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Transverse charge density waves in ladder systems

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We study a charge density wave instability in a three-leg ladder system using a tight-binding model. An excitonic instability which resembles a Peierls transition, but with displacements transverse to the density wave is shown to occur for 1/3 filling of the band. We discuss the application of this model to the dimerization transition observed recently in the Fe ludwigite system $Fe_3O_2BO_3$. The role of interactions to describe the complex magnetic and thermodynamic behavior of this system above and below the structural transition is pointed out.

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Low dimensional systems present a variety of interesting phenomena.[1,2] Among them the Peierls transition signals the instability of the one-dimensional electron gas to a distortion of the underlying lattice which, in the case of one-electron per site $(n=1)$, doubles the period of the atomic array.[3] This instability is related to a perfect nesting of the Fermi surface which occurs for strictly one-dimensional systems. If the increase in elastic energy of the lattice is compensated by the gain in energy of the electronic system, the transition actually takes place and has been observed in many systems.[4] The period doubling of the lattice opens a gap in the density of states and in general the Peierls transition is accompanied by a metal-insulator transition. Additional interactions in real materials maintain the stability of the Peierls distorted state at finite temperatures and these charge density wave (CDW) transitions are then observed at finite temperatures associated with many interesting modifications in the thermodynamic and transport properties.[4]

Similar to low dimensional metallic systems, *insulating*, one-dimensional magnetic materials may undergo a structural instability if the gain in *magnetic energy*, associated with the formation of singlet pairs, can account for the change in elastic energy due to the dimerization of the chain. These are the so-called spin-Peierls (SP) systems.[5,6]

Among other possible instabilities in low dimensional systems, we point out that of an excitonic transition, where a deformation of the lattice takes place due to electronic correlations.[7,8]

In low dimensional structures such as ladders, we may find distortions taking place in directions transverse to the direction of the wave. This was recently observed in the oxi-borate system $Fe_3O_2BO_3$.[9] This material has subunits in its structure, in the form of three leg ladders (3LL), which become unstable with decreasing temperature (see Fig. 1). The instability is such that the rungs dimerize in alternate directions *perpendicular* to the axis of the ladder [Fig. 1(b)]. The structural transition at $T_c \approx 283$ K is accompanied by an anomaly in the electrical resistivity.[9] An important distinction between $Fe_3O_2BO_3$ and the common Peierls systems is the existence of local moments of the Fe ions in the low dimensional structures of the former system. The magnetic character of the ions involved in the charge density wave has led Whangbo *et al.*[10] to suggest a magnetic mechanism as the cause of the structural instability of $Fe_3O_2BO_3$. This material in fact presents behavior associated with both, spin-Peierls and more conventional Peierls systems. Here we will focus mostly on the charge aspects of the problem where the itinerant electrons play the main role. This is the main mechanism determining the structural instability in $Fe_3O_2BO_3$ as suggested, for example, by the energy scales given in Table I which show that the BCS ratio, $2\Delta/k_BT_c$, for this material is anomalous, in common with other CDW materials. For SP systems this ratio is much closer to the theoretical value of ≈ 3.52. The differences from this value provide an estimation of the deviation from mean-field behavior.

The electron counting for the Fe ludwigite is such that the electronic configuration of the ladders corresponds to 2/3 of the Fe ions of the ladder in valence state Fe^{3+} and 1/3 in state Fe^{2+}. This allows us to view the ladders as being formed of a background of Fe^{3+} ions with an extra electron for every three ions. The distance between the Fe ions along the c axis of the ladder is $d_c = 3.071$ Å and along the rungs, in the high temperature phase, corresponds to $d_{Fe2/Fe4} = 2.786$ Å. These distances are not too large to avoid overlap among the $3d$ orbitals of the ions. Consequently, we adopt

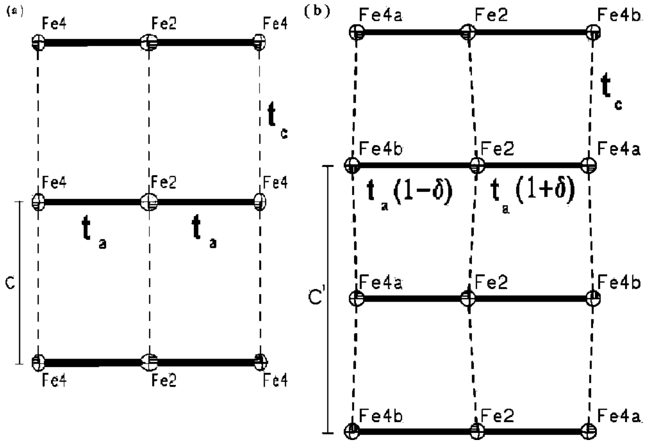

FIG. 1. The three leg ladder structure of $Fe_3O_2BO_3$, above (a) and below (b) the charge density wave transition. In the metallic phase (a), for $T > T_c$, the distance between ions in the rungs is $d_{Fe4/Fe2} = 2.786$ Å. The c-axis lattice parameter is $d_c = 3.071$ Å and doubles below T_c. In (b) the distances between ions are $d_{Fe4a/Fe2} = 2.616$ Å and $d_{Fe4b/Fe2} = 2.942$ Å.

TABLE I. Transition temperatures T_c, band gaps obtained from dc-resistivity measurements, and BCS parameters for some materials presenting CDW[11] (above the entry for $Fe_3O_2BO_3$). The systems below $Fe_3O_2BO_3$ are spin-Peierls materials for which Δ is a spin gap (Ref. 6 and references therein).

	T_C(K)	$2\Delta/k_B$(K)	$2\Delta/k_BT_c$
KCP	189	1400	7.41
$K_{0.3}MoO_3$	183	920	5.03
TaS_3	215	1600	7.44
$NbSe_3$	145	700 [a]	4.83
	59		11.86
$(TaSe_4)_2I$	263	3000	11.41
$Fe_3O_2BO_3$	283	5000	17.67
$CuGeO_3$	14	48	3.43
$TTF-CuBDT$	12	42.3	3.53
$TTF-AuBDT$	2.1	7.8	3.7
$MEM-(TCNQ)_2$	17.7	56	3.16

[a] Tunneling experiments.

here a model for the ladders which consists of itinerant electrons, in a tight-binding band, moving in a background of localized Fe^{3+} ions. Furthermore, we assume an infinite *local* Coulomb repulsion U between these itinerant electrons, such that, two of them can never sit at the same site. In this way we preclude the existence of the ionic configuration Fe^{1+} since there is not such an oxidation state for Fe ions. For the purpose of describing the charge density wave transition, occurring nearly at room temperature, we ignore the interaction between the localized and the itinerant $3d$ electrons at these temperatures.

The Hamiltonian describing itinerant tight-binding electrons in a three leg ladder is given by

$$H=t_c\sum_{ij\sigma} c^{\dagger}_{i\sigma}c_{j\sigma}+t_a\sum_{ij\sigma} c^{\dagger}_{i\sigma}c_{j\sigma}, \tag{1}$$

where t_c and t_a are the hopping terms along and perpendicular to the c axis, respectively.

The total density of states of the ladder, $\rho(\omega)$, obtained from the imaginary part of the one-electron Green's function is shown in Fig. 2 for a given value of t_a/t_c. For simplicity, we take in what follows $t_c=1$. The density of states exhibit van Hove–like singularities typical of one dimensional structures.

Notice that for noninteracting electrons the total number of electrons allowed in the band, per unit cell and spin direction, is $n=3$, such that, 1/3-band filling corresponds to two electrons per unit cell of the ladder. When double occupation is forbidden, 1/3 band filling is equivalent to one electron per cell as in the Fe ludwigite.

The dimerized phase [shown in Fig. 1(b)] is described by the tight-binding Hamiltonian

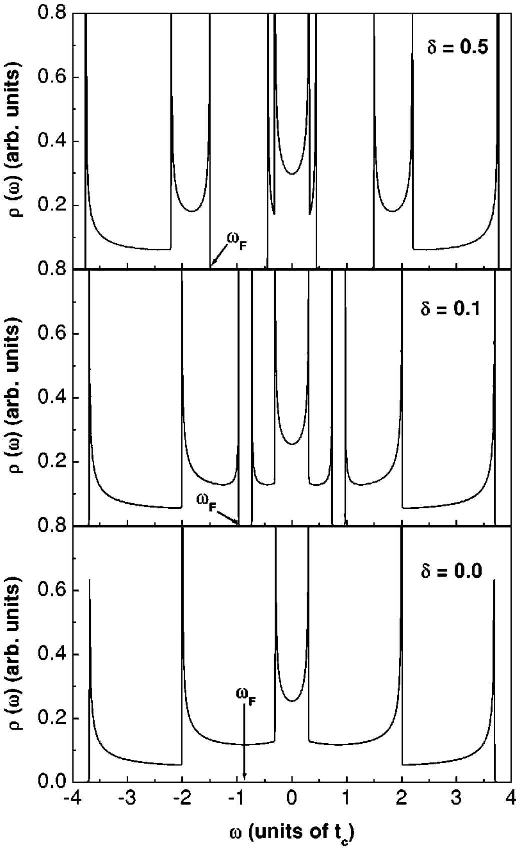

FIG. 2. Total density of states for the three leg ladder in the metallic $\delta=0$ and dimerized phases. The position of the Fermi level ω_F is shown for a 1/3-band filling. The hopping along the c axis is taken as $t_c=1$ and $t_a/t_c=1.2$.

$$H=t_c\sum_{ij\sigma} c^{\dagger}_{i\sigma}c_{j\sigma}+t_a(1+\delta)\sum_{ij\sigma} c^{\dagger}_{i\sigma}c_{j\sigma}+t_a(1-\delta)\sum_{ij\sigma} c^{\dagger}_{i\sigma}c_{j\sigma}, \tag{2}$$

where δ is introduced as a dimerization parameter which is related to the structural distortion. The total density of states of the dimerized phase of the ladder is shown in Fig. 2 for two values of the dimerization parameter and the same ratio, $t_a/t_c=1.2$, of the undistorted phase shown in the same figure. For any dimerization δ of the ladder, there are gaps, $\Delta(\delta)$, in the density of states which occur at 1/3- and 2/3-band-fillings, respectively. The intensity of these gaps as a function of δ is shown in Fig. 3. It is clear that the gaps increase linearly with the dimerization parameter δ, for small δ.

The Fermi level for 1/3 filling of the band is shown in Fig. 2. In the absence of dimerization the system is metallic for this occupancy. However, in the dimerized phase of the 3LL, for 1/3 filling, the Fermi level is located in a gap of the density of states and the system is insulating. The distortion of the ladder lowers the total electronic energy as shown in Fig. 4. This should compensate for the increase in elastic energy ($\propto|\delta|^2$) due to the dimerization.[2] In the case of the Fe ludwigite, there is a magnetic contribution to the total energy

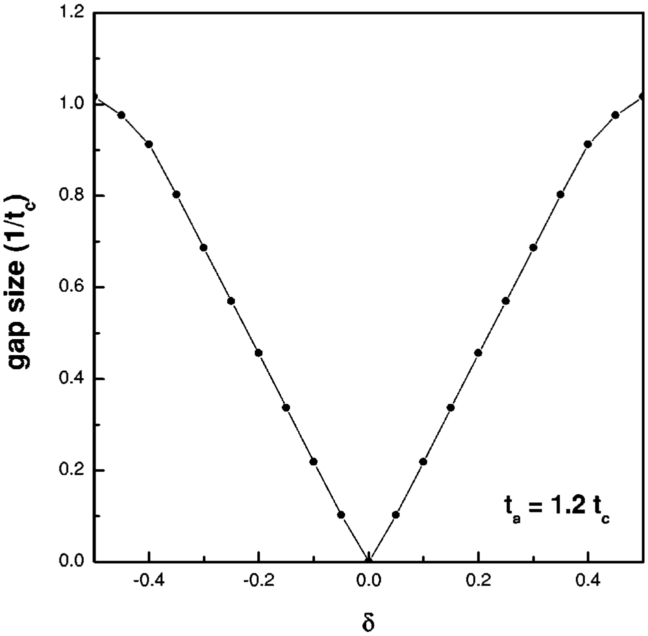

FIG. 3. Intensity of the gap Δ in the density of states for the tight-binding model, at 1/3- and 2/3- band fillings, as a function of the dimerization parameter δ $(t_a/t_c = 1.2)$.

due to antiferromagnetic pairs of local moments in the dimerized bonds[9] which should be included in the net energy balance.

The phenomenon discussed above can be alternatively approached from the point of view of k space. The dispersion relations for the undistorted 3LL is given by

$$\omega_1(k) = -2t_c \cos k_c a, \tag{3}$$

$$\omega_2(k) = -2t_c \cos k_c a + \sqrt{2} t_a \cos k_a b, \tag{4}$$

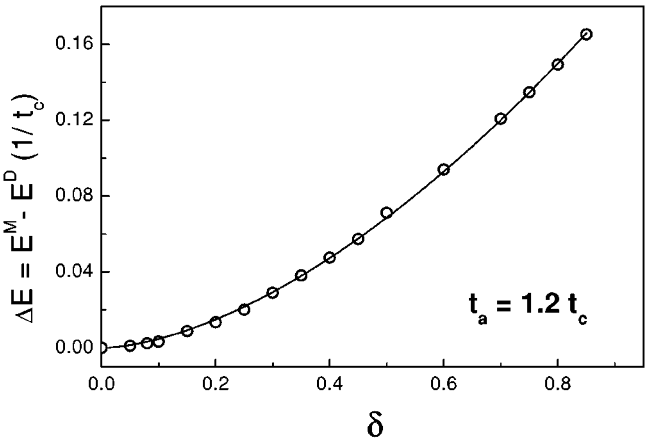

FIG. 4. Difference in total electronic energy between the metallic and dimerized phases, for 1/3-band filling, as a function of the dimerization parameter δ $(t_a = 1.2 t_c)$. The line through the points is a fit with the function, $\Delta E = A|\delta|^{5/3}$.

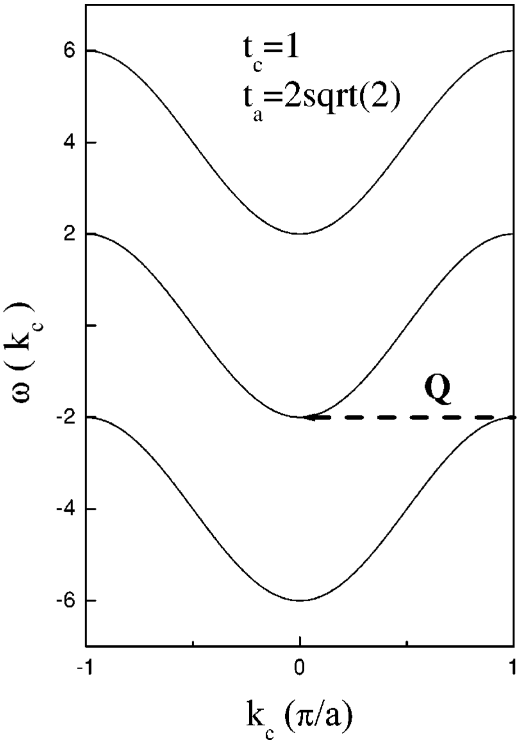

FIG. 5. Dispersion relation of the undistorted 3LL for $(t_a/t_c) = 2\sqrt{2}$. For 1/3-band filling the lower band $(k_a = \pi/a)$ is full. The vector **Q** connects the Fermi surface to the bottom of the conduction band.

where a and b are the atomic distances along and perpendicular to the axis of the ladder, respectively. Periodic boundary conditions imply that $k_a = n(\pi/b)$, such that the dispersion relation $\omega_2(k)$ correspond in fact to two bands given by

$$\omega_{2\pm}(k) = -2t_c \cos k_c a \pm \sqrt{2} t_a. \tag{5}$$

We can also use Eq. (4) to describe both bands $\omega_1(k)$ and $\omega_2(k)$ if we allow for values of k_a given by $k_a = n(\pi/2)b$. In Fig. 5 we plot these dispersion relations for the case $(t_a/t_c) = 2\sqrt{2}$ where the subbands, labeled by different values of k_a, just start to overlap. For occupation $n = 1/3$, the lower subband is full and we have plotted the wave vector **Q** connecting the bottom of the valence subband to the Fermi surface at $k_F = \pi/a$. Notice that these states are degenerate for this ratio of the hoppings. The vector **Q** has components $(Q_c = \pi/a,\ Q_a = -\pi/2b)$. Since $\mathbf{Q} = \mathbf{G}/2$ with G a reciprocal-lattice vector, in the presence of interactions between electrons labeled by different values of k_a, this nesting of the Fermi surface signals an instability of the 3LL to a new phase characterized by a charge distribution, $\rho(\mathbf{r}) \propto \cos \mathbf{Q} \cdot \mathbf{r} = \cos[(\pi/a)z]\cos[(\pi/2b)x]$, for values of $(t_a/t_c) \geqslant 2\sqrt{2}$. The charge distribution for the sites with coordinates $(z = na, x = 0), (z = na, x = b), (z = na, x = 2b)$, with $n = 0,1,2,3,\ldots,$ is given by

$$\begin{array}{ccc} -1 & 0 & +1 \\ +1 & 0 & -1 \\ -1 & 0 & +1 \\ +1 & 0 & -1 \\ & \cdots. & \end{array}$$

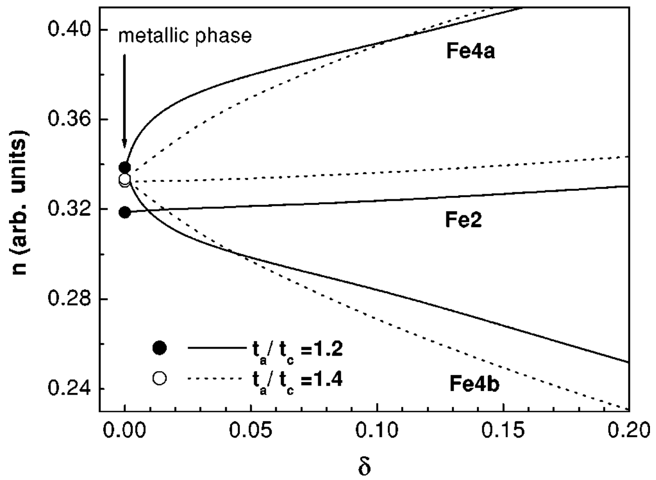

FIG. 6. Charge density (excluding the Fe^{3+} background) at different sites of the three leg ladder as a function of the dimerization parameter δ for two values of the ratio t_a/t_c. The sum of the charge on the three sites $n = n_{Fe2} + n_{Fe4a} + n_{Fe4b} = 1$. In the metallic phase, for $\delta = 0$ (circles), $n_{Fe4a} = n_{Fe4b} = n_{Fe4}$.

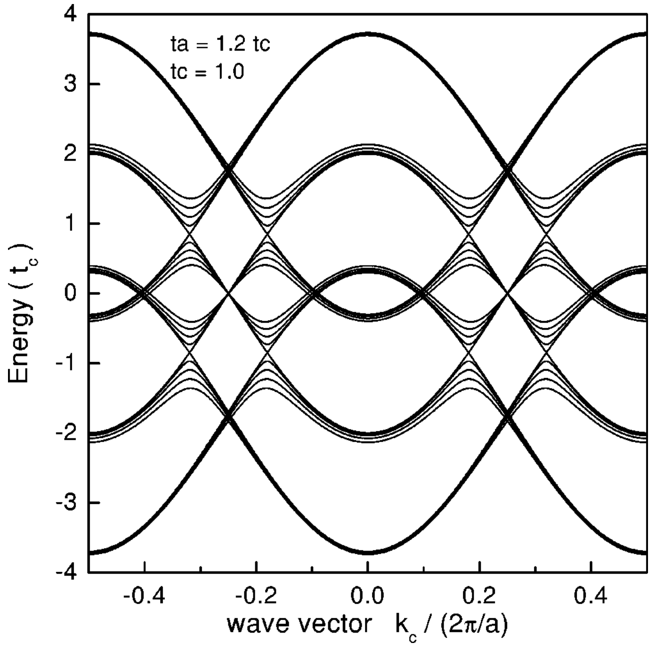

FIG. 7. Dispersion relations for the dimerized 3LL for different values of the dimerization parameter δ $(t_a/t_c = 1.2)$.

The *k* space approach leads us to recognize the transition to the distorted state as a *crystallization of excitons* which takes place in real space.[7,8] The electron-hole pairs alternate along the 3LL and the excitonic lattice has a period which is twice that of the original ladder. It also shows why the actual type of distortion is preferred among others, that double the period of the lattice, for this particular electron occupation.

We have obtained the local charge distribution for 1/3 filling, excluding the Fe^{3+} background, for different sites in a rung of the ladder, for both the metallic and dimerized configurations. The results are shown in Fig. 6. In the metallic phase, for the ratio $t_a/t_c = 1.2$, sites 4 have equal charges, larger than that of site 2. In the distorted phase, there is a charge transfer, essentially from site $4b$ to site $4a$ involved in the dimer. This is in agreement with the excitonic picture of electron-hole pairs forming in the rungs and which *crystallize* along the ladders with twice the period of the original lattice, as discussed above.

The $T = 0$ dimerization transition in the 3LL as described above is a quantum metal-insulator phase transition. The control parameter is the dimerization δ, which measures the distance to the quantum critical point (QCP) at $\delta = 0$. The gap exponent νz for this transition is defined by $\Delta \propto |\delta|^{\nu z}$ where Δ is the gap in the density of states. It takes the value $\nu z = 1$, as can be seen from the linear increase of the gap with δ, for small values of the control parameter, shown in Fig. 3. This suggests that the universality class of this transition is the same of the well studied band-filling or density-driven metal-insulator transition,[12] for which $\nu z = 1$, with $z = 2$ and $\nu = 1/2$ for the dynamic and correlation length exponents, respectively. Furthermore, the quantum hyperscaling relation,[12] $2 - \alpha = \nu(d + z)$, with $d = 1$ and the exponents above yield for the singular part of the free energy density close to the dimerization transition, $f_s \propto |\delta|^{3/2}$, since this quantity behaves as, $f_s \propto |\delta|^{2-\alpha}$. However, a closer look at the data of Fig. 4 shows that it can be very well fitted by $f_s \propto |\delta|^{5/3}$ for all δ. This, together with $\nu z = 1$ (as obtained from the numerical data for the gap) and the quantum hyperscaling relation with $d = 1$, implies the values $\nu = 2/3$ and $z = 3/2$ for these quantum critical exponents. We may identify the dimerization transition at $\delta = 0$ as a quantum Lifshitz point.[12] The dimerization gives rise to profound changes in the spectrum of the quasiparticles contributing to the density of states close to the gaps that appear with this phenomenon. In particular, the value $z = 3/2$ for the dynamic exponent leads to singularities in the density of states on the border of the gaps with the power-law behavior, $\rho(\omega) \propto \omega^{-1/3}$, instead of the usual square-root singularities of one-dimensional systems. The value for the dynamic exponent can be obtained directly calculating (numerically) the dispersion relation for the dimerized 3LL shown in Fig 7. It can be verified that the states contributing to the density of states on the border of the gaps which appear with dimerization are described by $\omega(k_c) \propto |k_c - k_0|^{3/2}$ where k_0 is an extremum of $\omega(k_c)$.

Finally let us point out that the *metallic phase* of $Fe_3O_2BO_3$ for $T > T_c \approx 283$ K has not been sufficiently investigated but, certainly, this is not a trivial phase. The low dimensionality of the ladders, the strongly correlated character of the electrons, the scattering by magnetic moments and the presence of small amount of disorder allow us to anticipate that the resistivity should be large and with a nontrivial temperature dependence. However, the existence of a well defined anomaly in the electrical resistivity at the temperature of the structural transition[9] and the clear thermally activated behavior of the electrical transport below T_c provide strong evidence that the structural transition is related to a significant change in the electronic properties as in the mechanism proposed here.

We have shown that a metal with a three leg ladder structure and 1/3-band filling is unstable to a dimerization transition which gives rise a doubling of the lattice period. This is a Peierls-like transition which can be viewed as the formation of an excitonic crystal. The structural transition gives rise to a metal-insulator transition with the opening of a gap in the density of states. This model provides a simple and appealing description of the structural transition that occurs in the Fe ludwigite and is accompanied by an anomaly in the electrical resistivity. Below this transition this material presents activated electronic transport. The description of the complex magnetic and thermodynamic behavior[9] below T_c must require taking into account the interaction among the local and itinerant electrons.

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