

ally insufficient for a higher order approximation. But for the central part of the Na-Cs composition range it is meaningful to take into account also the curvature of the older ρ -versus- T results. Then the values of $d\rho/dT$ given in Ref. 4 and repeated in Fig. 1 of this paper can be shown to apply effectively to temperatures lower than 100°C, down to 80°C. The discrepancy for pure cesium cannot be explained in this way.

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Nonlocal Exchange and Correlation Effects on the Fermi Surface of Metals*

Mark Rasolt and S. H. Vosko

Department of Physics and Erindale College, University of Toronto, Toronto, Ontario, Canada M5S 1A7

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The inhomogeneous-electron-gas theory of Hohenberg, Kohn, and Sham has been used to investigate the effects of nonlocal exchange and correlation on the Fermi surface of a simple cubic metal. The periodic lattice effects were represented by a realistic simple model pseudopotential. We find that the nonlocal terms substantially reduce the maximum Fermi-surface distortions, as experiments suggest.

Comparisons of experimental Fermi-surface (FS) distortions with first-principles calculations of these distortions result in significant discrepancies. A particularly striking example is the recent work of Janak, Williams, and Moruzzi,¹ who examined the effect of local exchange and correlation potentials on the FS of Cu. None of the potentials based on fundamental theory (Slater,² Kohn and Sham,³ and Hedin and Lundqvist⁴) resulted in agreement with experiment. It is especially disappointing that the local potential of Hedin and Lundqvist⁴ leads to no improvement over the simple local theory.³

There have been numerous calculations of the band structures and Fermi surfaces of the alkali metals. (For a recent review see Lee.⁵) The general tendency is for the theory to produce maximum distortions which are considerably larger than those observed. For example, Lawrence⁶ found that the FS of Cs touched the zone

boundary in the (1, 1, 0) direction. Other workers⁵ have found maximum distortions of order a factor 2 too large. In Li the maximum calculated distortions⁵ are again a factor 2 larger than the most recent experimental value.⁷ All the above first-principles calculations share one common approximation: They calculate the FS with a local exchange-correlation potential. Kane⁸ has recently investigated the effects of nonlocal exchange and correlation in the band structure of Si and found them to be substantial.

The primary objective of this work is to show by direct calculation with a realistic model that the FS given by a nonlocal many-body-type theory is significantly different than the corresponding local theory, both treated within the framework of the Hohenberg-Kohn-Sham^{3,9,10} theory of an inhomogeneous electron gas.

The general equation from which elementary excitations E_k of quasiparticles, and hence the corresponding FS, can be determined is¹⁰

$$(\hbar^2/2m) \nabla^2 \psi_{\mathbf{k}}(\mathbf{r}) + \int d^3r' \Sigma(\mathbf{r}, \mathbf{r}'; E_{\mathbf{k}}) \psi_{\mathbf{k}}(\mathbf{r}') = E_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}), \quad (1)$$

where Σ is the so-called mass operator. To exhibit explicitly the local and nonlocal components of Σ , write

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = V(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') + M(\mathbf{r}, \mathbf{r}'; E), \quad (2)$$

where $V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})$, $V_{\text{ext}}(\mathbf{r})$ is the applied external potential, $V_{\text{H}}(\mathbf{r})$ is the electrostatic potential (Hartree field) of the electrons, and M is the nonlocal (exchange and correlation) part of Σ

whose structural form is given by many-body theory.¹¹

The central result of the Hohenberg and Kohn⁹ theory is that any property of the ground state of a system of electrons is a unique functional of the density $n(\vec{r})$ of the ground state. In particular, Σ is such a functional. Thus, we turn our attention to finding $n(\vec{r})$ via the Kohn and Sham³ theory, which also gives a local theory for the determination of the FS. According to Kohn and Sham, $n(\vec{r})$ is obtained by finding the self-consistent solution of the equations

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + v_{xc}(\vec{r})\right)\varphi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\varphi_{\vec{k}}(\vec{r}), \quad (3)$$

$$n(\vec{r}) = \sum_{\vec{k}} |\varphi_{\vec{k}}(\vec{r})|^2 \theta(K_F - k), \quad (4)$$

where $V(\vec{r})$ has been defined in Eq. (2),

$$v_{xc}(\vec{r}) \equiv \delta E_{xc}[n]/\delta n(\vec{r}), \quad (5)$$

$E_{xc}[n]$ is the exchange and correlation functional which in principle includes all many-body effects, and $K_F \equiv K_F(\hbar)$ is the FS that encloses the correct number of electrons.

At this junction two remarks are in order:

(a) The $\varphi_{\vec{k}}(\vec{r})$ and $\epsilon_{\vec{k}}$ of Eq. (3) do not represent the quasiparticle states or excitation energies. Thus, it would be extremely fortuitous for Eq. (4) to give the correct FS [the solution of Eq. (1)

will]. (b) The self-consistent solution of Eqs. (3) and (4) would give the density $n(\vec{r})$ exactly if $E_{xc}[n]$ were known. It is this latter property which we wish to now exploit.

We emphasize that our interest is strictly the effect of nonlocality of M on the FS. Thus, we do not wish to investigate the effect of the local Hartree field $V_H(\vec{r})$, nor become involved with complicated self-consistent band-structure calculations. This is achieved as follows: Instead of starting with an external potential $V_{ext}(\vec{r})$ in Eq. (3) and constructing the corresponding self-consistent density distribution, the process is reversed; i.e., construct the external potential corresponding to a given self-consistent density distribution.¹² In other words, solve the equation

$$[-(\hbar^2/2m)\nabla^2 + V_m(\vec{r})]\varphi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\varphi_{\vec{k}}(\vec{r}), \quad (6)$$

where $V_m(\vec{r})$ is some (non-self-consistent) periodic model pseudopotential appropriately chosen, and construct the density according to Eq. (4). Equation (6) is easily solved since it is not a self-consistent equation and more important from our viewpoint gives the *exact density* $n(\vec{r})$ to be used in Eqs. (1) and (2).

The effect on $\Sigma(\vec{r}, \vec{r}'; E)$ of introducing $V_m(\vec{r})$ in Eq. (6) can be obtained by comparing Eqs. (3) and (6). Clearly

$$V(\vec{r}) = V_m(\vec{r}) - v_{xc}(\vec{r}), \quad (7)$$

$$\Sigma(\vec{r}, \vec{r}'; E) = V_m(\vec{r})\delta(\vec{r} - \vec{r}') + M(\vec{r}, \vec{r}'; E) - v_{xc}(\vec{r})\delta(\vec{r} - \vec{r}'). \quad (8)$$

[At first sight Eqs. (2) and (8) might appear contradictory to the theorem that Σ is a unique functional of n . This is however immediately resolved by recalling that $V(\vec{r})$ of Eq. (2) is also a unique functional of n .⁹] By substituting Eq. (8) in Eq. (1), we find

$$H_0\psi_{\vec{k}}(\vec{r}) + \hat{V}_p\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\psi_{\vec{k}}(\vec{r}), \quad (9)$$

where H_0 is the Hamiltonian in Eq. (6) and

$$\hat{V}_p\psi_{\vec{k}}(\vec{r}) \equiv \int d\vec{r}' [M(\vec{r}, \vec{r}'; E_{\vec{k}}) - v_{xc}(\vec{r}')\delta(\vec{r} - \vec{r}')] \psi_{\vec{k}}(\vec{r}'). \quad (10)$$

Equation (9), like Eq. (1), is exact; however, because of the complicated form of M neither is tractable without approximations which we now consider.

Sham and Kohn¹⁰ (SK) have suggested a number of approximations for M based on its functional dependence on $n(\vec{r})$. Their first approximation is

$$M(\vec{r}, \vec{r}'; E_{\vec{k}}) \approx M_h(\vec{r} - \vec{r}'; E_{\vec{k}} - V(\vec{r}_0); n(\vec{r}_0)), \quad (11)$$

where M_h is the self-energy operator of a uniform electron gas of density $n(\vec{r}_0)$, with $\vec{r}_0 \equiv (\vec{r} + \vec{r}')/2$. To remove the explicit dependence of $V(\vec{r}_0)$ in Eq. (11) and for FS calculations to remove the $E_{\vec{k}}$ dependence in M_h , SK use the relation

$$\mu = V(\vec{r}_0) + \mu_h(n(\vec{r}_0)), \quad (12)$$

where μ is the chemical potential and $\mu_h(n)$ is the chemical potential of a uniform gas of density n

with $V=0$. This yields

$$M(\vec{r}, \vec{r}'; E_{\vec{k}}) \approx M_h(\vec{r} - \vec{r}'; E_{\vec{k}} - \mu + \mu_h(n(\vec{r}_0)); n(\vec{r}_0)). \quad (13)$$

Since our objective is to solve Eq. (9) for $E_{\vec{k}}$ on the FS, i.e., $E_{\vec{k}} = \mu$, the $E_{\vec{k}}$ dependence on the right-hand side of Eq. (13) is removed so that for our purposes

$$M(\vec{r}, \vec{r}'; E_{\vec{k}}) \approx M_h(\vec{r} - \vec{r}'; \mu_h(n(\vec{r}_0)); n(\vec{r}_0)). \quad (14)$$

The particular form for M_h depends on the choice for the many-body contributions.

The corresponding approximation for $v_{xc}(\vec{r})$ is

$$v_{xc}(\vec{r}) \approx d(n\epsilon_{xc}(n))/dn, \quad (15)$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron of a uniform gas with density $n(\vec{r})$ and for consistency $\epsilon_{xc}(n)$ will be determined with precisely the same many-body corrections used to define M_h .

We are now in a position to define precisely what we mean by a Fermi surface derived from a local and a nonlocal theory: (a) Solve Eqs. (3) and (4) self-consistently for $\epsilon_{\vec{k}}$ and $n(\vec{r})$ with $v_{xc}(\vec{r})$ given by Eq. (15). From the $\epsilon_{\vec{k}}$'s of Eq. (3) determine the Fermi surface, which will be referred to as the local FS. (b) Use the density $n(\vec{r})$ in Eq. (14) to obtain M_h which would then be used in Eqs. (1) and (2) to determine $E_{\vec{k}}$ and the corresponding FS, which we will refer to as the nonlocal FS.

Actually, in the calculation which we present here the self-consistent calculation (a) has been replaced by Eq. (6) and the corresponding $n(\vec{r})$ it produces. The effect of nonlocality is contained in Eqs. (9) and (10), so that if the effect of nonlocality is small then \hat{V}_p of Eq. (10) will not per-

turb the local FS obtained from Eq. (6).

Noting that the model pseudopotential may be written as

$$V_m(\vec{r}) = \sum_{\vec{G}} V_m(\vec{G}) e^{i\vec{G}\cdot\vec{r}}, \quad (16)$$

where the \vec{G} 's are the reciprocal-lattice vectors, the solution for the local problem [part (a)] is obtained by expanding the wave function in plane waves (Ω is volume of the crystal),

$$\varphi_{\nu\vec{k}}(\vec{r}) = \Omega^{-1/2} \sum_{\vec{G}} A_{\vec{G}}(\nu\vec{k}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, \quad (17)$$

and substituting in Eq. (6). The energies $\epsilon_{\nu\vec{k}}$ and the expansion coefficients $A_{\vec{G}}(\nu\vec{k})$ are calculated in the standard procedure. Note that a band index and reduced zone scheme for \vec{k} has been introduced. In fact (see below), by a special choice of lattice and V_m in the model calculation presented here, this local band-structure calculation is made trivial.

The energies $E_{\vec{k}}$ for the nonlocal problem are obtained by expanding ψ in terms of $\varphi_{\nu\vec{k}}(\vec{r})$,

$$\psi_{\lambda\vec{k}}(\vec{r}) = \sum_{\nu} c_{\nu}(\lambda\vec{k}) \varphi_{\nu\vec{k}}(\vec{r}), \quad (18)$$

and substituting in Eq. (9). The energies are given by the solution of

$$\text{Det} | H_{\nu'\nu}(\vec{k}) - \delta_{\nu'\nu} E_{\vec{k}} | = 0, \quad (19)$$

$$H_{\nu'\nu}(\vec{k}) = \delta_{\nu'\nu} \epsilon_{\nu\vec{k}} + \langle \varphi_{\nu'\vec{k}} | \hat{V}_p | \varphi_{\nu\vec{k}} \rangle. \quad (20)$$

The whole nonlocal nature of the problem is now contained in the last term of Eq. (20). To evaluate this term within the approximation of Eqs. (14) and (15) we first note that

$$M_h(\vec{r} - \vec{r}'; \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) = \Omega^{-1} \sum_{\vec{p}} \tilde{M}(\vec{p}, \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) e^{i\vec{p}\cdot(\vec{r}-\vec{r}')}, \quad (21)$$

when $\tilde{M}(\vec{p}, \mu_h(n(\vec{r}_0)); n(\vec{r}_0))$ is the usual self-energy operator¹¹ in momentum-energy space for a homogeneous electron gas evaluated at $E = \mu_h(n(\vec{r}_0))$ with density $n(\vec{r}_0)$, i.e., the corresponding Fermi vector is

$$k_F(\vec{r}_0) = [3\pi^2 n(\vec{r}_0)]^{1/3}. \quad (22)$$

Then noting that the \vec{r}_0 dependence is periodic in the lattice and thus may be expressed as a Fourier series,

$$\tilde{M}(\vec{p}, \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) = \sum_{\vec{G}''} \tilde{M}'(\vec{p}; \vec{G}'') \exp(i\vec{G}''\cdot\vec{r}_0), \quad (23)$$

it is straightforward to show that

$$\langle \varphi_{\nu'\vec{k}} | \hat{V}_p | \varphi_{\nu\vec{k}} \rangle = \sum_{\vec{G}', \vec{G}} A_{\vec{G}'}^* (\nu'\vec{k}) \left[\tilde{M}'\left(\vec{k} + \frac{\vec{G}' + \vec{G}}{2}; \vec{G}' - \vec{G}\right) - v_{xc}(\vec{G}' - \vec{G}) \right]. \quad (24)$$

Equation (24) is completely general; however, $\tilde{M}(\vec{p}, E; n(\vec{r}_0))$ is, in general, very complicated¹¹ so that

we must make a definite approximation for $\tilde{M}(\vec{p}, E; n(\vec{r}_0))$. We choose the random-phase approximation (RPA) for Eq. (21) so that

$$\tilde{M}(\vec{p}, \mu_n(n(\vec{r}_0)); n(\vec{r}_0)) \approx \tilde{M}_x(\vec{p}; n(\vec{r}_0)) + \tilde{M}_{\text{RPA}}(\vec{p}, \mu_n(n(\vec{r}_0)); n(\vec{r}_0)), \quad (25)$$

where \tilde{M}_x is the Fock exchange:

$$\tilde{M}_x(\vec{p}; n(\vec{r}_0)) = -\frac{e^2 k_F}{\pi} \left[1 + \frac{k_F^2 - p^2}{2pk_F} \ln \left(\frac{k_F + p}{k_F - p} \right) \right]; \quad (26)$$

\tilde{M}_{RPA} is given by (see, for example, Hedin¹³)

$$\tilde{M}_{\text{RPA}}(\vec{p}, \mu_0; n(\vec{r}_0)) = -\frac{e^2 k_F^2}{\pi^2 p} \int_0^\infty \frac{dq}{q} \int_0^\infty dy \ln \left(\frac{[1 - (p/k_F - 2q)^2]^2 + 16y^2}{[1 - (p/k_F + 2q)^2]^2 + 16y^2} \right) \left(\frac{1}{\epsilon(q, iy)} - 1 \right), \quad (27)$$

and $\mu_0 = \hbar^2 k_F^2 / 2m$, with k_F defined in Eq. (22).

The consistent approximation for $v_{xc}(\vec{r})$, defined by $\delta E_{xc}(n) / \delta n$, when M is approximated by Eqs. (25)–(27) can easily be shown to be

$$\tilde{v}_{xc}(\vec{r}) = \tilde{M}_x(k_F; n(\vec{r}_0)) + \tilde{M}_{\text{RPA}}(k_F, \mu_0; n(\vec{r}_0)). \quad (28)$$

To avoid getting into a complicated band-structure calculation a simple cubic lattice was chosen (cube edge a) and all the Fourier coefficients in Eq. (16) were set equal to zero except for the first-nearest neighbors. The resulting pseudopotential is

$$V_m(\vec{r}) = 2V_1 \left(\cos \frac{2\pi}{a} x + \cos \frac{2\pi}{a} y + \cos \frac{2\pi}{a} z \right), \quad (29)$$

(the three-dimensional Mathieu potential) which makes Eq. (6) trivial to solve.

A variety of strengths for the Mathieu potential (different V_1 's), and a range of mean densities in the metallic regime have been considered. For each of these strengths and densities we have calculated the FS for the local theory and the effect of the nonlocal theory at a number of points on

the FS. The tendency in all cases seems to reduce substantially the radial distortions of the FS.

An example that was examined in detail is displayed in Fig. 1, where the spherical Fermi radius is denoted by K_0 and the corresponding Fermi energy $\epsilon_0 = \hbar^2 K_0^2 / 2m$. To simulate a physical situation somewhat similar to the alkali metals (e.g., Li), the lattice parameter, mean electron density, and strength of the pseudopotential were taken to be $K_0 = 0.8(\pi/a)$, $r_s = 3$, and $V_1 = \frac{15}{32} \epsilon_0$. A complete mapping of the radial distortions in the $(0, 0, 1)$ plane for the local and the nonlocal theories is plotted in Fig. 1. As clearly seen, the nonlocal effects are very large.

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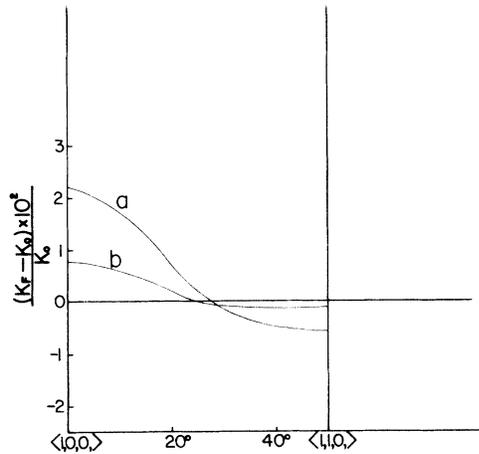


FIG. 1. The percentage of Fermi-surface distortion in the $(0, 0, 1)$ plane of a simple cubic metal: **a**, local FS; **b**, nonlocal FS.

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Polymorphism of the Mesomorphic Compound Terephthal-*bis*-Butylaniline (TBBA)

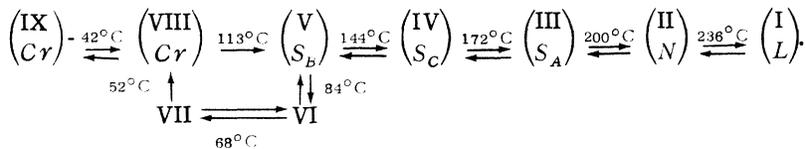
J. Doucet, A. M. Levelut, and M. Lambert

*Laboratoire de Physique des Solides, * Université Paris-Sud, 91405 Orsay, France*

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On the basis of x-ray monodomain and powder patterns, the structure of new identified terephthal-*bis*-butylaniline phases is described. These phases present a relatively high degree of order and appear as intermediate states between the smectic mesophases and the crystalline state.

TBBA (terephthal-*bis*-butylaniline) is known to present four stable liquid crystalline modifications, three of them being smectic mesophases: S_A , S_C , S_B .¹ Recently, it has been pointed out^{2,3} that two metastable phases appear when the S_B phase is cooled below 84°C, and before reaching the crystalline state. Moreover, we have identified two different crystalline states. The various transitions are shown here:



The different phases have thus been classified: TBBA I is the isotropic liquid and TBBA IX the low-temperature crystalline phase. The structure of TBBA V has already been described in a previous paper⁴ and it appears to be very similar to the structure of some of the plastic crystals: In short, no long-range order exists in the direction of the molecular axes; however, each smectic layer is relatively well ordered and the mass centers of the molecules build a "local" monoclinic lattice,⁵ with the c axis parallel to the molecules and a centered C face. It has also been shown that the difference between the two reticular spacings (110) and (200) is, in fact, very small, and the intersections of the molecular axes with a plane perpendicular to their directions approximately form a hexagonal lattice. From this experimental observation, and since a critical change in the lateral order of the parallel adjacent molecules occurs,⁶ it was suggested that the transition from the solid phase into the S_B phase was directly connected with a correlated motion of the molecules around their long axes. This motion, which explains the pseudohexagonal symmetry, has recently been observed in the S_B phase by means of NMR ex-

periments.²

In this Letter, we report new results concerning the structures of TBBA VI and VII modifications, yielded by x-ray experiments which were performed by using both powder and single-domain samples. It was relatively easy to obtain single domains of the different phases: A single crystal of the crystalline phase VIII, at room temperature, was progressively transformed into a single domain of modifications V, VI, VII, by successive heating and cooling.

Powder patterns were recorded by using a Guinier camera equipped with a heating stage⁷ and a focused monochromatic beam (crystal-reflected $\text{Cu } K\alpha_1$ radiation). The results of the analysis of the powder patterns performed with a Joyce microdensitometer MK III C are given in Fig. 1.

The main results are here reported: (a) The crystalline state is characterized by a large number of diffraction rings and mostly by large-angle rings which do not exist in patterns corresponding to the phases V, VI, and VII. The three phases present a "local" order rather than a long-range order. (b) These rings have been indexed on the basis of a monoclinic lattice suggested by