Electronic phase transitions due to correlation effects

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The part of the electron-electron interaction which stems from low-lying excitations of the ion cores and which is ignored in the ordinary band theory can lead to electronic phase transitions accompanied by sharp anomalies in the electronic and lattice properties of metals. Manifestations of these anomalies in transition metals and alloys and also upon electronic phase transitions in cesium are discussed.

It is generally believed that in most crystalline metals and semiconductors the electron-electron interaction, although not weak, does not cause the properties to differ radically from the band-theory predictions.[1] There are effects, however, in which this interaction is extremely important, e.g., superconductivity and the Kondo effect. In the present letter we show that correlation effects lead to some qualitatively new results (in comparison with those found in the single-electron approximation) in the case in which there is a narrow peak in the state density $N(E)$ near the Fermi energy

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E_F or in the case in which there are low-lying excited states of the ion cores of the metal or impurities. Under these conditions there is an additional electron-electron interaction (that reduces the Coulomb repulsion), which has been discussed by Geĭlikman[2] in connection with the problem of high-temperature superconductivity. In contrast with Ref. 2, we show here that these effects lead to some important nonanalytic additions to the electron and phonon spectra and thus to anomalies of the electronic-phase-transition type in the properties of metals.

Calculations on the band structure of transition metals[3] and, especially, their alloys[4] show that there are extremely narrow peaks in $N(E)$ near E_F. As a narrow peak in $N(E)$ approaches E_F, the transitions associated with this peak become progressively more important in the dielectric constant. The correction to the electron-electron interaction, attractive in nature, is described by $\delta\hat{V}_{\text{eff}} = -v_c\delta\hat{\Pi}v_c$, where $\delta\hat{\Pi}$ is the contribution of the corresponding transitions to the polarization operator, and v_c is the Coulomb interaction screened by the contributions of other transitions. Corresponding to this correction is a correction to the thermodynamic potential,

$$\delta\Omega = -\frac{T^2}{2}\sum_{\epsilon,\,\epsilon'} e^{i\epsilon 0}\, e^{i\epsilon' 0}\int d\mathbf{r}d\mathbf{r}'G(\mathbf{r},\mathbf{r}',i\epsilon)G(\mathbf{r}',\mathbf{r},i\epsilon')\,\delta V_{\text{eff}}(\mathbf{r},\mathbf{r}',i\epsilon - i\epsilon'), \quad (1)$$

where $\hat{G}$ is the single-electron Matsubara Green's function in the lattice potential, and T is the temperature. It follows from the calculation of (1) that in the case $\Delta \ll E_F$, where Δ is the distance from the center of the peak to E_F, a singular contribution Ω_s arises. At $T \ll \Delta$, it is described by

$$\Omega_s(T) = -\sum_{\lambda,\,\lambda'} f_{\lambda'}(1-f_\lambda)\left[(\epsilon_\lambda - \epsilon_{\lambda'})\ln|\epsilon_\lambda - \epsilon_{\lambda'}| + \frac{\pi^2 T^2}{3(\epsilon_\lambda - \epsilon_{\lambda'})}\right] \times \sum_{\mu,\,\nu}\delta(\epsilon_\mu - E_F)\delta(\epsilon_\nu - E_F) \times |<\nu\lambda|v_c|\mu\lambda'>|^2. \quad (2)$$

Here f_λ is the Fermi distribution function that depends on the energy ϵ_λ, and $|\lambda\rangle$ is one of the wave functions of the single-electron problem. In the limit $\Delta \to 0$, we see that there is a singularity $\sim\Delta^2\ln|\Delta|$ in Ω_s; this singularity is cut off at $\Delta \sim \Gamma$, where Γ is the width of the peak ($\Gamma \ll E_F$). In the elastic moduli c_{ik} there is accordingly a singularity $\sim\ln|\Delta|$, and in the thermal-expansion coefficient there is a singularity Δ^{-1}. The electronic and lattice contributions to the specific heat increase with decreasing Δ in proportion to $-\ln|\Delta|$.

The correction to the exchange-correlation energy in (2) gives rise to a singular contribution to the Stoner exchange parameter, which can be calculated by the method of Ref. 5. The corresponding contribution to the paramagnetic susceptibility $\chi(T)$ can be written $\chi_s(T) = \chi_s(0) + \delta\chi_s(T)$ for $\Delta \ll E_F$ we have $\chi(0) \sim -\ln|\Delta|$, while $\delta\chi_s(T)$ increases with increasing T in proportion to T^2/Δ^2 at $T \ll \Delta$, or it falls off in proportion to Δ^2/T^2 at $T \gtrsim \Delta$.

The anomalies in Ω_s lead to nonanalytic contributions to the generalized susceptibility $\hat{\chi} = \delta^2\Omega/\delta\hat{V}\delta\hat{V}$ ($\hat{V}$ is the external potential), which directly determines the

phonon spectrum[6] $\omega_{\nu\mathbf{q}}$. It follows from (2) that the singular contribution $\omega_{\nu\mathbf{q}}^{(s)} \sim \Delta \ln|\Delta|$ corresponds to a softening of the "overall" phonon spectrum, in contrast with the anomalies in $\omega_{\nu\mathbf{q}}$ which arise upon a change in the topology of the Fermi surface and which are analyzed in Ref. 7. The corresponding contribution to the free energy of the phonon subsystem, F_{ph}, including the zero-point vibration energy, is $\sim\Delta \ln|\Delta|$. This result means that although F_{ph} is small, proportional to the small parameter θ_D/E_F (θ_D is the Debye temperature), the anharmonic contributions to the pressure p and to $c_{ik}(T)$ should be significant because of their pronounced singularity.

The anomalies found in the thermodynamic characteristics of the metal are related to singularities in the electron energy spectrum, as can be seen from the expression for the singular contribution to the mass operator, $\hat{\Sigma}_s = \delta\Omega_s/\delta\hat{G}$, which depends strongly on the energy E and which has singularities $\sim(E-E_c)\ln|E-E_c|$ at $E_c = E_F \pm \Delta$. As a filled level E_λ approaches a vacant level E_λ, (or in the case of two narrow bands), all the singularities are intensified: $\Omega_s \sim -\Delta \ln|\Delta|$ and $\Sigma_s \sim \ln|(E-E_F+\Delta)/(E-E_F-\Delta)|$. It follows that at $E = E_F \pm \Delta$ the electron spectrum changes substantially, and an energy gap forms. Since the correction to the chemical potential has the behavior $\sim\ln|\Delta|$, E_F shifts toward this "gap." In this case, of course, the first correction in (2) is not sufficient. This circumstance should be regarded as a tendency for a possible change in the initial increase, $N(E)\sim\Delta^{-1}$, to a sharp decrease.

These anomalies are of the nature of an electronic phase transition. Such changes are usually associated with changes in the topology of the Fermi surface[1]; there are anomalies in the thermodynamic and kinetic characteristics.[8,9] Anomalies of both types apparently occur; the effects that we are discussing here are stronger. For example, the singularity in $N(E_F)$ is of the type $\sim\ln|\Delta|$, instead of $\Delta^{1/2}$. In the limit $\Delta\to 0$, the bulk modulus can formally go negative, indicating a first-order transition.

These arguments may explain the jump in the volume and the anomalies in the Grüneisen parameter $\gamma(T)$ upon the electronic phase transition in Cs near $p_c \approx 43$ kbar (Ref. 10). This transition apparently occurs because a narrow d-state peak approaches E_F; we know[11] that this peak is near E_F even at $p = 0$. It follows from the estimates above that the parameter $\gamma \sim [(1/\Delta)(d\Delta/dp)]$; ($d\Delta/dp < 0$; the peak comes closer during compression) falls off rapidly as $p\to p_c$ and then increases.

As mentioned earlier, the anomalies associated with the change in the topology of the Fermi surface, which have been called upon[12] in order to explain the electronic phase transition in cesium, are weaker. In particular, they apparently could not explain the sharp anomalies observed experimentally in the resistance of cesium.[13]

These anomalies may also be associated with magnetic phase transitions, as follows from the logarithmic increase in the Stoner exchange parameter I as $\Delta\to 0$, as shown above. In nearly ferromagnetic metals of the Pd type, even a slight increase in I can lead to a ferromagnetism. Such an increase in I occurs when impurities are added to quasilocal levels near E_F of the host metal. It is possible that this argument could explain the transition of Pd to a ferromagnetic state caused by just a 2% admixture of nickel.[14]

The phenomena discussed here may be observed in alloys as well as pure metals.

It was hypothesized in Ref. 15, on the basis of an analysis of experimental data on the alloys of $3d$ metals with titanium, that the narrow impurity d bands are slightly hybridized with electronic states of titanium. At a certain critical impurity concentration, according to Ref. 15, a Mott-Hubbard transition occurs in the impurity subsystem. According to the hypothesis and the arguments of the present letter, the pronounced anomalies in these alloys at $x \approx x_c$, e.g., a sharp decrease in the state density,[15] and the anomalies in the elastic properties[16] can be attributed to the convergence of two narrow peaks that belong to the upper and lower Hubbard subbands.

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