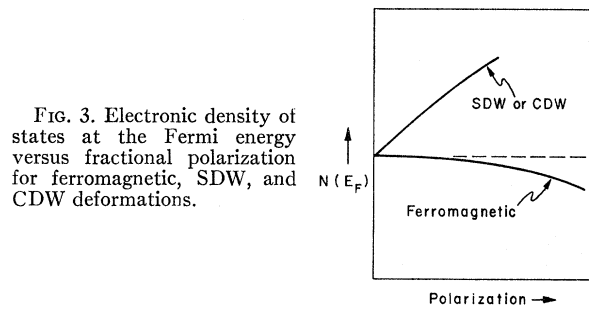


FIG. 3. Electronic density of states at the Fermi energy versus fractional polarization for ferromagnetic, SDW, and CDW deformations.

at the Fermi surface. Thus the correlation energy is reduced in magnitude, inhibiting the deformation. The $N(E_F)$ decrease is a contributing factor to the suppression of a ferromagnetic instability by correlation corrections. An argument is frequently advanced that SDW instabilities will be suppressed by correlation corrections analogous to the ferromagnetic case. We emphasize that the deformations have opposite behavior in a very crucial aspect, so no analogy exists.

We have shown that the two common arguments for discounting the likelihood of anomalous conduction-electron ground states are incorrect.⁹ This by no means establishes the contrary. The energy differences between paramagnetic, CDW and SDW states are probably much smaller than the accuracy of many-body calculations. Experimental evidence¹⁰ will possibly provide the only information on such questions for the near future.

The negative cusp in correlation energy that occurs when the Fermi surface is near critical contact with an energy gap should be a general phenomenon. Sato and Toth¹¹ have established experimentally that the periodicity of the long-period superlattice in CuAu and other alloys is governed by such a critical-contact requirement. The generality of their results is hard to explain without a cusplike term in the energy versus super-

⁹ Herring (Ref. 2, p. 114) presents a third argument, but because of a logical error, this is also incorrect. He invokes a lemma, proved on p. 15, that electron correlations eliminate any energy contributions from repulsive δ -function interactions. He then argues: Real interactions can be divided into high- q and low- q components. The latter determine the plasma frequency, which is independent of magnetic deformation. Appeal is then made to the lemma to show that the high- q components can have negligible effect on magnetic stability. However, we observe that proof of the lemma does not derive from the high- q components of a δ function. It depends on the fact that a δ function is a precisely phased synthesis of low- q and high- q components. A δ function with its low- q parts deleted would have no such lemma.

¹⁰ In a subsequent paper, the author will summarize the extensive, yet still inconclusive, evidence that alkali metals have anomalous electronic ground states.

¹¹ H. Sato and R. S. Toth, Phys. Rev. **124**, 1844 (1961); **127**, 469 (1962). M. Tachiki and K. Teramoto [J. Phys. Chem. Solids **27**, 335 (1966)] have attempted to explain the behavior by treating the superlattice potential in perturbation theory. They found relatively smooth and shallow minima in energy versus Q for superlattice Q 's near the required values. However, they neglected several Q -dependent contributions to the energy which will probably shift the minima and spoil agreement.

lattice periodicity. The effect we have described provides a promising explanation.

II. MATRIX-ELEMENT CONTRIBUTIONS TO THE CORRELATION ENERGY

In Sec. I, we have discussed qualitatively the effect of energy-level shifts on the correlation energy (4). Here we shall estimate the effect of matrix-element changes for virtual excitation of electron-hole pairs. We shall find that these are also important.

To achieve perspective, consider again a half-filled conduction band with fractional ferromagnetic polarization P . The number of parallel-spin pairs per unit volume is

$$n_P = \frac{1}{8}[(1+P)^2 + (1-P)^2]\rho_0^2 = \frac{1}{4}\rho_0^2(1+P^2),$$

where ρ_0 is the electron density. Since the exchange energy is proportional to n_P (if all exchange integrals are taken equal),

$$W_{\text{ex}}(P)/W_{\text{ex}}(0) \sim 1+P^2. \quad (9)$$

The increase of $|W_{\text{ex}}|$ with P^2 is the major contribution favoring magnetic instability. As is well known, the correlation energy opposes such a tendency. This is easily understood by considering Eq. (4). The dominant contributions to the sum over virtual states are those from electron-hole-pair excitations having antiparallel spin. (The parallel-spin pairs have smaller matrix elements because of cancellation by an exchange term.) If wave-vector conservation is ignored, the total number of antiparallel-spin electron-hole excitations in a half-filled band is

$$n_A = (\frac{1}{2}\rho_0)^4(1+P)(1-P)(1-P)(1+P).$$

Since the correlation energy is crudely this number multiplied by an average matrix element and divided by an average-energy denominator,

$$W_c(P)/W_c(0) \sim (1-P^2)^2 \sim 1-2P^2. \quad (10)$$

The last approximation is limited to small P . The decrease of $|W_c|$ with P^2 only partially cancels the increase of $|W_{\text{ex}}|$, since generally $|W_c(0)|$ is three or four times smaller than $|W_{\text{ex}}(0)|$.

The foregoing analyses of exchange- and correlation-energy changes fail when exchange-instability waves [Eq. (1)] are considered. In this case, the numbers of spin-up and spin-down electrons remain the same when the amplitude p of the fractional modulation deviates from zero. It is clear, however, that variations similar to (9) and (10) must still occur. These are to be found instead in matrix elements, as we now show. Suppose, for the sake of simplicity, that all of the modulated wave functions for occupied states can be written

$$\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}(1 + \frac{1}{2}p \cos \mathbf{Q}\cdot\mathbf{r}) / (1 + \frac{1}{8}p^2)^{1/2}. \quad (11)$$

The exchange energy associated with two of these func-

tions is, by a tedious evaluation,

$$\langle \mathbf{k}, \mathbf{k}' | U | \mathbf{k}', \mathbf{k} \rangle \cong U(\mathbf{k}' - \mathbf{k}) + \frac{1}{4}p^2[U(\mathbf{k}' - \mathbf{k} + \mathbf{Q}) + U(\mathbf{k}' - \mathbf{k} - \mathbf{Q})], \quad (12)$$

with p^4 and higher terms neglected. $U(\mathbf{k})$ is the Fourier transform of $U(\mathbf{r})$. If we were to neglect the \mathbf{k} dependence of $U(\mathbf{k})$, we would have

$$\langle \mathbf{k}, \mathbf{k}' | U | \mathbf{k}', \mathbf{k} \rangle \approx U(\mathbf{k}' - \mathbf{k})(1 + \frac{1}{2}p^2).$$

This agrees with (9), since $\frac{1}{2}p^2$ is the mean-square fractional polarization for SDW deformations and correspond to P^2 in the ferromagnetic case.

The correlation energy involves the matrix element for processes in which two electrons in occupied states \mathbf{k}, \mathbf{k}' (having opposite spin) are virtually excited to empty states $\mathbf{k} + \mathbf{q}, \mathbf{k}' - \mathbf{q}$. It is important to know whether these latter states are above or below the energy gap. Assume first that they are both below, which is the predominant case. Then both $\psi_{\mathbf{k}}$ and $\psi_{\mathbf{k}+\mathbf{q}}$ can be taken to have the form (11). For an SDW deformation, $\psi_{\mathbf{k}'}$ and $\psi_{\mathbf{k}'-\mathbf{q}}$ will have the form

$$\psi_{\mathbf{k}'} = e^{i\mathbf{k}'\cdot\mathbf{r}}(1 - \frac{1}{2}p \cos \mathbf{Q}\cdot\mathbf{r}) / (1 + \frac{1}{8}p^2)^{1/2}, \quad (13)$$

since the down-spin modulation is 180° out of phase with the spin-up modulation. The matrix element of the virtual excitation can be evaluated directly (all but 19 of the 81 terms which arise are 0):

$$\langle \mathbf{k}' - \mathbf{q}, \mathbf{k} + \mathbf{q} | U | \mathbf{k}', \mathbf{k} \rangle \cong U(q) - \frac{1}{4}p^2[U(\mathbf{q} + \mathbf{Q}) + U(\mathbf{q} - \mathbf{Q})], \quad (14)$$

where p^4 and higher terms have again been neglected. Were we to neglect the \mathbf{q} dependence of $U(\mathbf{q})$,

$$|\langle \mathbf{k}' - \mathbf{q}, \mathbf{k} + \mathbf{q} | U | \mathbf{k}', \mathbf{k} \rangle|^2 \approx U(q)^2[1 - 2(\frac{1}{2}p^2)],$$

which agrees with (10). (It is the behavior of the square-matrix element that must be compared in this case.) Naturally, it is not correct to assume that all $\psi_{\mathbf{k}}$ have the same p [or, for that matter, that the $\exp(i\mathbf{Q}\cdot\mathbf{r})$ and $\exp(-i\mathbf{Q}\cdot\mathbf{r})$ components of the modulation have equal coefficients], as we have done for the sake of simplicity. Matrix elements of general validity, corresponding to (12) and (14), can with patience be written down, but that is not necessary for the present purpose; as long as $U(q)$ is positive, all of the correction terms that would arise have the same sign.

We have shown that the usual suppression of a ferromagnetic instability by correlation energy persists in the SDW case, but manifests itself as a decrease in magnitude of the matrix elements appearing in Eq. (4). In Sec. I, we showed that this decrease is partly compensated by an increase resulting from changes in $N(E)$, provided Q has the value required for critical contact. Such cancellation cannot occur for a ferromagnetic polarization.

Consider now the behavior of the correlation energy for a CDW deformation. The only difference from the SDW case above is that the modulation of the spin-up

and spin-down wave functions are now in phase. Since the most numerous excited states are again those for which both virtually excited electrons are below the energy gap, all four states which determine the matrix element can be taken to have the form (11). We then find

$$\langle \mathbf{k}' - \mathbf{q}, \mathbf{k} + \mathbf{q} | U | \mathbf{k}', \mathbf{k} \rangle \cong U(q) + \frac{1}{4} p^2 [U(\mathbf{q} + \mathbf{Q}) + U(\mathbf{q} - \mathbf{Q})]. \quad (15)$$

The correction terms are all positive. This result is important because it shows that correlation energy enhances a CDW instability, opposite to the behavior in the magnetic case. This is in sharp contrast to the exchange-energy trend, which is always the same. [Equation (12) applies generally, irrespective of the phase φ in Eq. (1).]

The foregoing conclusions are easy to anticipate physically. The correlation energy is a consequence of virtual scattering of pairs of electrons having (predominantly) antiparallel spin. Wave-function deformations which partially localize both probability densities in identical regions magnify this mechanism. Deformations which localize them in contiguous but separate regions diminish it.

Contemporary literature in the theory of metals is often characterized by a total neglect of exchange and correlation effects, presumably based on a naive hope they always almost cancel. Many workers pretend that correlation effects are somehow adequately accounted for by carrying out Hartree-Fock calculations with screened interactions.¹² We have shown that such an artifice can be qualitatively wrong. Phonon spectra and electron-phonon interaction are examples of phenomena that are sensitive, and probably need reinvestigation. If a modified-interaction artifice must be employed for pragmatic reasons, "antiscreening" will sometimes be the appropriate choice. The alternatives depend on wave vector, as we now show.

When $Q \geq 2k_F$, which is the case we have been considering, almost all low-lying excited states are below the energy gap. This can be understood from Fig. 1. The contribution to $N(E)$ from states below the gap corresponds to the area of the curve below an extended horizontal line running through points A and B. The only excited states that are above the gap (so the spatial phase of their modulation is reversed) are those above the line, to the right of point B. Such states of low excitation energy are obviously very few in number. This is no longer the case if Q is small, allowing energy gaps to cut through the occupied region of k space. In this case, virtual excitations for which one or both excited states lie above the gap must be evaluated. If only one excited state is above,

$$\langle \mathbf{k}' - \mathbf{q}, \mathbf{k} + \mathbf{q} | U | \mathbf{k}', \mathbf{k} \rangle \cong U(q)(1 - \frac{1}{4} p^2), \quad (16)$$

¹² Most workers seem content to screen the Fock term without also screening the Hartree term.

instead of (14) or (15). If both excited states are above (and both initial states below),

$$\langle \mathbf{k}' - \mathbf{q}, \mathbf{k} + \mathbf{q} | U | \mathbf{k}', \mathbf{k} \rangle \cong U(q)(1 - \frac{1}{2} p^2). \quad (17)$$

The results given by (16) and (17) are obtained for both SDW and CDW modulations. Consequently, for such excitations, the correlation energy is diminished by the modulation. Numerous other cases must also be evaluated, since the locations of all four states relative to the energy gaps are pertinent.

The general trend is indicated. Exchange and correlation reinforce one another for charge modulations with Q sufficiently large. The value of Q at which virtual transitions having this property tend to predominate is likely near $Q = k_F$, for which the probabilities of low-energy excitations being above and below the gap are equal.

The ability of exchange and correlation to reinforce one another rather than cancel when spin-up and spin-down modulations are in phase has been emphasized previously in a different context.¹³

III. PARALLEL-SPIN CORRELATION AND UMKLAPP CORRELATION

We were primarily concerned, in the previous sections, with the variations in antiparallel-spin correlation caused by an exchange-instability wave. Parallel-spin correlation (in excess of the exchange energy that arises directly from the Pauli exclusion principle) is considerably smaller in magnitude. This can be seen by the following argument. Consider the excited states $\{|i\rangle\}$ that enter Eq. (4). They are enumerated by three wave vectors \mathbf{k} , \mathbf{k}' , and \mathbf{q} . \mathbf{k} and \mathbf{k}' are the one-electron states emptied by excitation to $\mathbf{k} + \mathbf{q}$, $\mathbf{k}' - \mathbf{q}$. There are $\frac{1}{4}\rho_0^2$ initial pairs of parallel spin, half for spin-up pairs and half for spin-down. This is the same number of \mathbf{k} , \mathbf{k}' pairs having antiparallel spin. It seems at first sight that the total number of excited states $|i\rangle$ would be the same. However, for parallel-spin pairs, the final state $\mathbf{k} + \mathbf{q}$, $\mathbf{k}' - \mathbf{q}$ is the same as $\mathbf{k}' - \mathbf{q}$, $\mathbf{k} + \mathbf{q}$. Consequently, the number of distinguishable excited states is fewer by a factor of 2.

Furthermore, square-matrix elements of parallel-spin excitations are smaller on the average than their antiparallel-spin counterparts, since direct and exchange terms have opposite sign:

$$|\langle 0 | U | i \rangle|^2 = [U(\mathbf{q}) - U(\mathbf{k}' - \mathbf{k} - \mathbf{q})]^2.$$

Suppose, for example, that the probability distribution for $|U(q)|$ were uniform in an interval $(0, U_m)$. For antiparallel-spin pairs,

$$\langle U^2 \rangle_{av} = U_m^2 \int_0^1 x^2 dx = \frac{1}{3} U_m^2.$$

¹³ A. W. Overhauser, Phys. Rev. 156, 884 (1967).

For parallel-spin pairs,

$$\langle U^2 \rangle_{\text{av}} \approx U_m^2 \int_0^1 \int_0^1 (x-y)^2 dx dy = \frac{1}{6} U_m^2,$$

which is smaller by a factor of 2. Combining all factors, we conclude that parallel-spin correlation is approximately 20% of the total correlation energy. This estimate depends on the probability distribution assumed above, but is not very sensitive to reasonable modifications.

Our present interest is the parallel-spin correlation-energy changes introduced by ferromagnetic, SDW, and CDW deformations. A crude argument for the ferromagnetic case, similar to that employed in obtaining Eq. (10), leads again to Eq. (10). This result is understandable. For a half-filled band with $P=1$, no virtual excitations within the band are possible, so each contribution to the correlation energy must decrease as $P \rightarrow 1$.

Matrix-element changes for SDW and CDW parallel-spin excitations are identical, and are given by Eq. (15). Both the direct and exchange terms, say, U and U' , are increased in magnitude to $U+p^2u$, $U'+p^2u'$. The square-matrix element to order p^2 is

$$(U-U')^2 + 2p^2(u-u')(U-U').$$

Because the wave vector \mathbf{Q} appearing in Eq. (15) is large, the relative magnitudes of U and u and of U' and u' will be uncorrelated. Consequently, there will be no predictable trend in the sign of the p^2 correction term above. For this case, we conclude that the over-all effect of the density modulation via matrix elements is negligible. However, the Fermi-energy density-of-states effect, discussed in Sec. I, plays a proportionate role here also, enhancing the correlation energy of CDW-SDW states attributable to parallel-spin excitations.

For the paramagnetic and ferromagnetic states, the one-electron states are eigenfunctions of momentum, and the virtual excitations conserve momentum. This is not the case for CDW and SDW ground states. We still catalog the one-electron wave functions with wave-vector labels, but they are no longer eigenfunctions of momentum. The most important virtual excitations are those which conserve wave-vector label; and these are the only ones we have discussed until now. These excitations can still be shown to conserve expectation value of momentum; but one must introduce the entire metal center-of-mass coordinate and include its recoil. The recoil energy is of course completely negligible and does not affect the correlation energy.

Modulation of the one-electron wave function by the CDW-SDW potential introduces an entirely new class of virtual excitations that contribute to the correlation energy, namely, those for which

$$(\mathbf{k}, \mathbf{k}') \rightarrow (\mathbf{k} + \mathbf{q}, \mathbf{k}' - \mathbf{q} \pm \mathbf{Q}).$$

The matrix elements of these umklapp excitations will be proportional to p . They necessarily enhance the correlation energy of an exchange-instability wave by an amount proportional to p^2 . We shall refer to this contribution as umklapp correlation. It favors CDW or SDW instability. Which type benefits more is hard to assess. There are also virtual excitations for which wave-vector label is nonconserved by $\pm 2\mathbf{Q}$, $\pm 3\mathbf{Q}$, and $\pm 4\mathbf{Q}$. The matrix elements are of higher order in p , so that their contributions can be neglected.

IV. CHARGE-DENSITY-WAVE INSTABILITIES

The pertinent contributions to the exchange instability of an electron gas are summarized in Table I for ferromagnetic, SDW, and CDW deformations. There is always an increase in total kinetic energy, together with a countervailing increase in magnitude of the exchange energy. The SDW-instability theorem⁴ proves that the latter always dominates the former for CDW and SDW deformations. Only for a low-density electron gas can this occur in the ferromagnetic case. The effect of correlation energy differs for all three cases. It suppresses a ferromagnetic instability and enhances a CDW instability. The net effect in the SDW case is uncertain because the correlation contributions have opposite sign. The degree of cancellation cannot be determined without an elaborate numerical calculation.

Perhaps the most surprising conclusion of the present analysis is the strongly indicated possibility that CDW instabilities can occur in a simple metal. The (unfavorable) electric-field energy $\mathcal{E}^2/8\pi$ will be cancelled in large part by a displacement of the positive ions from their normal equilibrium sites. The fractional charge modulation of the electrons is

$$p = (3G/4E_F) \{1 + [(1-u^2)/2u] \ln[(u+1)/(u-1)]\}, \quad (18)$$

where

$$u \equiv Q/2k_F \approx 1 + (G/4E_F).$$

The last equality is equivalent to Eq. (7). The result (18) is obtained by perturbation theory and differs insignificantly from an exact calculation. Suppose now, that the ions of a monovalent metal have normal lattice sites $\{\mathbf{L}\}$. If the displacement $\mathbf{s}(\mathbf{L})$ of the ions from

TABLE I. Energy contributions to ferromagnetic, SDW, and CDW instabilities. F indicates a favorable and U an unfavorable contribution.

Energy contribution	Ferro	SDW	CDW
Kinetic	U	U	U
Exchange	F	F	F
$\mathcal{E}^2/8\pi$	U
Correlation, $N(E_F)$	U	F	F
Correlation, $ \langle 0 U i\rangle ^2$	U	U	F
Correlation, spin	U	F	F
Correlation, umklapp	...	F	F

these sites is

$$\mathbf{s}(\mathbf{L}) = (p\mathbf{Q}/Q^2) \sin \mathbf{Q} \cdot \mathbf{L}, \quad (19)$$

the positive-ion charge modulation will just cancel the electronic CDW. The electrostatic potential arising from this modulation must of course be included in the one-electron potential (2).

Naturally the ion displacements will not be quite so large as that given by (19). The Born-Mayer ion-ion interactions will resist a static phononlike modulation of the lattice periodicity. However, it is well known that in alkali metals this interaction is very weak and, for example, contributes little to the bulk modulus. For this reason alkali metals are perhaps the best candidates for the occurrence of CDW instabilities. The Coulomb interaction between ions, dielectrically screened by the conduction electrons, will also be altered by the lattice modulation. This change, which excludes contributions from Fourier components $\pm \mathbf{Q}$, will also be small compared to the $\mathcal{E}^2/8\pi$ energy that can be eliminated by the lattice modulation (19). The importance of the aforementioned ion-ion interactions, though small, lies in their dependence on the orientation of \mathbf{Q} relative to the crystal axes. Determination of the optimum direction of \mathbf{Q} is an important problem.

Modulation of the positive-ion lattice, given approximately by (19), will necessarily accompany a CDW ground state of the conduction-electron system. This will give rise to satellite Bragg reflections of neutrons or x rays. Observation of satellites would provide unambiguous evidence for such a state. However, the expected intensities are very weak, as we now show.

Consider a monatomic Bravais lattice of point ions. The positive-ion density is

$$\rho(\mathbf{r}) = \sum_{\mathbf{L}} \delta[\mathbf{r} - \mathbf{L}],$$

where $\delta[\mathbf{r}]$ is a δ function. Suppose the lattice positions are modulated according to (19). Then

$$\rho(\mathbf{r}) = \sum_{\mathbf{L}} \delta[\mathbf{r} - \mathbf{L} - (p\mathbf{Q}/Q^2) \sin \mathbf{Q} \cdot \mathbf{L}]. \quad (20)$$

Bragg reflections are found by taking the Fourier transform of (20):

$$\rho(\mathbf{K}) = \int \rho(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) d^3r.$$

Integration yields

$$\rho(\mathbf{K}) = \sum_{\mathbf{L}} \exp\{i\mathbf{K} \cdot [\mathbf{L} + (p\mathbf{Q}/Q^2) \sin \mathbf{Q} \cdot \mathbf{L}]\}.$$

The second term of the exponential can be expanded in a power series in p , which allows the sum over $\{\mathbf{L}\}$ to be performed. One obtains a nonzero result only for scattering vectors,

$$\mathbf{K} = 2\pi\mathbf{G}, 2\pi\mathbf{G} + \mathbf{Q}, 2\pi\mathbf{G} - \mathbf{Q},$$

where $\{\mathbf{G}\}$ are the reciprocal lattice vectors. If the Bragg-reflection intensity of the unmodulated lattice is I_0 , the intensities of the allowed reflections for the

modulated lattice are

$$I(2\pi\mathbf{G}) = [1 - \frac{1}{2}p^2(2\pi\mathbf{G} \cdot \mathbf{Q}/Q)^2]I_0, \quad (21a)$$

$$I(2\pi\mathbf{G} \pm \mathbf{Q}) = \frac{1}{4}p^2[(2\pi\mathbf{G} \pm \mathbf{Q}) \cdot \mathbf{Q}/Q^2]^2 I_0. \quad (21b)$$

The satellite intensities (21b) are weak if experimental data are used to determine p . For potassium, the instability-wave energy gap is 0.62 eV,⁵ and $E_F = 2.1$ eV. Equation (18) predicts $p = 0.17$; so that $I(2\pi\mathbf{G} \pm \mathbf{Q})/I_0 \sim 0.007$.

This relatively small intensity could be obtained only if the sample were a "single- \mathbf{Q} " crystal. A "poly- \mathbf{Q} " crystal, containing modulation domains of at most 24 different (but equivalent) orientations, would have individual satellite intensities $\sim 3 \times 10^{-4} I_0$. Obviously these would be quite difficult to observe, even if the favored orientations of \mathbf{Q} were known in advance.

In the absence of direct observation by Bragg reflection, indirect evidence for electronic ground states of the SDW-CDW type can occur in varied phenomena. Anomalous behavior, otherwise unexplained, has been reported in the alkali metals. Quantitative interpretation is possible in five areas: (a) optical absorption,⁵ (b) magnetoresistance,¹⁴ (c) de Haas-van Alphen periodicity,^{10,15} (d) helicon wave absorption,¹⁶ and (e) positron annihilation.¹⁷ Only the optical absorption depends sensitively on the phase angle φ of the CDW-SDW admixture [Eq. (1)]. The theoretical treatment of this effect⁵ assumed implicitly that the phase of the exchange-instability wave (regarded at the time as a pure SDW) was pinned to the positive-ion lattice. It was emphasized subsequently¹⁸ that the absorption could not occur without pinning. The present investigation began as a theoretical study of SDW pinning, by incorporation of a CDW component. The surprisingly favorable correlation energy of the CDW component, shown in Sec. II, leads to the conclusion that exchange-instability waves in simple metals are more likely of the pure-CDW type.

The foregoing conjecture solves a difficulty pointed out in the original work on SDW instabilities.¹⁹ Large nuclear hyperfine fields (~ 500 kG in Cs) should be manifest, at least in a time-averaged, vestigial way. For the alkali metals, such evidence has never been found in nuclear-magnetic-resonance (NMR) experiments nor in the Mössbauer effect.²⁰

¹⁴ P. A. Penz and R. Bowers, *Solid State Commun.* **5**, 341 (1967). The theory of this effect will be published by J. R. Reitz and the author.

¹⁵ D. Shoenberg and P. J. Stiles, *Proc. Roy. Soc. (London)* **A281**, 62 (1964).

¹⁶ A. W. Overhauser and S. Rodriguez, *Phys. Rev.* **141**, 431 (1966). Conflicting evidence from ultrasonic absorption is vitiated by severe elastic stress of specimens.

¹⁷ D. R. Gustafson and G. T. Barnes, *Phys. Rev. Letters* **18**, 1 (1967).

¹⁸ J. J. Hopfield, *Phys. Rev.* **139**, A419 (1965).

¹⁹ A. W. Overhauser, *Phys. Rev. Letters* **4**, 462 (1960).

²⁰ A. J. F. Boyle and G. J. Perlow, *Phys. Rev.* **151**, 211 (1966).

APPENDIX

A well-known difficulty of Eq. (4) is that W_c diverges when the matrix elements of e^2/r are employed. This is caused by the small-momentum-transfer singularity of Rutherford scattering, and arises from the long-range tail of the Coulomb interaction. Collective-screening effects in a metal prevent the dominance of virtual scattering by small-angle events. This restraint can be incorporated into the perturbed-ground-state wave function ψ by letting

$$\psi \cong |0\rangle - \sum_i |i\rangle \langle i| U_{sc} |0\rangle / (E_i - E_0), \quad (\text{A1})$$

where $|0\rangle$ is the ground-state Slater determinant, and $\{|i\rangle\}$ are those of higher energy having two electrons excited above the Fermi surface. U_{sc} is some appropriate screened Coulomb interaction between all electron pairs. It is clear, however, that U_{sc} cannot be used to calculate the energy. Only the exact Hamiltonian $T+U$ can be employed. In other words, we interpret (A1) as a variational wave function. Accordingly, the energy is

$$E = \langle \psi | T + U | \psi \rangle / \langle \psi | \psi \rangle. \quad (\text{A2})$$

Naturally, the question arises about the choice of U_{sc} . From the variational point of view, this is discretionary. One might employ, for example,

$$U_{sc} = e^2 \sum_{ij} \exp(-\mu r_{ij}) / r_{ij}, \quad (\text{A3})$$

and determine the optimum value of μ by minimizing (A2). The results of such a calculation would provide an interesting comparison with other estimates of the correlation energy.²¹

In the event that $\langle \psi | \psi \rangle$ does not deviate too much from unity, (A2) can be expanded in powers of U and U_{sc} . To second order, we obtain

$$E \approx E_0 - \sum_i [\langle 0 | U | i \rangle \langle i | U_{sc} | 0 \rangle + \langle 0 | U_{sc} | i \rangle \langle i | U | 0 \rangle - |\langle 0 | U_{sc} | i \rangle|^2] / (E_i - E_0), \quad (\text{A4})$$

where $E_0 \equiv \langle 0 | T + U | 0 \rangle$. By way of illustration, suppose (A3) were used for U_{sc} . Then the correction term of (A4) becomes

$$W_c \approx - (4\pi e^2)^2 \sum_i (q_i^2 + 2\mu^2) / q_i^2 (q_i^2 + \mu^2)^2 (E_i - E_0), \quad (\text{A5})$$

where $\hbar q_i$ is the momentum transfer involved in the transition to $|i\rangle$. Comparison of Eqs. (4) and (A5) provides an explicit (though somewhat arbitrary) interpretation of the matrix element appearing in (4):

$$\langle 0 | U | i \rangle = 4\pi e^2 (q^2 + 2\mu^2)^{1/2} / q (q^2 + \mu^2). \quad (\text{A6})$$

²¹ A computation similar to that proposed here has already been carried out and gives reasonable values for the correlation energy [W. Macke, Z. Naturforsch. **5a**, 192 (1950)].

The advantage of this identification is that long-range screening effects, as they effect small-angle virtual excitations, are incorporated by wave-function modification, as it should be done, and by keeping the exact Hamiltonian intact. The sum appearing in Eq. (4) will of course converge.

Ideally, the energy of a CDW-SDW state should be computed by an *ab initio* repetition of the perturbation-variation scheme described above. The reason is that the optimum parameter μ of the screened interaction for the CDW-SDW state may differ from the value μ_0 that minimizes the energy of the paramagnetic state. The resulting correction to the CDW-SDW-state energy, however, is fourth order in p , the fractional modulation of the exchange-instability wave, as we now show. The total energy, to relevant order in p and $\mu - \mu_0$, is

$$W(p, \mu) = A + B(\mu - \mu_0)^2 + p^2 [C + D(\mu - \mu_0)], \quad (\text{A7})$$

where A , B , C , and D are appropriate parameters. This is optimized with respect to μ by setting $\partial W / \partial \mu = 0$. Accordingly,

$$\mu = \mu_0 - D p^2 / 2B.$$

Inserting this result back into (A7), we obtain

$$W(p) = A + C p^2 - (D^2 / 4B) p^4,$$

which differs from $W(p, \mu_0)$ only by a term in p^4 . Consequently, in calculating correlation-energy changes associated with CDW-SDW deformations, we may employ the effective matrix elements, e.g., (A6), derived for the paramagnetic state.

Finally, it should be appreciated that the approximate expression [Eq. (4)] for the correlation energy is not a correction term in a standard Rayleigh-Schrödinger perturbation scheme. Rather, it is the term caused by first-order configuration-interaction corrections to a Hartree-Fock state. Brillouin's theorem²² shows that the only configurations connected to a Hartree-Fock state in first order are those determinantal functions differing from the Hartree-Fock state by just two orbitals. Consequently, the only term in the Hamiltonian which can contribute to such matrix elements is the electron-electron interaction. One might suspect that this involves some double counting of the interaction, since the Hartree-Fock potential includes already some effects of the interaction. This is not so. The potential terms in the Hartree-Fock equations are one-electron operators; so that even if they were to be subtracted from U , they could not contribute to the configuration mixing allowed by Brillouin's theorem.

²² J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963), Vol. I, p. 259.