Exchange instabilities in an *n*-type silicon inversion layer*

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We investigate the possibility that in a semiconducting surface inversion layer the ground state has charge-density waves in each of the two equivalent subbands. The two charge-density waves are identical except that they are completely out of phase with each other. Such a state, referred to as a valley-density wave (VDW), need not be accompanied by a lattice distortion. A density-functional formalism is used to study the instability toward formation of a VDW ground state. It is found that under certain conditions the VDW state has a lower energy than the paramagnetic state. A similar conclusion is drawn on the basis of Hartree-Fock treatment of VDW state.

INTRODUCTION

Experimental studies of *n*-type Si inversion layer suggest that at an interface between Si(100) and SiO_2 the electrons occupy two of the six conduction bands along ⟨100⟩ axis of the bulk Brillouin zone.[1] The ground state of such a system is thought to be paramagnetic with two conduction bands equally and uniformly populated. We have investigated whether this paramagnetic uniform occupancy of the two bands is in fact the ground state of the system. We find that under certain circumstances there exists another state, which we call a valley-density-wave (VDW) state, having a lower energy than the paramagnetic state of the system. The VDW state consists of two identical charge-density waves (CDW) that are completely out of phase with each other. Each of the CDW originates in one of the two valleys. Owing to the identical nature of the conduction valleys, it is possible to have two identical charge-density waves. The condition that they be out of phase ensures that there will be no net charge density and no lattice distortion. The presence of a VDW state will modify single-particle energy spectrum and create an energy gap just as charge- and spin-density waves do. As in the case of those instabilities the modification of single-particle energy spectrum should strongly affect the magnetoresistance of the surface channel, the quantum oscillations in the surface conductance, the cyclotron effective mass, and the optical absorption of the inversion-layer electrons.

We use two different approaches to investigate the energy difference between a VDW state and a paramagnetic state. The first approach is based on the density-functional formalism of Hohenberg-Kohn-Sham,[2,3] and the second approach is similar to the one used by Chan and Heine for finding the condition for a spin-density wave (SDW) or CDW instability.[4]

DENSITY-FUNCTIONAL APPROACH

Let us suppose that there are two identical CDW's, each originating from one of two equivalent bands in a semiconductor. Then, the density $\rho_\nu(\vec{r})$ associated with the CDW in valley ν can be written

$$\rho_\nu(\vec{r}) = \tfrac{1}{2}[\rho(\vec{r}) + \xi_\nu \Delta\rho(\vec{r})] \ , \tag{1}$$

where $\xi_\nu = \pm 1$, depending upon whether ν denotes valley 1 or 2. In Eq. (1), $\rho(\vec{r})$ is the total density in the system and $\Delta\rho(\vec{r})$ is the density of the oscillatory part of a CDW. The fact that $\xi_\nu = +1$ for valley 1 and -1 for valley 2 ensures that the two CDW will be out of phase with each other. Consequently, a VDW state will not be accompanied by any periodic lattice distortions. It follows from Eq. (1) that

$$\rho(\vec{r}) = \sum_\nu \rho_\nu(\vec{r})$$

and (2)

$$\Delta\rho(\vec{r}) = \sum_\nu \xi_\nu \rho_\nu(\vec{r}) \ .$$

Following Hohenberg and Kohn,[2] it can be easily shown that the ground-state energy E of the system is a unique functional of the densities $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ in valleys 1 and 2, respectively. Equivalently, we can regard E as a unique functional of $\rho(\vec{r})$ and $\Delta\rho(\vec{r})$ and demand that E should be minimum with respect to variations in $\rho(\vec{r})$ and $\Delta\rho(\vec{r})$. In the presence of external potentials $V_A(\vec{r})$ and $V_D(\vec{r})$, which couple with $\rho(\vec{r})$ and $\Delta\rho(\vec{r})$, respectively, the ground-state energy of the system can be expressed as

$$E[\rho, \Delta\rho] = \int d\vec{r}[V_A(\vec{r})\rho(\vec{r}) + V_D(\vec{r})\Delta\rho(\vec{r})] + \left(\frac{1}{2}\right)\int\int d\vec{r}\, d\vec{r}\,' \frac{\rho(\vec{r})\rho(\vec{r}\,')}{\kappa|\vec{r}-\vec{r}\,'|} + G[\rho, \Delta\rho] \ , \tag{3}$$

where κ is the static dielectric constant of the semiconductor and $G[\rho, \Delta\rho]$ is a universal functional. It is apparent that the classical Coulomb energy in Eq. (3) is the same as for the paramagnetic state. Thus, the VDW state will not have any periodic lattice distortions.

Under the assumption that $\Delta\rho(\vec{r})$ is small, we expand $G[\rho, \Delta\rho]$ and retain terms that are quadratic in $\Delta\rho$:

$$G[\rho, \Delta\rho] = G[\rho] + \frac{1}{2}\int d\vec{r}\int d\vec{r}\,' G[\vec{r}, \vec{r}\,';\rho]\,\Delta\rho(\vec{r})\Delta\rho(\vec{r}\,') \quad , \tag{4}$$

where

$$G[\vec{r}, \vec{r}\,';\rho] = \left.\frac{\delta^2 G[\rho, \Delta\rho]}{\delta\Delta\rho(\vec{r})\delta\Delta\rho(\vec{r}\,')}\right|_{\Delta\rho=0} \quad . \tag{5}$$

Substituting Eq. (4) into Eq. (3) and minimizing with respect to $\Delta\rho$, we obtain

$$\Delta\rho(\vec{r}) = -\int d\vec{r}\,' G^{-1}[\vec{r}, \vec{r}\,';\rho]\, V_D(\vec{r}\,') \quad . \tag{6}$$

Equation (6) is an expression for the linear response of the oscillatory part of a VDW state. For self-sustaining valley density waves we find that the difference in energy between the VDW state and paramagnetic state is given by

$$E[\rho, \Delta\rho] - E[\rho] = \frac{1}{2}\int d\vec{r}\int d\vec{r}\,' G[\vec{r}, \vec{r}\,';\rho]\,\Delta\rho(\vec{r})\Delta\rho(\vec{r}\,') \quad . \tag{7}$$

The quantity of main interest is the functional $G[\vec{r}, \vec{r}\,';\rho]$. If the right-hand side of Eq. (7) is negative, then the ground state of the system is obviously a VDW state and not the paramagnetic state. As $G[\vec{r}, \vec{r}\,';\rho]$ approaches zero the response function, $G^{-1}[\vec{r}, \vec{r}\,';\rho]$ becomes singular as one would expect.

The functional $G[\vec{r}, \vec{r}\,';\rho]$ is a sum of two contributions: (i) kinetic energy term $G_s[\vec{r}, \vec{r}\,';\rho]$, and (ii) exchange and correlation term $G_{xc}[\vec{r}, \vec{r}\,';\rho]$. Since the VDW state is similar to a spin-polarized electron liquid, we follow the approach of Vosko and Perdew[5] and obtain the following expression for the response function $G^{-1}[\vec{r}, \vec{r}\,';\rho]$:

$$G^{-1}[\vec{r}, \vec{r}\,';\rho] = G_s^{-1}[\vec{r}, \vec{r}\,';\rho] - \int\int d\vec{r}\,'' d\vec{r}\,''' G_s^{-1}[\vec{r}, \vec{r}\,'';\rho] \times G_{xc}[\vec{r}\,'', \vec{r}\,''';\rho] G^{-1}[\vec{r}\,''', \vec{r}\,';\rho] \quad . \tag{8}$$

The kinetic part of G^{-1}, i.e., $G_s^{-1}[\vec{r}, \vec{r}\,';\rho]$, can be obtained from a knowledge of eigenfunctions and eigenvalues of Schrödinger equation for the paramagnetic state. Thus, the band-structure effects can be incorporated in the functional $G_s^{-1}[\vec{r}, \vec{r}\,';\rho]$. Following Vosko and Perdew's method[5] for a spin-polarized system, it is straightforward to show that the expression for G_s^{-1} reads

$$G_s^{-1}[\vec{r}, \vec{r}\,';\rho] = 2\sum_{i,j}\left(\frac{\theta(\mu-\epsilon_i) - \theta(\mu-\epsilon_j)}{\epsilon_j - \epsilon_i}\right) \times \phi_i^*(\vec{r})\phi_j^*(\vec{r}\,')\phi_i(\vec{r}\,')\phi_j(\vec{r}) \quad , \tag{9}$$

where ϵ_i are the single-particle energies, ϕ_i's are the single-particle orbitals, μ is the chemical potential in the paramagnetic state, and $\theta(\mu-\epsilon_i)$ is the Fermi function at zero temperature.

The many-body effects are lumped in the exchange and correlation functional G_{xc}. In order to evaluate $G_{xc}[\vec{r}, \vec{r}\,';\rho]$ we assume that the electrons in the conduction valleys constitute a homogeneous two-component electron gas. The response function G_h^{-1} of the system is given by

$$\Delta\rho(\vec{r}) = -\int d\vec{r}\,' G_h^{-1}(\vec{r}-\vec{r}\,';\rho_0)\, V_D(\vec{r}\,') \quad , \tag{10}$$

where ρ_0 is the homogeneous density. Introducing a function $\chi_h(\vec{r}-\vec{r}\,';\rho_0)$, such that

$$\chi_h(\vec{r}-\vec{r}\,';\rho_0) = -G_h^{-1}(\vec{r}-\vec{r}\,';\rho_0) \quad , \tag{11}$$

and substituting Eqs. (10) and (11) in Eq. (8), we obtain in the q space

$$G_{xc}(\vec{q};\rho_0) = -(\chi_h^{-1}(\vec{q}, \rho_0) - \chi_s^{-1}(\vec{q}, \rho_0)) \quad , \tag{12}$$

where

$$\chi_s(\vec{q}, \rho_0) = -G_s^{-1}(\vec{q}, \rho_0) \quad . \tag{13}$$

The function $G_{xc}(\vec{r}-\vec{r}\,';\rho)$ is then obtained by taking the Fourier transform of right-hand side of Eq. (12) and replacing the homogeneous density ρ_0 by $\rho(\vec{r})$. It shoud be observed that the long-wavelength limit of Eq. (12) corresponds to local-density approximation for $G_{xc}(\vec{r}-\vec{r}\,';\rho)$.

For the purpose of evaluating $\chi_h(\vec{q};\rho_0)$ we assume that there are external potentials $\{\phi_v^{\rm ext}(\vec{r})\}$, each of which couples only with the density of particles in valley v. It is easy to infer from Eqs. (2) and (3) that

$$\phi_v^{\rm ext}(\vec{r}) = \tfrac{1}{2}[V_A(\vec{r}) + \xi_v V_D(\vec{r})] \quad . \tag{14}$$

The induced density of component v can be written[6]

$$\langle\rho_v(\vec{q})\rangle = \chi_s^v(\vec{q})\left(\phi_v^{\rm ext}(\vec{q}) + \sum_{v'}\Psi_{v,v'}(\vec{q})\,\langle\rho_{v'}(\vec{q})\rangle\right) \quad , \tag{15}$$

where the effective field $\Psi_{v,v'}(\vec{q})$ is defined by

$$\Psi_{v,v'}(\vec{q}) = \phi(\vec{q})[1 - \mathcal{G}_{v,v'}(\vec{q})] \quad . \tag{16}$$

In Eq. (16), $\phi(\vec{q})$ is the Fourier transform of Coulomb potential The quantity $\mathcal{G}_{\nu,\nu'}(q)$ is often referred to as local-field correction. It is a measure of short-range exchange-correlation effects. Physically, $\mathcal{G}_{\nu,\nu'}$ represents a local exchange and correlation hole surrounding each electron. For example, in the Hubbard approximation in two dimensions,

$$\mathcal{G}_{\nu,\nu'}(q) = \delta_{\nu,\nu'}\{q/[4(q^2+q_F^2)]^{1/2}\} ,$$

where q_F is the Fermi wave vector of the system.

Owing to the identical nature of conduction valleys, we have

$$\chi_s^1(\vec{q}) = \chi_s^2(\vec{q}) = \chi_s(\vec{q}) ,$$

$$\mathcal{G}_{11}(\vec{q}) = \mathcal{G}_{22}(\vec{q}) = \mathcal{G}_{\text{intra}}(\vec{q}) , \quad (17)$$

and

$$\mathcal{G}_{12}(\vec{q}) = \mathcal{G}_{21}(\vec{q}) = \mathcal{G}_{\text{inter}}(\vec{q}) .$$

From Eqs. (14)–(17), we obtain

$$\chi_h(\vec{q}) = \frac{\Delta\rho(\vec{q})}{V_D(\vec{q})} = \frac{\chi_s(\vec{q})}{1+\phi(\vec{q})[\mathcal{G}_{\text{intra}}(\vec{q}) - \mathcal{G}_{\text{inter}}(\vec{q})]\chi_s(\vec{q})} . \quad (18)$$

Comparing Eq. (18) with Eq. (12), we find

$$G_{xc}(\vec{q};\rho_0) = -\phi(\vec{q})[\mathcal{G}_{\text{intra}}(\vec{q},\rho_0) - \mathcal{G}_{\text{inter}}(\vec{q},\rho_0)] . \quad (19)$$

The oscillatory part of a CDW of wave vector $\vec{q}$ is given by

$$\Delta\rho(\vec{r}) = \alpha\cos(\vec{q}\cdot\vec{r}) , \quad (20)$$

where α denotes the amplitude of the CDW. Substituting Eq. (20) into Eq. (7) and assuming translational invariance, we find that in order to have a self-sustaining VDW state at lower energy than the paramagnetic state,

$$G(\vec{q};\rho_0) \leq 0 . \quad (21)$$

By definition,

$$G(\vec{q};\rho_0) = G_s(\vec{q};\rho_0) + G_{xc}(\vec{q};\rho_0) .$$

Using Eq. (19) for $G_{xc}(\vec{q};\rho_0)$, we obtain the following condition for a VDW instability;

$$\phi(q)[\mathcal{G}_{\text{intra}}(\vec{q},\rho_0) - \mathcal{G}_{\text{inter}}(\vec{q},\rho_0)] \geq G_s(\vec{q},\rho_0) . \quad (22)$$

$G_s^{-1}(\vec{q},\rho_0)$ can be easily obtained from Eq. (9). It is obvious that $G_s^{-1}(\vec{q};\rho_0)$ is a non-negative quantity and that

$$\mathcal{G}_{\text{intra}}(\vec{q};\rho_0) > \mathcal{G}_{\text{inter}}(\vec{q};\rho_0) .$$

Thus it is possible to satisfy the condition expressed in Eq. (22) for some wave vector q and concentration ρ_0, and whenever that happens the ground state of the system will be a VDW state.

Stern has evaluated the noninteracting response function of a two-dimensional system.[7] Using his expression for $G_s^{-1}(\vec{q};\rho_0)$ and Hubbard approximation for local-field correction, we find that for $q < 2q_F$ the VDW instability condition in $Si(100)/SiO_2$ becomes $4a_B{}^{*-1} \geq (q^2+q_F^2)^{1/2}$, where $a_B{}^*$ is the effective Bohr radius of the system. This condition can be satisfied for a wide range of densities and wave vectors.

Overhauser has suggested that the optimum q at which an exchange instability manifests itself is close to $2q_F$.[8] In other words, the total response function of the system should exhibit at least a peak around $q = 2q_F$. Since both $G_s^{-1}(\vec{q};\rho_0)$ and the Hubbard approximation for local-field correction show no structure around $2q_F$, one would not expect a peak in the response function around $q = 2q_F$. Should one assume that the particles respond to effective field as free particles, the only way in which one can obtain a peak at $q = 2q_F$ is by constructing a local-field correction having a maximum at that particular wave vector. For example, in a three-dimensional (3D) electron gas the local-field correction of Geldart and Taylor exhibits a structure at $q = 2q_F$.[9]

In the absence of translationl invariance, one needs to evaluate the functional $G[\vec{r},\vec{r}';\rho]$. Knowing the eigenfunctions and eigenvalues of Schrödinger equation for the paramagnetic state, it is straightforward to obtain the kinetic part of $G[\vec{r},\vec{r}';\rho]$ from Eq. (9). The exchange and correlation contribution to $G[\vec{r},\vec{r}';\rho]$, is obtained from Eq. (19) by taking its Fourier transform with respect to q and then replacing ρ_0 by $\rho(\vec{r})$. Having obtained $G_s[\vec{r},\vec{r}';\rho]$ and $G_{xc}[\vec{r},\vec{r}';\rho]$, one can evaluate the right-hand side of Eq. (7) for the specific form of $\Delta\rho(\vec{r})$, given by Eq. (20). If the right-hand side is negative, the ground state of the system will be a VDW state and not a paramagnetic state.

HARTREE-FOCK APPROACH

Within the Hartree-Fock (HF) approximation, Chan and Heine have obtained the condition for an SDW or CDW instability.[4] These authors note that the condition for a CDW instability cannot be satisfied unless there is a periodic lattice distortion (PLD). Since in the VDW state the two charge-density waves are out of phase, the net lattice distortion in the system is zero. Thus, one would expect that the direct Coulomb energy should remain the same as in the paramagnetic state. In this respect, a VDW state is very much like a SDW state and, therefore, the condition for the existence of a VDW state is expected to be similar to that for an SDW instability.

The Hartree-Fock energy of the system can be simply written

$$E(\phi)=\sum_{\sigma}\int d\vec{r}\left[\frac{p^2}{2m}+V_L(\vec{r})\right]\langle\phi|\psi_\sigma^\dagger(\vec{r})\psi_\sigma(\vec{r})|\phi\rangle+\sum_{\sigma\sigma'}\int d\vec{r}\int d\vec{r}\,'\,U(\vec{r},\vec{r}\,')\langle\phi|\psi_\sigma^\dagger(\vec{r})\psi_\sigma(\vec{r})|\phi\rangle$$
$$\times\langle\phi|\psi_{\sigma'}^\dagger(\vec{r}\,')\psi_{\sigma'}(\vec{r}\,')|\phi\rangle-\sum_{\sigma\sigma'}\int d\vec{r}\int d\vec{r}\,'\,V(\vec{r},\vec{r}\,')\left|\langle\phi|\psi_\sigma^\dagger(\vec{r})\psi_{\sigma'}(\vec{r}\,')|\phi\rangle\right|^2 , \tag{23}$$

where $|\phi\rangle$ is the Hartree-Fock ground state of the system. In Eq. (23), $\psi_\sigma(\vec{r})$ is a field operator, $V_L(\vec{r})$ is the lattice potential, $U(\vec{r},\vec{r}\,')$ is the direct Coulomb potential, and $V(\vec{r},\vec{r}\,')$ is the exchange potential.

The Hartree-Fock ground state is acceptable only if the energy corresponding to it is minimum with respect to variations in $|\phi\rangle$. However, the HF energy is only assured to be stationary with respect to the variations in $|\phi\rangle$. Thus, it is conceivable that the paramagnetic state obtained from the solution of HF equations may not be the ground state of the system.

In order to find the condition for a VDW instability, we shall examine the behavior of energy of a paramagnetic state in its neighborhood. Let us assume that $\phi^{o}_{\vec{K},\nu,\sigma}(\vec{r})$ represents a Block orbital of an occupied state in valley ν and spin σ. We can mix the occupied orbitals $\phi^{o}_{\vec{K},\nu,\sigma}(r)$ with unoccupied orbitals $\phi^{e}_{\vec{K}+\vec{q},\nu,\sigma}(\vec{r})$ to form a new set of orthonormal orbitals:

$$\psi^{\alpha}_{\vec{K},\nu,\sigma}(\vec{r})=\phi^{o}_{\vec{K},\nu,\sigma}(\vec{r})\cos\theta_{\vec{K},\nu}+\phi^{e}_{\vec{K}+\vec{q},\nu,\sigma}(\vec{r})\sin\theta_{\vec{K},\nu}$$

and (24)

$$\psi^{\beta}_{\vec{K},\nu,\sigma}(\vec{r})=-\phi^{o}_{\vec{K},\nu,\sigma}(\vec{r})\sin\theta_{\vec{K},\nu}+\phi^{e}_{\vec{K}+\vec{q},\nu,\sigma}(\vec{r})\cos\theta_{\vec{K},\nu} ,$$

where the parameter $\theta_{\vec{K},\nu}$ is a measure of mixing between the occupied and unoccupied orbitals. Since we are interested in examining the change in energy in the neighborhood of paramagnetic state, we shall be concerned with only small values of $\theta_{\vec{K},\nu}$. It is easy to show that the new set of orbitals $\psi^{\alpha}_{\vec{K},\nu,\sigma}(\vec{r})$ and $\psi^{\beta}_{\vec{K},\nu,\sigma}(\vec{r})$ give rise to a CDW in each valley. In order to have two canceling CDW's we should impose the condition

$$\theta_{\vec{K},\nu}=\xi_\nu\theta_{\vec{K}} , \tag{25}$$

where $\xi_\nu=\pm1$ for valleys 1 and 2, respectively. To obtain the condition for the existence of a VDW state, we need to find the HF energy in the deformed state $|\bar{\bar{\psi}}\rangle$, which consists of orbitals $\psi^{\alpha}_{\vec{K},\nu,\sigma}$ and $\psi^{\beta}_{\vec{K},\nu,\sigma}$. For small values of $\theta_{\vec{K},\nu}$, the difference of the HF energy between the deformed state $|\bar{\bar{\psi}}\rangle$ and the paramagnetic state $|\phi\rangle$ has only quadratic terms in $\theta_{\vec{K},\nu}$; the linear terms in $\theta_{\vec{K},\nu}$ vanish because of the stationary property of the Hamiltonian. Treating the difference in energy as an eigenmode problem, it is easy to show that the instability toward the formation of a VDW state occurs only if

$$V_{\vec{q}}^{\text{intra}}-V_{\vec{q}}^{\text{inter}}\geq 1/\chi_0(\vec{q}) , \tag{26}$$

where $V_{\vec{q}}^{\text{intra}}$ and $V_{\vec{q}}^{\text{inter}}$ are the local values of intravalley and intervalley exchange energies and

$$\chi_0(\vec{q})=\sum_{\vec{K}}\frac{f_{\vec{K}}-f_{\vec{K}+q}}{\epsilon_{\vec{K}+q}-\epsilon_{\vec{K}}} . \tag{27}$$

In Eq. (27), $\epsilon_{\vec{k}}$'s are the single-particle energies in the HF approximation and $f_{\vec{K}}$ is the Fermi-distribution function. Since both the numerator and denominator in Eq. (27) have the same signs, $\chi_0(\vec{q})$ is always a non-negative quantity. Furthermore, the intravalley exchange is always expected to dominate the intervalley exchange term. Thus, within the HF approximation the VDW state will constitute the ground state of the system, if the difference between the intravalley and intervalley exchange is greater than or equal to the inverse of the single-particle response function of the paramagnetic state.

CONCLUSION

Using the density-functional formalism, we have shown that under certain conditions the ground state of a two valley system will consist of two identical charge-density waves that are completely out of phase with each other. Such a state of the system will not be accompanied by any periodic lattice distortions. The instability condition for valley-density waves depends critically on the magnitude of intravalley and intervalley exchange and correlation effects. We have shown that the valley-density waves form the ground state only when the difference between the intravalley and intervalley exchange and correlation effects become equal to or exceed the inverse of single-particle response function for the paramagnetic state. A similar result is also obtained in the Hartree-Fock approximation.

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