Structural and magnetic instabilities in a twofold-degenerate band

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The question of coexistence of cubic-to-tetragonal structural transition and both paramagnetic-to-ferromagnetic and -antiferromagnetic transitions in a twofold-degenerate band is studied under the Hartree-Fock approximation of the Hubbard Hamiltonian. The phase diagrams for both the transitions have been worked out at $T=0$ coupling of electrons to the tetragonal shear mode. The results show the absence of tetragonal and ferromagnetic states simultaneously for any filling of the band whereas both tetragonal and antiferromagnetic transitions are possible if the splitting of the center of gravity of the band to the tetragonality is more than that due to the antiferromagnetic ordering.

I. INTRODUCTION

Many intermetallic compounds undergo structural transition from cubic to tetragonal symmetry on cooling.[1–5] The transition is favorable for the system where the Fermi level in the cubic phase lies in a narrow degenerate band, e.g., d band. The coupling of lattice with local electron density lifts the degeneracy of the band and the electron redistribution between the split bands causes the lowering of electronic band energy. The transition occurs when the decrease of the band energy is more than the increase of elastic energy due to tetragonal distortion. Structural transition due to this band Jahn-Teller mechanism has been studied by Pytte[6] for the threefold band and Ghatak *et al.*[7] for the twofold (e_g) band. As the lowering of electronic energy depends on the density of states at the Fermi level in cubic phase, the transition is mostly favored for the narrow-band solid. It is also known that the itinerant magnetic phase appears for the solids with the narrow band and, therefore, it calls for analysis of the coexistence of magnetic and distorted phases.

The question of the coexistence becomes more relevant with reference to the observed strong decrease of cubic to tetragonal transition temperature with external magnetic field in La_3S_4 and La_3Se_4.[8] As the magnetic field induces uniform moment, it appears from above that the ferromagnetism would inhibit the distortion. Below, we examine the coexistence of magnetic and distorted phases at $T=0$ K in a system with the Fermi level lying in the twofold (e_g) band.

II. MODEL

We consider the case of the twofold degenerate e_g band in presence of electron-lattice coupling. The Hamiltonian for such a case can be written as

$$H=H_e+H_L+H_{e\text{-}L} \ . \tag{1}$$

H_e, being essentially the Hubbard Hamiltonian for electrons in a twofold-degenerate band in a rotationally invariant form in the spin space:[9]

$$H_e=\sum_{\vec{K},\alpha,\sigma}(\epsilon_{\vec{K}\alpha\sigma}-\mu)C^{\dagger}_{\vec{K}\alpha\sigma}C_{\vec{K}\alpha\sigma}+U\sum_{i,\alpha}\hat{n}_{i\alpha+}\hat{n}_{i\alpha-} + \left[U'-\frac{J}{2}\right]\sum_{i,\sigma}\hat{n}_{i1\sigma}\hat{n}_{i2\sigma'}-2J\sum_i\vec{S}_{i1}\cdot\vec{S}_{i2} \ , \tag{2}$$

where $\epsilon_{\vec{K}\alpha\sigma}$ is the energy of electron with momentum $\vec{K}$ and spin σ in αth ($\alpha=1,2$) band and $\hat{n}_{\vec{K}\alpha\sigma}=C^{\dagger}_{\vec{K}\alpha\sigma}C_{\vec{K}\alpha\sigma}$ is the number operator. The on-site intraorbital and interorbital Coulomb repulsions are U and U', respectively, and J is the exchange integral. The chemical potential is represented by μ, H_L represents the lattice energy corresponding to the tetragonal strain

$$H_L=\tfrac{1}{2}NC_0e^2 \ , \tag{3}$$

where elastic constant $C_0=(\frac{3}{2})(C_{11}-C_{12})$ and N, being the number of atoms. The last term is electron-lattice coupling which is responsible for band Jahn-Teller (JT) effect,[6,7]

$$H_{e\text{-}L}=Ge\sum_{i,\sigma}(\hat{n}_{i2\sigma}-\hat{n}_{i1\sigma}) \ . \tag{4}$$

Here, the lattice is coupled to the electron through the difference of population of two orbitals, and G is the relevant electron-phonon coupling constant.[7] In the following Hamiltonian H_e is treated in the Hartree-Fock approximation. In order to study the interplay between different phases we define order parameters as

$$n_2-n_1=n\delta \ , \tag{5}$$

$$n_+-n_+=nm \ , \tag{6}$$

where $n_{2,1}$ refers to average occupation per atom of band 2 and 1, respectively, and n_+, to that of up- and down-spin bands. The average occupation per atom is $n=n_2+n_1=n_++n_-$.

The parameter δ is related to strain through $\delta = C_0 e/Gn$ and thus is a measure of tetragonality, e and m is uniform magnetization. The phases are then characterized by (1) cubic paramagnetic (CP): $\delta = m = 0$, (2) cubic-ferromagnetic (CF): $\delta = 0$; $m \neq 0$, and (3) tetragonal paramagnetic (TP): $\delta \neq 0$; $m \neq 0$. To characterize the antiferromagnetic or spin-density wave (SDW) with wave vector, $Q = \pi/a$, a being lattice constant we define an order parameter:

$$b_{\alpha\sigma} = \sum_{\vec{K}} \langle C_{\vec{K}+\vec{Q},\alpha\sigma} C_{\vec{K}\alpha\sigma} \rangle , \tag{7}$$

we also take

$$n_{\alpha\sigma} = n_{\alpha-\sigma} = n/2 \quad \text{and} \quad b_{\alpha\sigma} = -b_{\alpha-\sigma} = b_\alpha \tag{8}$$

to have maximum amplitude of SDW and zero amplitude of charge-density wave vector $\vec{Q}$. The fractional moment amplitude m_Q per atom is then related to b_α through the relative $nm_Q = \sum_\alpha b_\alpha$. Therefore, the nonvanishing values of b and δ determines the tetragonal-antiferromagnetic (TAF) phase. Below, we consider the situations at $T=0$ separately.

III. PHASE DIAGRAM AT $T=0$

A. Tetragonal and ferromagnetic phase

In the Hartree-Fock approximation, the Hamiltonian (2) reduces to

$$H_{\rm HF} = \sum_{\vec{K},\alpha,\sigma} E_{\vec{K}\alpha\sigma} \hat{n}_{\vec{K}\alpha\sigma} + E_{\rm HF} . \tag{9}$$

The energies $E_{\vec{K}\alpha\sigma}$ for four bands are given by

$$\begin{aligned} E_{\vec{K}1\pm} &= \epsilon_{\vec{K}} - \mu + Ge + (U-5J)\frac{n\delta}{4} \pm \frac{U+J}{4} nm , \\ E_{\vec{K}2\pm} &= \epsilon_{\vec{K}} - \mu - Ge - (U-5J)\frac{n\delta}{4} \pm \frac{U+J}{4} nm . \end{aligned} \tag{10}$$

The constant shift of all bands by $(3U-5J/4)n$ does not play any role in determining the phases, and, therefore, will not be considered below. Due to strain and consequent orbital population differences the center of gravity of two bands are shifted. Similarly, the homogeneous moment splits up- $(+)$ and down- $(-)$ spin bands. The splitting of the bands appear at the same point of Brillouin zone (BZ), e.g., at $\vec{K}=0$ and two processes compete with each other. In deriving Eq. (10), U' is taken as $U-2J$ for the e_g band. The last term of Eq. (9) is given by

$$E_{\rm HF} = \tfrac{1}{8}(U+J)n^2m^2 + \tfrac{1}{8}(U-5J)\delta^2 n^2 , \tag{11}$$

where the part that is independent of order parameters is dropped in Eq. (11). The energy difference between the TF phase and CP phase can be written as

$$\Delta E = \int_{\mu_0}^{\mu_{1\pm}} + \int_{\mu_0}^{\mu_{2\pm}} \epsilon\rho(\epsilon)d\epsilon - \tfrac{1}{2}I\delta^2 - \tfrac{1}{2}jm^2 , \tag{12}$$

where $\mu_{1+} = \mu - I\delta \pm jm$ and $\mu_{2+} = \mu + I\delta + jm$ and μ and μ_0 the Fermi levels for TF and CP phases, respectively. The density of state $\rho(\epsilon)$ of subbands refers to initial CP phase. The last two terms are the consequence of the mean field approximation. The parameters I and j are given by

$$I = \tfrac{1}{4}(U - 5J + 4G^2/C_0) \quad \text{and} \quad j = \tfrac{1}{4}(U+J).$$

The occupations of subbands are then determined by the equations

$$\begin{aligned} n_{1\pm} &= \frac{n}{4}(1-\delta \pm m) = \int_{\mu_{-w}}^{\mu_{1\pm}} \rho(\epsilon)d\epsilon , \\ n_{2\pm} &= \frac{n}{4}(1+\delta \pm m) = \int_{\mu_{-w}}^{\mu_{2\pm}} \rho(\epsilon)d\epsilon . \end{aligned} \tag{13}$$

Next, we consider the simple form of density of state for $\rho(\epsilon)$ as

$$\rho(\epsilon) = \frac{3}{4W}(1 - \epsilon^2/w^2) . \tag{14}$$

Using this density of states in Eq. (13), μ's can be expressed in terms of order parameters δ and m. As δ and m are less than unity and, moreover, near the phase boundary they tend to be small, the change in Fermi energy compared to that of CP phase can be expanded in terms of δ and m. A straightforward calculation then gives the energy in terms of leading powers of m and δ:

$$\Delta E = \tfrac{1}{2}Am^2 + \tfrac{1}{4}Bm^4 + \tfrac{1}{2}Cm^2\delta^2 + \tfrac{1}{2}A_1\delta^2 + \tfrac{1}{4}B_1\delta^4 \tag{15}$$

where

$$\begin{aligned} A &= \frac{n^2}{4\rho_0}(1 - 4j\rho_0) , \\ A_1 &= \frac{n^2}{4\rho_0}(1 - 4J\rho_0) , \\ B &= \frac{n^4}{81}\left[1 - 4\left[\frac{\mu_0}{w}\right]^2 - 5\left[\frac{\mu_0}{w}\right]^4\right]\frac{1}{[1-(\mu_0/w)^2]^6} = B_1 , \end{aligned} \tag{16}$$

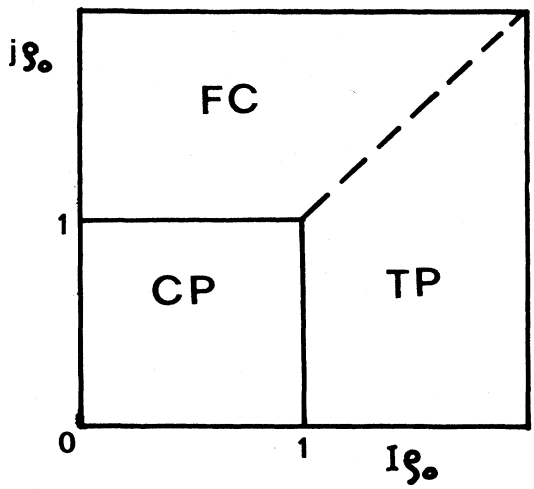

FIG. 1. Phase diagram for structural and ferromagnetic transitions. FC represents ferromagnetic-cubic phase, CP represents cubic and paramagnetic phase, TP represents tetragonal-paraphase, j and I are defined in the text.

and

$$C=3B\ .$$

Here, ρ_0 is the density of states at the Fermi level μ_0 for the cubic-paramagnetic phase. We note that the coefficients B and C are positive for all values of filling of the band as $|\mu_0/w|<1$. Therefore, the coupling between magnetization and the strain increases the energy and so the interplay is of destructive nature. This is the consequence of appearance of band splittings due to strain and magnetization at the same point $K=0$. It is also to be noted that both order parameters are of infinite wavelength. The phase diagram in j-I parameter space as follows from Eqs. (15) and (16) are shown in Fig. 1. The CF phase is given by usual Stoner criterion $(U+J)\rho_0>1$. Similarly, the TP phase boundary is determined by $(U+4J-5J)\rho_0>1$. It follows that the effect of exchange is to reduce the tendency of distortion. As the coefficient $C>B$, the tetragonal distortion and ferromagnetism are mutually exclusive of each other. Similar results have been obtained earlier for a one-dimensional system with a half-filled band where the Peierl's distortion and SDW (both with same wavelength) do not coexist.[10]

B. Tetragonal and antiferromagnetic phase

The Hartree-Fock form of the Hamiltonian $H_e+H_{e\text{-}L}$ for this case becomes

$$H_{\rm HF}=\sum_{\vec{K},\alpha,\sigma}\epsilon_{\vec{K}\alpha}C^{\dagger}_{\vec{K}\alpha\sigma}C_{\vec{K}\alpha\sigma}+\sum_{\alpha,\vec{K}}\gamma_{\alpha}(C^{\dagger}_{\vec{K}+\vec{Q},\alpha\sigma}C_{\vec{K}+\vec{Q},\alpha\sigma}+\text{H.c.})+E_{\rm HF} \tag{17}$$

with band energies

$$\begin{aligned}\epsilon_{\vec{K}1}&=\epsilon_{\vec{K}}-\mu+Ge+\frac{Un_1}{2}+\left[U-\frac{5J}{2}\right]n_2\ ,\\ \epsilon_{\vec{K}2}&=\epsilon_{\vec{K}}-\mu-Ge+\frac{Un_2}{2}+\left[U-\frac{5J}{2}\right]n_1\ ,\end{aligned} \tag{18}$$

where again the constant shift proportional to n is dropped on Eq. (18). The quantities γ's are given by

$$\gamma_{1,2}=-(Ub_{1,2+}+Jb_{2,1+})\ . \tag{19}$$

The amplitudes of the SDW for two orbitals are expected to be different in presence of tetragonal distortion. But their differences to a first order can be neglected when the band splitting due to distortion is small. Using the assumption $b_{\alpha\sigma}=-b_{\alpha-\sigma}$ [Eq. (8)], the Hamiltonian (17) for such system can be put into diagonal form

$$H_{\rm HF}=\sum_{\vec{K},\alpha,\pm}E_{\vec{K}\alpha\pm}d^{\dagger}_{\vec{K}\alpha\pm}d_{\vec{K}\alpha\pm}+E_{\rm HF} \tag{20}$$

with the band energies of four bands

$$\begin{aligned}E_{\vec{K}1\pm}&=E_{01}\pm(\epsilon^2_{\vec{K}}+\gamma^2)^{1/2}\ ,\\ E_{\vec{K}2\pm}&=E_{02}\pm(\epsilon^2_{\vec{K}}+\gamma^2)^{1/2}\ ,\end{aligned} \tag{21}$$

where

$$E_{01,2}=\epsilon_{\vec{K}1,2}-\epsilon_{\vec{K}}$$

and $\gamma=-(U+J)b$; $b=\frac{1}{2}\sum_{\alpha}b_{\alpha+}$. In deriving the above results, the complete nesting $\epsilon_{\vec{K}}=-\epsilon_{\vec{K}+\vec{Q}}$ is assumed. Due to strain, the band centers are shifted and the SDW order produces an energy gap at band centers. The operators d's is given by canonical transformation

$$\begin{aligned}d_{\vec{K}\alpha+}&=h_{\vec{K}\alpha}C_{\vec{K}\alpha}+g_{\vec{K}\alpha}C_{\vec{K}+\vec{Q},\alpha}\ ,\\ d_{\vec{K}\alpha-}&=g_{\vec{K}\alpha}C_{\vec{K}\alpha}-h_{\vec{K}\alpha}C_{\vec{K}+\vec{Q},\alpha}\ ,\end{aligned} \tag{22}$$

with

$$h_{\vec{K}\alpha}=\left[\frac{1}{2}\left[1+\frac{\epsilon_{\vec{K}}}{(\epsilon^2_{\vec{K}}+\gamma^2_{\alpha})^{1/2}}\right]\right]^{1/2},$$

$$g_{\vec{K}\alpha}=\left[\frac{1}{2}\left[1-\frac{\epsilon_{\vec{K}}}{(\epsilon^2_{\vec{K}}+\gamma^2_{\alpha})^{1/2}}\right]\right]^{1/2},$$

and the energy

$$E_{\rm HF}=\tfrac{1}{2}(U+J)b^2+\tfrac{1}{2}\left[U-\frac{5J}{2}\right]n^2\delta^2/4\ .$$

As the strain e is related through $\partial E/\partial e=0$ to the parameter δ by $e=G/C_0n\delta$, the energies $E_{\vec{K}}$'s can be expressed in terms of parameter δ and b as

$$\begin{aligned}E_{\vec{K}1\pm}&=I\delta-\mu\pm[\epsilon^2_{\vec{K}}+(U+J)^2b^2]^{1/2}\ ,\\ E_{\vec{K}2\pm}&=-J\delta-\mu\pm[\epsilon^2_{\vec{K}}+(U+J)^2b^2]^{1/2}\ .\end{aligned} \tag{23}$$

The band centers are shifted by strain and bands are split due to the presence of the SDW.

The self-consistent equation for the order parameters can be easily obtained from Eqs. (20)—(22) and are given by

$$1=-\frac{U+J}{4}\sum_{\vec{K},\alpha}\left[[f(E_{\vec{K}\alpha+})-f(E_{\vec{K}\alpha-})]\times\frac{1}{(\epsilon^2_{\vec{K}}+\gamma^2)^{1/2}}\right]_{T\to0} \tag{24}$$

for energy gap γ and

$$\Delta=I\delta=I\sum_{\vec{K},\sigma=\pm}[f(E_{\vec{K}2\sigma})-f(E_{\vec{K}1\sigma})]_{T\to0} \tag{25}$$

for splitting Δ.

The function $f(\epsilon)=(1+e^{E/k_BT})^{-1}$ is the Fermi function. The chemical potential μ is governed by electron-number conservation

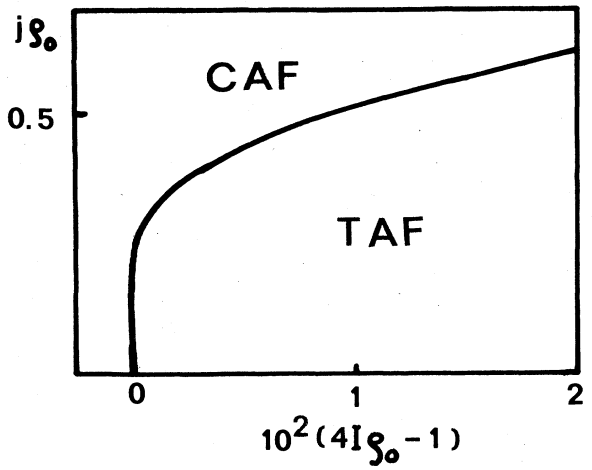

FIG. 2. Phase diagram for structural and antiferromagnetic transitions for the half-filled-band case.

$$n=\sum_{\vec{K},\alpha,\sigma} f(E_{\vec{K}\alpha\sigma}) . \tag{26}$$

These three coupled equations [(24)—(26)] are to be solved in a self-consistent fashion to obtain the phase diagram.

Below we consider the situation at $T=0$ and for the half-filled-band case which can be solved easily. As the band is symmetric around the band center, the chemical potential remains stationary for all phases and is given by $\mu=0$. The above equations (24) and (26) reduce to

$$\begin{aligned} &1=(U+J)\int_0^B \frac{\rho(\epsilon)}{(\epsilon^2+\gamma^2)^{1/2}}d\epsilon \quad \text{for } A>\gamma , \\ &\Delta=4I\int_0^{(\Delta^2-\gamma^2)^{1/2}} \rho(\epsilon)d\epsilon \quad \text{for } A>\gamma \end{aligned} \tag{27}$$

and

$$\begin{aligned} &1=(U+J)\int_0^B \frac{\rho(\epsilon)d\epsilon}{(\epsilon^2+\gamma^2)^{1/2}} \quad \text{for } \Delta<\gamma , \\ &\Delta=0 \quad \text{for } \Delta<\gamma . \end{aligned} \tag{28}$$

This means that when the half-filled system is antiferromagnetic, the tetragonality would be inhibited. On the other hand, antiferromagnetism can appear if the tetragonality already exists in the system. The existence of either tetragonality or antiferromagnetism depends on the relative magnitude of parameters I, $(U+J)$, and $\rho(\epsilon)$. The phase boundary is governed by the condition

$$\gamma_0=\Delta_0 ,$$

where subscript 0 refers to the value of 1 when the other is absent in the system. Using symmetric density of states Eq. (14), and from Eqs. (27) and (28) the above phase-boundary condition leads to an equation $(U+J)\rho_0$:

$$(U+J)\rho_0=-\frac{2}{1+2\ln(\sqrt{3}/2)(1-1/4I\rho_0)^{1/2}} \tag{29}$$

which is shown in Fig. 2.

The transition from the TAF phase across the phase boundary is of second order. The phase boundary has sharp variation around the critical value of tetragonality.

In the presence of SDW, the tetragonality decreases and for small amplitude of SDW, the strain can be expressed as

$$e=e_0(1-\gamma^2/\Delta_0^2)^{1/2} .$$

IV. DISCUSSION

In this paper, a twofold-degenerate narrow band (e_g) represented by Hubbard Hamiltonian together with electron-lattice coupling is treated to examine the coexistence of SDW and distortion within the system. The absence of tetragonal and ferromagnetic state is the consequence of particular mechanism to produce these phases. Here, Jahn-Teller effect lifts the degeneracy of band and so splitting between two subbands appears at center of BZ. Similarly, in Hartree-Fock approximation the spontaneous homogeneous moment splits the spin-up and spin-down band. The redistribution of electrons in two subbands due to band JT effect and that due to magnetism work in opposite direction in changing band energy. The former tends to decrease whereas the latter increases the band energy. As these changes are produced at the same point of the band they interfere destructively. These results would be drastically modified for different mechanism of tetragonal distortion like Gor'kov's mechanism or for t_{2g} band and will be reported elsewhere.

In a system with half-filled band the antiferromagnetic (SDW) state is favored for any finite value of U or J because the splitting due to SDW always lowers the electronic energy in this case. The coexistence of tetragonality and SWD is possible if the splitting of the center of gravity of bands due to tetragonality is more than the splitting of band due to SDW. In this case, the energy is lowered when both the order parameters are finite. In presence of SDW, the Fermi level for half-filled system lies at the energy gap created by SDW and if splitting due to strain is less than that due to SDW the total energy cannot be further lowered by distortion. The situations will be different for more than or less than half-filled cases and are being studied.

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