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Electron correlations and electron-lattice interactions in the metal-insulator, ferroelastic transition in VO_2: A thermodynamical study

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We present a model of the VO_2 phase transition which incorporates both electron-electron and electron-lattice interactions and accounts for the presence of two d bands (π^* and $d_{\parallel}$) overlapping at the Fermi level of the metallic phase. Attention is given to the crystallographic symmetry change at the transition and to the properties of the associated order parameter. To take into account electron-electron interaction, we use the functional-integral treatment of the Hubbard Hamiltonian. Then, to account for the electron-lattice interaction, the center of gravity and the shape of the d bands are chosen so as to depend explicitly on the lattice distortion. Finally spin-spin interactions are described in terms of an Ising-like model. This treatment leads to a free energy expression which, at a given temperature, depends on two variational parameters: the mean amplitude of the local moment μ and the amplitude of the lattice distortion η. Minimization of the free energy with respect to η and μ leads to the temperature dependence of these quantities. The transition which is a first-order one, appears to be driven by electron correlations which, below the transition temperature, stabilize a distorted phase with paired local magnetic moments on the vanadium sites and a density of states gap between the lower Hubbard $d_{\parallel}$ and the π^* band. Our model lends itself to discussion of the magnetic susceptibility which, in the insulating phase, is governed by the pairing of the local magnetic moments, induced by the electron-lattice interaction. Using accepted values of the electronic structure parameters, we find a fairly quantitative agreement with experiment. We account for all the features of the ferroelastic, metal-insulator transition of VO_2.

I. INTRODUCTION

Vanadium dioxide offers one of the most studied examples of a compound undergoing an insulator-to-metal transition. This transition, at 340 K, is a first-order one, its striking feature being to display lattice, electronic, and magnetic aspects. Indeed there is a spontaneous lattice distortion (i.e., a symmetry change) and a discontinuous variation of both the electrical conductivity and the magnetic susceptibility with such a large amplitude that none of these changes may be considered as a marginal consequence of the primary mechanism inducing the others.

Despite the obvious interactions of these three aspects, the VO_2 transition has long been taken as a prototype of the metal-insulator transition induced by the crystalline distortion, which opens a gap in the electronic density of states.[1] This general scheme has been substantiated by Goodenough[2] who has put forward a band-structure model in which the nature of the relevant bands and the two electron-phonon coupling mechanisms, associated with the displacement of the vanadium ions (interband deformation-potential coupling and intraband Peierls-dimerization coupling), were identified. Later on, detailed studies of the effect of Cr doping on magnetic properties,[3] showing in particular the formation of magnetic moments localized on a vanadium chain in two intermediate phases of VO_2, have emphasized the primary importance of electron-electron correlations as they are accounted for in the Hubbard model.[4] These various aspects have been synthetized in the Zylbersztejn-Mott[5] model which incorporates the electronic structure, the lattice distortion, and the Hubbard interaction in quantitative agreement with experiments but which is relying on an implicit thermodynamical calculation (e.g., calculation of the free energy versus lattice distortion) which has not been implemented. Finally, a recent electronic-structure calculation[6] has confirmed previous conjectures but went back to electron-lattice mechanisms by suggesting the formation of a charge-density wave accompanied by a periodic lattice distortion, i.e., a mechanism which postulates the softening of a normal phonon mode at the transition.

In the meantime Evanson, Schrieffer, and Wang[7] (to be refered to as ESW) and Cyrot[8] have devised a method of handling the thermodynamics of the Hubbard model in terms of a functional integral. On this basis, approximation schemes may be specified which enable one to perform explicit calculations; using this method, specific problems like the one involving the lattice[9] or the spin-polaron formation[10] have been studied. It thus seems that one has at one's disposal all that is needed to tackle a complex problem like the one of the VO_2 transition which involves (i) a multiband structure, (ii) various types of electron-lattice coupling, and (iii) important electron-electron interactions.

The aim of this paper is to attempt such a comprehensive analysis in which all the relevant interactions are introduced on the same footing, with due attention given to the self-consistency requirements. Essential to our analysis is the fact that our starting point is an unbiased one; i.e., our model does not introduce any implicit hypothesis regarding which of the interactions is the leading one.

To account for the symmetry change at the transition, one is bound to introduce the crystallographic order parameter; deduced from the symmetry requirements,[11] this parameter η is identified with the static amplitude of a normal phonon mode. On the other hand, the ESW-Cyrot treatment of the Hubbard model naturally introduces another parameter μ, which specifies the electronic degrees of freedom and which is identified with the average amplitude of the local magnetic moments. Thus the thermodynamics of our Hamiltonian derives from the η and μ dependence of the free energy of the system.

We do not find it necessary to review the abundant literature of the VO_2 transition, a subject which has been carefully covered by previous authors, most noticeably in Refs. 5, 6, and 12. In the course of our discussion, we will need actual values of some parameters, for most of them we will use accepted values taken from this literature.

Although the basic method we use, namely, the functional-integral method, has been put on a sound basis by the work of ESW,[7] Cyrot,[8] and others,[10] its implementation for the specific problem of VO_2 has led us to introduce some improvements which are worth quoting here. These are (i) the influence of the Peierls dimerization on the distorted band in terms of order-parameter η-dependent moments of the density of states, (ii) a Hartree-like incorporation of the interband on-site electron-electron interaction which self-consistently accounts for the energy shift of the center of gravity of the relevant bands as a function of their mutual filling. With a set of parameters taken from the literature, our model leads to quantitative results in fair agreement with experiments regarding the transition temperature, the latent heat, the temperature dependence of the electronic gap, the lattice distortion, and the spin-correlation function in the insulating phase. Variations in a wide range of the values of the set of parameters we use, do not change the qualitative behavior of the transition. Our thermodynamical analysis makes it clear that the transition is a first-order one and allows us to conclude that electron-electron interactions are the leading mechanism of the phase transition: the growing of local moments (paired in the insulating phase) under cooling triggers the lattice distortion. Our statement, we believe, draws its strength from the "unbiased" character of the Hamiltonian we start from.

The organization of the paper is as follows. In Sec. II, we review the background of the model. This model is presented in Sec. III: the specific Hamiltonian is constructed (Sec. III A), the functional-integral method is recalled to justify the approximations made (Sec. III B), then the coherent-potential approximation, used to solve the equivalent alloy problem (Sec. III C) and the way we account for the Peierls dimerization (Sec. III D) are presented; finally the exchange interactions between localized moments are discussed in terms of an Ising-like model (Sec. III E). The thermodynamics of the model is elaborated in Sec. IV in which numerical results are presented. The magnetic properties in both phases are discussed in Sec. V, where some comments are made on improvements to be carried on the description of the correlated metallic phase. Our results are summarized and briefly commented on in Sec. VI. Some ancillary developments regarding the scaling of the electron-electron interaction constants, the sketch of the transfer matrix method in the Ising problem, and the comparison with the phenomenological theory of "triggered" phase transitions are deferred to the Appendixes. Preliminary accounts of this work have been given in Ref. 13.

II. BACKGROUND OF THE MODEL

A. Symmetry consideration

The high-temperature phase of VO_2 exhibits the rutile structure: the unit cell has two unequivalent vanadium atoms, each of them being at the center of a slightly distorted octahedron, these two vanadium atoms belonging to two unequivalent chains parallel to the *c* axis. The space group of the rutile structure is $P4_2/mnm$. The low-temperature (M_1) phase belongs to the space symmetry $P2_1/c$, the twofold monoclinic axis being perpendicular to the tetragonal axis of the rutile phase lost at the transition: the unit cell has then four unequivalent vanadium atoms. As shown by Brews,[11] the transition can be described by an order parameter transforming like an irreducible representation of the $P4_2/mnm$ space group, associated to the R point $(0,\frac{1}{2},\frac{1}{2})$ of the primitive tetragonal Brillouin zone. This representation is a four-dimensional one: two dimensions for the small representation multiplied by the two branches of the star of the wave vector. Let us call η_1 and η_2 the order-parameter components associated with the subspace relative to a single branch of the star. The $R \rightarrow M_1$ phase transition corresponds to spontaneous values of the order parameter $\eta_1 = \pm \eta_2 \neq 0$. However spontaneous values $\eta_1 = 0$ and $\eta_2 \neq 0$ or $\eta_1 \neq 0$ and $\eta_2 = 0$ would lead to another monoclinic phase (space group $B2/m$) and $\eta_1 \neq 0$, $\eta_2 \neq 0$ with $\eta_1 \neq \eta_2$ to a triclinic phase (space group $P\bar{1}$). These phases, M_2 and T, respectively, have been evidenced[14,15] in Cr-doped VO_2 and in pure VO_2 under uniaxial stress.[16] Other possibilities, associated with spontaneous values for the four components of the order parameter, would correspond to other phases with fourfold multiplication of the unit cell which has not been evidenced. By looking at the symmetry of the lattice modes, one finds three modes of vanadium displacements corresponding to the symmetry of the order parameter but no oxygen displacement mode having this symmetry. The atomic displacements at the $R \rightarrow M_1$ transition have been identified as corresponding to both a pairing of V atoms along V chains and a tilt of these atoms perpendicular to the c axis, this complex motion being common to the two unequivalent chains. It is worth pointing out that, contrary to the conjecture in Ref. 2, the two displacement components of the V atoms are not independent. Indeed symmetry arguments require that the tilt of the V atom on chain 1 be associated to pairing on chain 2; we may call η_1 the common amplitude of these displacements, and conversely the tilt on chain 2 has to be associated to pairing on chain 1 with amplitude η_2 (see Fig. 1). One sees that atomic displacements at the $R \rightarrow M_1$ transition transform like the abstract order parameter. One also verifes that the ($\eta_1 = 0$, $\eta_2 \neq 0$) and ($\eta_1 \neq 0$, $\eta_2 = 0$) possibilities correspond to both the symmetry change and the atomic displacements at the $R \rightarrow M_2$ transition and that the ($\eta_1 \neq 0$, $\eta_2 \neq 0$, $\eta_1 \neq \eta_2$) possibility corresponds to the atomic displacements in the T phase which must possess the ($P\bar{1}$) space symmetry. From a crystallographic viewpoint, the $R \rightarrow M_1$ transition must be described by the abstract order parameter, itself identified with the rutile normal modes we have just described. Any thermodynamic description of the transition is bound to use this order parameter, the intermediate phases M_2 and T naturally appearing as internal possibilites of such a description. In what follows, we will limit ourselves to study the $R \rightarrow M_1$ transition, calling η the common value of η_1 and η_2.

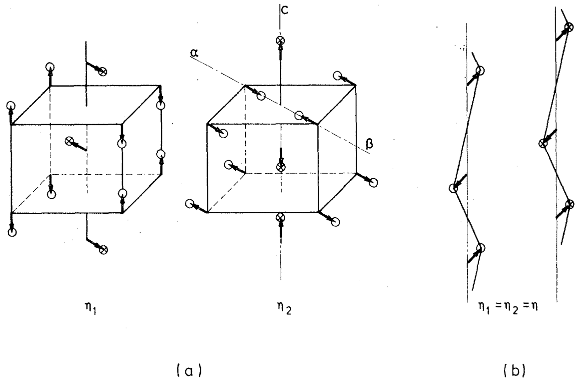

FIG. 1. (a) Motion of the vanadium atoms associated with the normal-mode components transforming as η_1 and η_2. Circles and crossed circles are nonequivalent atoms forming nonequivalent chains, parallel to the c axis in the rutile phase. Interchange of η_1 and η_2 corresponds to interchange between tilt and pairing on a given chain. (b) Sketch of the actual atomic displacement occurring at the phase transition in the $\alpha\beta$, c plane. This displacement corresponds to $\eta_1 = \eta_2 = \eta$ and the same combination of tilt and pairing on the two nonequivalent chains.

B. Electron-electron correlations (Hubbard) versus electron-lattice interactions (Peierls)

Crystal-field and bonding considerations,[2] cluster calculations,[17] and band-structure calculations[6,18] agree on the qualitative features of the metallic VO_2 electronic structure: the conduction band is made of crystal-field-split vanadium d orbitals, which, depending on their symmetry, are differently hybridized with oxygen p orbitals. The Fermi level falls within two degenerate bands, a narrow $d_{\parallel}$ one essentially made of d orbital overlapping along the c axis and accomodating two electrons per vanadium, and a wider antibonding π^* band, made of d orbitals pointing towards oxygen atoms and hybridized with their p orbitals and accomodating four electrons per vanadium. The d^1 configuration of the V^{4+} ion allows a single electron to be shared by these $d_{\parallel}$ and π^* bands. Owing to (i) their different widths and (ii) their different anisotropies ($d_{\parallel}$ band is highly anisotropic while π^* is more spherical), these two bands are expected to respond in a different way either to electron-electron interactions (significant only for the narrow $d_{\parallel}$ band) or to a lattice distortion.

As first conjectured by Goodenough[2] and confirmed by cluster calculation,[17] due to the lattice distortion the antibonding π^* band raises above the Fermi level and the $d_{\parallel}$ band becomes half filled. Further $d_{\parallel}$-band splitting may originate from either vanadium pairing along the c axis (Peierls mechanism) or from the opening of a correlation gap (Hubbard mechanism). There has been an active debate to ascertain the relative importance of each mechanism: the occurrence of localized spin-$\frac{1}{2}$ moments on one chain in the M_2 phase strongly favors the Hubbard mechanism[3,5]: on the other hand, recent band-structure and generalized susceptibility $\chi(\vec{q})$ calculations[6] emphasize the nesting features of the metallic Fermi surface and suggest the formation of a charge-density wave associated to a lattice periodic distortion with wave vector $\vec{q}=\Gamma R$ (Γ being the center of the Brillouin zone). Let us notice that the peak in $\chi(\vec{q})$ for $\vec{q}=\Gamma R$ results only from the $d_{\parallel}$-band contribution.

The Peierls mechanism acting alone seems unable to account for all the features of the transition for the following reasons. In the first place, current estimates of both the bandwidth[6,18] and the electron-lattice interaction term[17] hardly lead to the opening of a gap within the half-filled $d_{\parallel}$ band. More precisely, this mechanism would be very efficient for a distortion acting on uncoupled chains whereas nesting arguments[6] imply interchain coupling (i.e., nonvanishing interchain-hopping integrals) and the actual distortion with wave vector $\vec{q}=\Gamma R$ is expected to open only local gaps in the Fermi surface but not one in the density of states. Secondly, this mechanism cannot account for the formation of local moments in the M_2 phase nor for the temperature dependence of the magnetic susceptibility in the metallic phase. One may notice that a charge-density-wave mechanism would be sensitive to any change in the Fermi surface and especially to that brought about by Cr doping which is expected to introduce an extra electron and thus to raise the Fermi level.[19] Cr doping is known to induce new phases while keeping the temperature range of the metallic phase stability unchanged. Finally, the latent heat associated with the R-M_1 and R-M_2 transitions (i.e., metal-insulator transitions) are much larger than those corresponding to M_2-T and T-M ones (crystallographic transitions between insulating phases), a phenomenon which would hardly be understood on a simple Peierls mechanism basis. At this point, it is worth noticing that, beside the electron-lattice interactions (namely, the π^*-$d_{\parallel}$ band splitting and Peierls distortion), there is experimental evidence for electron-phonon interactions leading to a global softening of the phonon modes in the metallic phase. The strongest one coming from Debye-Waller factor measurements.[20]
There is, however, no indication that the transition is driven by a strong softening of lattice modes associated with the R point of the Brillouin zone.

However, the description of the transition in terms of the Hubbard model alone suffers from obvious deficiencies. First, a lattice distortion is required to lift the $d_{\parallel}$-π^* degeneracy and previously developed symmetry arguments show that a tilt of vanadium atoms also implies their pairing. More generally, a Hubbard mechanism cannot break any crystallographic symmetry nor account for the symmetry properties of the order parameter. Finally, the vanishing magnetic susceptibility in the M_1 phase implies some spin-dimerization mechanism which originates in vanadium pairing.

To summarize, any theory attempting to account for the major features of the transition, namely, symmetry breaking, gap opening, and magnetic properties, and to give a quantitative thermodynamical analysis must incorporate both mechanisms on an equal footing.

C. Electronic-structure parameters

In this section, we will extract from the literature a set of data on which the authors seem to agree and which will constitute the framework of our model.

In the first place, we assume the metallic phase Fermi level to lie 0.44 eV above the bottom of the $d_{\parallel}$-π^* complex which has itself a width of 2 eV.[6,18] In this configuration the $d_{\parallel}$ band accomodates 0.75 electrons per vanadium. Symmetry considerations show that the upward motion of the π^* band and the downward motion of the $d_{\parallel}$ band must be a quadratic function of the order parameter η, the center of gravity of the $d_{\parallel}$-π^* complex being stationary. Using the cluster calculation of Sommers *et al.*,[17] we take for the deformation potential constant the value $\Xi=30$ eV/Å [see Eqs. (4.6) and (4.7) below]. Finally for the value of the $d_{\parallel}$ electron Hubbard interaction term we will use $U_{\parallel}=1.1$ eV, which is close to the estimate that Sommers and Doniach[21] obtained from a self-consistent, unrestricted Slater $X\alpha$ cluster calculation.

III. MODEL

A. Hamiltonian

Within the spirit of the Hubbard model, the most general Hamiltonian suited to our problem is

$$H=H_{0\parallel}+H_{0*}+H_{e\text{-}e}+H_{\text{latt}} , \tag{3.1}$$

where $H_{0\parallel}$ and H_{0*} are tight-binding terms describing, respectively, the $d_{\parallel}$ and π^* band in the absence of electron-electron interactions:

$$H_{0\parallel}=\sum_{i,\sigma}\epsilon_{\parallel}(\eta)a_{i\sigma}^{\dagger(\parallel)}a_{i\sigma}^{(\parallel)}+\sum_{i,j,\sigma}t_{ij}^{(\parallel)}(\eta)a_{i\sigma}^{\dagger(\parallel)}a_{j\sigma}^{(\parallel)}\ ,\tag{3.2a}$$

$$H_{0*}=\sum_{\substack{i,\sigma\\ l=1,2}}\epsilon_{*}(\eta)a_{i\sigma}^{\dagger(*l)}a_{i\sigma}^{(*l)}+\sum_{\substack{i,j,\sigma\\ l=1,2}}t_{ij}^{(*)}a_{i}^{\dagger(*l)}a_{j}^{(*l)}\ ,\tag{3.2b}$$

in which the η dependence of $\epsilon_{\parallel}$ and ϵ^* and of $t_{ij}^{(\parallel)}$ accounts for the deformation potential acting on the $d_{\parallel}$ and π^* bands and for the distortion dependence of the $d_{\parallel}$ hopping integral; creation and destruction operators operate on Wannier states with spin σ localized on site i and made from d_{xy} wave functions for $a_{i\sigma}^{\dagger(\parallel)}$ and $a_{i\sigma}^{(\parallel)}$, and from d_{yz} (d_{xz}, respectively), wave functions for $a_{i\sigma}^{\dagger(*1)}$ and $a_{i\sigma}^{(*1)}$ (respectively, $a_{i\sigma}^{\dagger(*2)}$ and $a_{i\sigma}^{(*2)}$), accounting for the degeneracy of the π^* band. The sum runs over the N lattice sites of the crystal. $H_{e\text{-}e}$ describes the electron-electron interaction and, under its most general form, $H_{e\text{-}e}$ is written:

$$H_{e\text{-}e}=\sum_{\substack{i,j,k,l\\ \alpha,\beta,\gamma,\delta}}U_{ijkl}^{\alpha\beta\gamma\delta}a_{i\alpha}^{\dagger}a_{j\beta}^{\dagger}a_{k\gamma}a_{l\delta}\ ,$$

where i, j, k, and l are site indices and α, β, γ, and δ label both the orbital and the spin state of the d wave functions: electrostatic interactions with the core electrons are implicitly accounted for in the $\epsilon_{\parallel}$ and ϵ_* energies. In keeping with the spirit of the Hubbard approximation, we retain only the interactions on a single site, namely $i=j=k=l$. Among the selected terms, we retain only those including pairs of associated creation and destruction operators $n_i^{(\alpha)}=a_i^{\dagger(\alpha)}a_i^{(\alpha)}$, forgetting about more complex spin and charge fluctuations. We are then left with

$$\begin{aligned}H_{e\text{-}e}=\sum_{i}[&U_{\parallel}n_{i\uparrow}^{(\parallel)}n_{i\downarrow}^{(\parallel)}+U_{*}(n_{i\uparrow}^{(*1)}n_{i\downarrow}^{(*1)}+n_{i\uparrow}^{(*2)}n_{i\downarrow}^{(*2)})+W_{**}(n_{i\uparrow}^{(*1)}+n_{i\downarrow}^{(*1)})(n_{i\uparrow}^{(*2)}+n_{i\downarrow}^{(*2)})\\&+W_{*\parallel}(n_{i\uparrow}^{(\parallel)}+n_{i\downarrow}^{(\parallel)})(n_{i\uparrow}^{(*1)}+n_{i\downarrow}^{(*1)}+n_{i\uparrow}^{(*2)}+n_{i\downarrow}^{(*2)})]\ ,\end{aligned}\tag{3.3}$$

where $U_{\parallel}$ and U_* are the specific Hubbard terms describing the Coulomb interaction of two electrons of like orbitals and opposite spins and W_* and $W_{*\parallel}$ account for the interactions of electrons of unlike orbitals. We do not distinguish, as formally we would have to do, between direct and exchange terms in $W_{*\parallel}$ and W_{**} which are expected to have the same order of magnitude and which will be handled within a mean-field approximation whereas, for the prevailing $U_{\parallel}$ term, we will go beyond the Hartree-Fock approximation. The relative importance of the $U_{\parallel}$ term with respect to the other ones comes about from the fact that (i) $U_{\parallel}$ is larger than U_* because the $d_{\parallel}$ wave functions are expected to be more localized than the π_* ones which are more hybridized with p oxygen wave functions, and (ii) $U_{\parallel}$ is larger than $W_{*\parallel}$ which describes electrostatic interactions between nearly orthogonal wave functions; these arguments will be used to scale U_*, W_{**}, and $W_{*\parallel}$ with respect to $U_{\parallel}$, using the respective radii R_* and $R_{\parallel}$ of the d wave functions (see Appendix A).

Finally, H_{latt} describes the bare potential energy associated with the normal phonon mode which is the order parameter of the transition, but does not encompass the changes in the other phonon modes which accompany the change of the electronic spectrum[22]

$$H_{\text{latt}}=C\eta^2+D\eta^4\ ,\tag{3.4}$$

where C and D coefficients are, respectively, the harmonic and anharmonic contributions; symmetry properties preclude the occurrence of η^3 terms.

B. Decoupling and approximations

It may first be necessary to recall the procedure commonly used in dealing with the Hubbard Hamiltonian in its simplest form:

$$H_H=\sum_{i,j,\sigma}t_{ij}a_{i\sigma}^{\dagger}a_{j\sigma}+U\sum_{i}n_{i\uparrow}n_{i\downarrow}\ ,$$

where t_{ii} takes the value ϵ_0 and t_{ij} ($i\neq j$) depends only on $\vec{R}_i-\vec{R}_j$. Difficulties arise from the second two-particle term which may be expressed as a sum of squares of operators:

$$Un_{i\uparrow}n_{i\downarrow}=\tfrac{1}{4}U[(n_{i\uparrow}+n_{i\downarrow})^2-(n_{i\uparrow}-n_{i\downarrow})^2]\ .\tag{3.5}$$

The partition function may then be transformed in a functional integral of partition functions for uninteracting electrons in fluctuating fields[7,8,10,23,24]:

$$Z=\int\prod_{i}D\mu_i(s)D\zeta_i(s)\,\mathrm{tr}\,T_s\left[\exp\left(-\int_0^{\beta}\Phi(s)\,ds\right)\right]\ ,\tag{3.6}$$

with $\beta = 1/k_B T$ and

$$\begin{aligned}\Phi(s) = &\sum_{i,j,\sigma} t_{i,j} a^{\dagger}_{i,\sigma}(s) a_{j,\sigma}(s)\\ &-\tfrac{1}{2}U \sum_i \mu_i(s)[n_{i\uparrow}(s) - n_{i\downarrow}(s)]\\ &+\tfrac{1}{2}U \sum_i \zeta_i(s)[n_{i\uparrow}(s) + n_{i\downarrow}(s)]\\ &+\tfrac{1}{4}U \sum_i [\mu_i^2(s) - \zeta_i^2(s)] \ ,\end{aligned}$$

where T_s is the chronological operator, and $\mu_i(s)$ and $\zeta_i(s)$ being the magnetic moments and electric charge fields, respectively, fluctuating with the (fictitious) time s. On this ground, approximations may be made, the first one being to neglect time fluctuations; this static approximation transforms functional integrals into conventional ones. The second approximation is to neglect electric charge fluctuation

$$\zeta_i(s) = \langle n_{i\uparrow} + n_{i\downarrow} \rangle = \bar{n} \ .$$

The partition function is then approximated by

$$Z = \int \prod_i d\mu_i Z_0(\{\mu_i\}) \ , \tag{3.7a}$$

with

$$\begin{aligned}Z_0(\{\mu_i\})\\ = \operatorname{tr}\exp\Bigg[-\beta\Bigg(&\sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} - \tfrac{1}{2}U \sum_i \mu_i (n_{i\uparrow} - n_{i\downarrow})\\ &+\tfrac{1}{2}U\bar{n} \sum_i (n_{i\uparrow} + n_{i\downarrow})\\ &+\tfrac{1}{4}U \sum_i (\mu_i^2 - \bar{n}^2)\Bigg)\Bigg] \ .\end{aligned} \tag{3.7b}$$

One then uses the Landau (or steepest-descent) approximation, which consists in choosing the prevailing term in Eq. (3.7a)

$$Z \simeq [\max_{\{\mu_i\}} Z_0(\{\mu_i\})] g_{\{\mu_i\}} \ ,$$

where the degeneracy factor $g_{\{\mu_i\}}$ accounts for the volume of the μ_i space in which Z_0 takes its maximum value. Each of these μ_i distributions satisfy the equation

$$\frac{\partial Z_0}{\partial \mu_i} = 0 \ ,$$

a condition which turns out to be identical to $\mu_i = \langle n_{i\uparrow} - n_{i\downarrow} \rangle$. An additional simplification is to simulate the unknown μ_i distribution by the one of an equivalent alloy, specified by a variational probability distribution $\mathcal{P}(\{\mu_i\})$ to be defined. Then,

$$Z \simeq [\max_{\{\mu_i\}} Z_0(\{\mu_i\})] g_{\{\mu_i\}} \simeq \max_{\mathcal{P}} [\langle Z_0(\{\mu_i\}) \rangle g_{\mathcal{P}}] \ , \tag{3.8}$$

where $\langle Z_0 \rangle$ is the alloy average of the electronic partition function Z_0 given by Eq. (3.7b) and where the degeneracy factor $g_{\mathcal{P}}$ is related to the alloy-configuration entropy. In the absence of the magnetic field and for $\bar{n} = 1$, the symmetry of the Hubbard problem (i.e., the electron-hole symmetry) suggests the probability distribution

$$P_\mu(\{\mu_i\}) = \prod_i [\tfrac{1}{2}\delta(\mu_i - \mu) + \tfrac{1}{2}\delta(\mu_i + \mu)] \ , \tag{3.9}$$

that is, the distribution

$$\mathcal{P}_\mu(\{\mu_i\}) = \mathcal{P}(\mu, \{\epsilon_i\}) \ ,$$

where $\mu_i = \epsilon_i \mu$ and where ϵ_i takes at random the value $+1$ or -1 on site i, $\mathcal{P}_\mu$ depends only on the variational parameter μ. In Eq. (3.8a), $g_{\mathcal{P}}$ no longer depends on μ which is chosen from

$$\frac{\partial \langle Z_0(\mu, \{\epsilon_i\}) \rangle}{\partial \mu} = 0 \ , \tag{3.10}$$

which is still identical to

$$\mu = \frac{1}{N} \sum_i \epsilon_i \langle n_{i\uparrow} - n_{i\downarrow} \rangle \tag{3.11}$$

as far as Z_0 is exactly calculated; μ appears as the alloy-average amplitude of the local magnetic moment. The free energy estimated from Eq. (3.8) is

$$F = -k_B T \ln\langle Z_0 \rangle - k_B T \ln g_{\mathcal{P}} \ , \tag{3.12}$$

$\mathcal{P}_\mu$ being specified by Eq. (3.9)

$$\ln g_{\mathcal{P}} = -N \ln 2 \ ;$$

that is F includes beside the electronic term a magnetic moment entropy as long as μ given by Eq. (3.11) is nonvanishing. Finally, we will estimate $\langle Z_0 \rangle$ using the coherent-potential approximation[25] which involves no correlation between different ϵ_i and within which the alloy-average electronic free energy equals that estimated from the alloy-average density of states.[26]

Note that more sophisticated approximations like the self-consistent sublattice approximation[10,27] would imply others $\mathcal{P}(\{\epsilon_j\})$ involving correlations between nearest neighbors as additional parameters.

When one returns to our Hamiltonian Eq. (3.3) and assumes that the $d_{\parallel}$ electrons only need to be considered beyond the Hartree-Fock approximation, the previous decoupling procedure leads to

$$\begin{aligned} H = {} & H_{0\parallel} + H_{0*} + H_{\text{latt}} \\ & + \sum_i \left[\tfrac{1}{2} U_{\parallel} \bar{n}^{(\parallel)} n_i^{(\parallel)} - \tfrac{1}{2} U_{\parallel} \epsilon_i \mu \left(n_{i\uparrow}^{(\parallel)} - n_{i\downarrow}^{(\parallel)} \right) \right. \\ & \qquad \left. + W_{*\parallel} \left(\bar{n}^{(\parallel)} n_i^{(*)} + \bar{n}^{(*)} n_i^{(\parallel)} \right) \right] \\ & + \sum_i \left(-\tfrac{1}{4} U_{\parallel} \bar{n}^{(\parallel)2} + \tfrac{1}{4} U_{\parallel} \mu^2 - \tfrac{1}{8} U_* n^{(*)2} \right. \\ & \qquad \left. - \tfrac{1}{4} W_{**} \bar{n}^{(*)2} - W_{*\parallel} \bar{n}^{(*)} \bar{n}^{(\parallel)} \right) , \end{aligned} \tag{3.13a}$$

where

$$\begin{aligned} \bar{n}^{(\parallel)} &= \langle n_{i\uparrow}^{(\parallel)} + n_{i\downarrow}^{(\parallel)} \rangle , \\ \bar{n}^{(*)} &= \langle n_{i\uparrow}^{(*1)} + n_{i\downarrow}^{(*1)} \rangle + \langle n_{i\uparrow}^{(*2)} + n_{i\downarrow}^{(*2)} \rangle , \end{aligned} \tag{3.13b}$$

and where $H_{0\parallel}$ and H_{0*} are defined by Eqs. (3.2a) and (3.2b). μ is a variational parameter associated with the local $d_{\parallel}$ moments only; i.e., we neglect the local π^* moments. Let us notice that, within this formalism, the condition

$$\bar{n}^{(\parallel)} + \bar{n}^{(*)} = 1$$

leads to the constraint

$$0 \leq \mu \leq \bar{n}^{(\parallel)} . \tag{3.14}$$

The fifth term of Eq. (3.13a), which contains only the c numbers $\bar{n}^{(*)}$, $\bar{n}^{(\parallel)}$, and μ is a consequence of our decoupling procedure but expresses simply the necessity of not counting twice the interaction energies.

We will assume that, when the $d_{\parallel}$ and π^* bands overlap at the Fermi level, the probability distribution of the local $\mu_{\parallel}$ moments is still given by Eq. (3.9). Note that in that case, minimization of the partition function of the whole system with respect to μ no longer implies Eq. (3.11).

At this stage, we find it convenient to introduce a fictitious configuration in which $d_{\parallel}$ and π^* bands do overlap in absence of both lattice distortion and magnetic moments, at $T=0$; this configuration corresponds to the band-structure calculation for the metallic phase. Denoting then by N_0 the $d_{\parallel}$ electron concentration associated with the configuration, we may rewrite H as:

$$\begin{aligned} H = {} & \tilde{H}_{0\parallel}(\eta) + \tilde{H}_{0*}(\eta) + \sum_i \tfrac{1}{2} U_{\parallel} \epsilon_i \mu \left(n_{i\uparrow}^{(\parallel)} - n_{i\downarrow}^{(\parallel)} \right) \\ & + \sum_i \left[\left(\tfrac{1}{2} U_{\parallel} - W_{*\parallel} \right) \left(\bar{n}^{(\parallel)} - N_0 \right) n_i^{(\parallel)} \right. \\ & \qquad \left. + \left(W_{*\parallel} - \tfrac{1}{4} U_* - \tfrac{1}{2} W_{**} \right) \left(\bar{n}^{(\parallel)} - N_0 \right) n_i^{(*)} \right] \\ & + \Delta E_{\text{int}} + H_{\text{latt}} \end{aligned} \tag{3.15a}$$

with

$$\begin{aligned} \Delta E_{\text{int}} = {} & \sum_i \left[\tfrac{1}{4} U_{\parallel} \mu^2 - \left(\tfrac{1}{4} U_{\parallel} + \tfrac{1}{8} U_* - W_{*\parallel} \right) \left(\bar{n}^{(\parallel)2} - N_0^2 \right) \right. \\ & \qquad \left. + \left(W_{*\parallel} - \tfrac{1}{4} U_* - \tfrac{1}{2} W_{**} \right) \left(\bar{n}^{(\parallel)} - N_0 \right) \right] , \end{aligned} \tag{3.15b}$$

where $\tilde{H}_{0\parallel}(\eta)$ and $\tilde{H}_{0*}(\eta)$ incorporate the Hartree-Fock energies corresponding to the N_0 configuration, energy shifts in the fourth and fifth terms being estimated with respect to this configuration. It is worth pointing out that the way we take into account the $d_{\parallel}$-π^* interaction strictly follows the prescription given by Hubbard,[4(a)] who states that the unperturbed band energies of the electrons he considers incorporate the interaction with the electrons of all other bands. The fourth term shows explicitly that, owing to the electron-electron interaction, the positions of the $d_{\parallel}$ and π^* bands depend on their respective populations. Finally, H depends on two parameters, namely, the amplitude of the static distortion η and the one of the local moment μ. The task is to estimate, at any temperature, the partition function Z or the free energy F associated to H, the equilibrium state of the system being defined by the values of η and μ which miminize F or Z.

C. CPA density of states

From H, we may extract

$$H_{\text{alloy}} = \tilde{H}_{0\parallel}(\eta) + \sum_i \tfrac{1}{2} U_{\parallel} \epsilon_i \mu \left(n_{i\uparrow}^{(\parallel)} - n_{i\downarrow}^{(\parallel)} \right) ,$$

which corresponds to the propagation of independent spin ↑ or spin ↓ electrons in presence of a set of static and, in our approach, uncorrelated scattering potentials $\pm \frac{1}{2} U_{\parallel} \mu$.

The average propagation in such a random field is generally described in terms of an effective medium which is defined by the condition that a single scatterer embedded in this effective medium should produce no further scattering on the average.[25] The propagation of an electron in the effective medium is described by the Green's function $G(z)$

$$G(z) = G_0(z - \Sigma(z)) ,$$

where $G_0(z)$ is the Green's function of the unperturbed medium, i.e.,

$$G_0(z) = [z - \tilde{H}_{0\parallel}(\eta)]^{-1} ,$$

and where the self-energy $\Sigma(z)$ is defined by a self-consistency relation. With the probability distribution Eq. (3.9) this relation takes the simple form:

$$\Sigma(z) = [(\tfrac{1}{2} U_{\parallel} \mu)^2 - \Sigma(z)^2] \mathcal{G}(z) , \tag{3.16}$$

where

$$\mathcal{G}(z)=\langle i|G(z)|i\rangle=\frac{1}{N}\,\mathrm{tr}G(z)\ ,$$

$$\mathcal{G}(z)=\frac{1}{N}\sum_{k}\frac{1}{z-\epsilon_k-\Sigma(z)}$$

$$=\int\frac{\rho_0^{\|}(E)}{z-E-\Sigma(z)}\,dE\ , \tag{3.17}$$

where ϵ_k are the Bloch state eigenenergies associated with $H_{0\|}(\eta)$ and $\rho_0^{\|}(E)$ is the correponding density of states per atom. Furthermore, the actual density of states per atom is given by

$$\rho_{\mathrm{CPA}}^{\|}(E)=-\frac{1}{\pi}\,\mathrm{Im}\mathcal{G}(E+i0)\ . \tag{3.18a}$$

From the preceding equation, it is clear that the solution of the CPA equation does not involve the full band structure ϵ_k but only the unperturbed density of states $\rho_0^{\|}(E)$.

A well-known consequence of the CPA is the opening of a gap in the density of states when the scattering potential exceeds a critical value; the gap opening condition depends only on the product $U_{\|}\mu$ and on the unperturbed density of states $\rho_0^{\|}(E)$. As pointed out before, since $H_{0\|}$ depends on the amplitude η of the deformation, we only need to account for the part of this dependence which is due to the hopping integral $t_{ij}(\eta)$ via a suitable parametrization of $\rho_0^{\|}(E,\eta)$. Then, implementing the CPA calculation gives us

$$\rho_{\mathrm{CPA}}^{\|}(E)=\rho_{\mathrm{CPA}}^{\|}(E,\eta,\mu)\ , \tag{3.18b}$$

D. Model density of states and Peierls dimerization

As regards the $d_{\|}$ band, we know that its shape depends primarily on coupling between adjacent vanadium along a chain, the eight interchain hopping terms t_0 being smaller than the intrachain one t or, in the distorted phase, the t_s and t_l associated with the short and long bounds, respectively. According to previously given arguments, we assume that the lattice distortion, acting alone, is not able to open a gap in the $d_{\|}$ density of states, however, it will distort it. A simple way to account for this effect is to introduce a model density of states under the form of an even fourth-degree polynomial in energy:

$$\rho_0^{\|}(E)=\frac{1}{\Delta^{(\|)3}(\frac{2}{5}-\frac{1}{3}b)}\times\left[\frac{1}{\Delta^{(\|)2}}(\Delta^{(\|)4}-E^4)+b(E^2-\Delta^{(\|)2})\right]\ ,\quad\text{if } -\Delta^{(\|)}\leqslant E\leqslant\Delta^{(\|)}$$

$$=0,\quad\text{otherwise}\ , \tag{3.19}$$

which depends on two parameters, the half-bandwidth $\Delta^{(\|)}(\eta)$ and $b(\eta)$. As stated above, we assume that there is no density-of-states gap induced by the Peierls dimerization alone, so one has $0\leqslant b\leqslant 1$ with $b(\eta=0)=0$ implying no distortion, and $b(\eta)=1$ the onset of a gap opening. We make contact with the hopping terms and their distortion dependence assuming

$$\text{(i) } t_0 \text{ independent of } \eta\ ,$$

$$\text{(ii) } t_s=t\exp(2\eta/R)\ , \tag{3.20}$$

$$t_l=t\exp(-2\eta/R)\ ,$$

where R is a typical Slater radius for the $d_{\|}$ wave function, and using the following relations

$$\Delta^{(\|)}(\eta)=8t_0+t_l+t_s\ , \tag{3.21a}$$

$$M_2(\eta)=t_s^2+t_l^2+8t_0^2\ , \tag{3.21b}$$

deduced from a nearest-neighbor tight-binding approximation. M_2 is the second moment of the density of states

$$M_2=\int E^2\rho_0^{(\|)}(E)\,dE\ . \tag{3.22}$$

It is worth emphasizing that the knowledge of $\Delta^{(\|)}(\eta=0)$ and of $\rho_0^{\|}(\eta=0)$ is equivalent to the one of t_0 and t, the values of the former quantities imply a ratio $t/t_0=8.1$ of the intrachain to the interchain hopping term.

Introducing Eq. (3.20) in Eq. (3.21) and Eq. (3.19) in Eq. (3.22) gives $\Delta^{\|}(\eta)$ and $b(\eta)$. Note that the strength of the electron-phonon interaction is introduced via the η dependence of t_s and t_l, i.e., via the Slater radius R. An advantage of the model density of states Eq. (3.19) is that, for such a symmetric unperturbed shape the gap-opening condition may be shown, following Ref. 25(b), to depend only on the second moment M_2, namely,

$$U_{\|}\mu\geqslant 2(M_2)^{1/2}\ , \tag{3.23}$$

so that our parametrization combines the electron-phonon and electron correlation coupling mechanisms in the most direct and simplest way.

For the π^* density of states $\rho_0^*(E)$ which is not distorted, we will assume the same form as in Eq. (3.19) with $b = 0$ and a half-bandwidth $\Delta^{(*)}$.

A second effect of the distortion is to shift the π^* band with respect to the $d_{\parallel}$ one, this effect is introduced via the η dependence of $\epsilon_{\parallel}$ and ϵ_* in Eq. (3.2), i.e., via the previously discussed deformation potential. However the η dependence of $H_{0\parallel}$ and H_{0*} includes, besides this explicit dependence, the implicit one which is associated with the change in band populations.

E. Exchange interactions

It has been made clear by several authors that, especially as regards the thermodynamics, the basic feature of the Hubbard problem[8, 10] as well as of the problem of metal magnetism[24] is the formation of local magnetic moments. However the coupling between magnetic moments needs to be accounted for. The specificity of the VO_2 problem relies on (i) the quasi-one-dimensional character of the coupling between vanadium ions and (ii) the electron-phonon coupling which induces a quasidimerization of vanadium atoms (along a chain) which is also a quasidimerization of their spins.

The magnetic coupling may be estimated in terms of an effective coupling J_{ij} between spins, either perturbatively from the functional-integral formalism[23, 28] or from a sophisticated alloy approximation involving intersite correlations.[10] Either of these methods would be very difficult to implement in a situation where hopping integrals t_{ij} are not equivalent and depend on the distortion parameter η. We will thus estimate this antiferromagnetic exchange interaction

$$H_{\text{exch}} = \sum_{i,j} J_{ij}\mu^2\epsilon_i\epsilon_j \tag{3.24}$$

from a two-atom Hubbard model.[3] In this model, the energy difference between the (singlet) ground state and the first (triplet) excited one is

$$\Delta E = (\tfrac{1}{4}U_{\parallel}^2 + 4t_{ij}^2)^{1/2} - \tfrac{1}{2}U_{\parallel} = 2J_{ij} \ . \tag{3.25}$$

In the distorted phase, one has to distinguish between intradimer J_s and interdimer J_l

$$J_{s(l)}(\eta) = [\tfrac{1}{16}U_{\parallel}^2 + t_{s(l)}^2(\eta)]^{1/2} - \tfrac{1}{4}U_{\parallel} \ .$$

In this model we have neglected the interchain exchange coupling, owing to the smallness of t_0.

The onsite Hartree-Fock interaction between $d_{\parallel}$ and π^* electrons could generate an effective exchange interaction between the two bands, which, however, has been discarded. Note that Eq. (3.25), which describes some Anderson superexchange, is, strictly speaking, only valid for a half filled band with $\mu \sim 1$, which, as will be shown, corresponds to the situation found in the insulating (M_1) phase of VO_2. In the metallic phase of VO_2, where we shall find a fractional occupation of the $d_{\parallel}$ band ($\bar{n}_{\parallel} \sim 0.8$) and small moments ($\mu \sim 0.3$), these terms, although giving a poor description of the exchange energy, do represent but a small correction.

Thermodynamics of the linear Ising chain may be performed exactly using the transfer-matrix method[29] (see Appendix B), leading to a spin contribution to the free energy

$$F_{\text{spin}} = -\tfrac{1}{2}k_BT\ln(4\cosh\beta J_s\mu^2\cosh\beta J_l\mu^2) \ . \tag{3.26}$$

In F_{spin}, one may separate an internal energy contribution from an entropy one; at the limit $J_{s(l)} \rightarrow 0$, the former contribution vanishes and the latter one tends towards the $-k_BT\ln 2$ term discussed in Eq. (3.2). In other words, accounting for the exchange interactions (i.e., for the correlations between moments) introduces corrective terms which are not present in the CPA calculations of the orbital free energy.

IV. THERMODYNAMICS OF THE MODEL

Having specified the model Hamiltonian, we are in a position to write down the free energy F as the sum of orbital, spin, and lattice contributions:

$$F = F_{\text{orb}} + F_{\text{spin}} + F_{\text{latt}} \tag{4.1}$$

and to define the equilibrium state at a given temperature T by the values of μ and η which minimize F, subjected to the constraint Eq. (3.14). In Eq. (4.1), $F_{\text{spin}} = F_{\text{spin}}(T, \eta, \mu)$ has been previously defined by Eq. (3.26) and F_{latt} is reduced to the potential energy Eq. (3.24). We get F_{orb} from

$$F_{\text{orb}}(T, \eta, \mu) = E_F - k_BT\int_{-\infty}^{+\infty}\rho_{\text{tot}}(E;\eta,\mu) \times\ln(1 + e^{\beta(E_F - E)})\,dE + \Delta E_{\text{int}}(\eta, \mu, T) \ , \tag{4.2}$$

where ΔE_{int} has been defined in Eq. (3.15b), the total density of states $\rho_{\text{tot}}(E, \eta, \mu)$ is

$$\rho_{\text{tot}}(E;\eta,\mu) = \rho^{\parallel}(E;\eta,\mu) + \rho^*(E;\eta,\mu) \ , \tag{4.3}$$

and the Fermi energy E_F is specified by the condition

$$\int_{-\infty}^{+\infty}\rho_{\text{tot}}(E;\eta,\mu)f(E,E_F;T)\,dE = 1 \ , \tag{4.4}$$

f being the Fermi function. The π^* density of states, normalized to four electrons is

$$\rho^*(E;\eta,\mu) = \rho_0^*(E - \Omega_*(\eta,\mu)) \ ,$$

with

$$\rho_0^*(x)=\begin{cases}\dfrac{5}{2\Delta^{*5}}(\Delta^{*4}-x^4), & \text{for } |x|\le\Delta^*\\ 0, & \text{otherwise}\ ,\end{cases}$$

where the center of the π^* band, $\Omega_*(\eta,\mu)$, depends explicitly on η via the deformation potential and implicitly on both η and μ through the Hartree-Fock terms. The $d_{\parallel}$ density of states, normalized to two electrons is

$$\rho^{\parallel}(E;\eta,\mu)=2\rho_{\parallel,\mathrm{CPA}}(E-\Omega_{\parallel}(\eta,\mu))\ ,$$

and depends on η and μ via (i) the dependence of the center of the $d_{\parallel}$ band $\Omega_{\parallel}(\eta,\mu)$ and (ii) the dependence of $\rho_{\parallel,\mathrm{CPA}}$, given in Eq. (3.18) and which is obtained from the self-consistent calculation discussed in Sec. III C and III D. Let us emphasize that, for each couple (η,μ) of variational parameters, we have first to self-consistently solve the CPA equations (3.16) and (3.17) at each energy. A second step of self-consistently is, for a given couple (η,μ) and at given temperature T, to specify $\Omega_*(\eta,\mu)$ and $\Omega_{\parallel}(\eta,\mu)$ via the $d_{\parallel}$- and π^*-band occupations given by Eqs. (4.3) and (4.4):

$$\bar{n}^{(\parallel)}=\int_{-\infty}^{+\infty}\rho_{\parallel}(E;\eta,\mu)p(E,E_F;T)\,dE\ , \tag{4.5}$$

from

$$\Omega_*(\eta,\mu)=\Omega_{*0}+\tfrac{1}{3}\Xi\eta^2 +(W_{*\parallel}-\tfrac{1}{4}U_*-\tfrac{1}{2}W_{**})(\bar{n}^{(\parallel)}-N_0)\ , \tag{4.6}$$

and

$$\Omega_{\parallel}(\eta,\mu)=\Omega_{\parallel 0}-\tfrac{2}{3}\Xi\eta^2 +(\tfrac{1}{2}U_{\parallel}-W_{*\parallel})(\bar{n}^{(\parallel)}-N_0)\ . \tag{4.7}$$

In Eqs. (4.6) and (4.7), the relative position of the two band centers, $\Omega_{\parallel 0}$ and Ω_{*0}, in the N_0 configuration will be defined below, the second terms include the deformation potential Ξ, and the third terms correspond to Hartree-Fock potentials. In order to specify the model completely, we need the parameters of the N_0 reference configuration. We first take for convenience $\Omega_{\parallel 0}=0$, then, in keeping with the discussion of Sec. II, we take

$$\int_{-\infty}^{E_F}\rho_0^{\parallel}(E,\eta=0)\,dE=0.75\ ,$$

$$\int_{-\infty}^{E_F}\rho_0^*(E-\Omega_{*0})\,dE=0.25\ ,$$

and from Ref. 6, $E_F+\Delta_{\parallel}=0.44$ eV and $\Delta_{\parallel}(\eta=0)+\Delta_*+\Omega_{*0}=2$ eV. Solving these equations, we find $\Delta_{\parallel}(\eta=0)=0.55$, $\Delta_{*0}=0.89$, and $\Omega_{*0}=0.56$ eV. We then take $U_{\parallel}=1.10$ eV, close to the estimate $U_{\parallel}=1.22$ eV of the cluster calculation.[21] Note that the ratio $U_{\parallel}/2\Delta_{\parallel}(\eta=0)$ is larger than the one which is needed to open a correlation gap within a single-band, undistorted Hubbard system. The scaling of Hartree-Fock terms on $U_{\parallel}$ (see Appendix A) gives $U_*=0.55$, $W_{*\parallel}=0.61$, and $W_{**}=0.49$ eV. The radius R which in Eq. (3.20) defines the strength of the Peierls coupling is chosen so as to introduce, for the value of η which corresponds to the distorted phase, a significant deformation of the density of states but no gap opening ($b<1$), namely, $R=0.5$ Å. Finally, with the previous choice of electronic parameters, the constants C and D in Eq. (3.4) are determined from the knowledge of the transition temperature $T_c=340$ K and of the distortion at the transition $\eta_c=0.105$ Å; we get $C=17.3$ eV Å^{-2} and $D=260$ eV Å^{-4}.

The value of C is close to the one which would have been obtained by taking the eigenfrequency of the normal mode associated with the lattice distortion in the calculated lattice dispersion curve of rutile,[30] $\omega=5.10^{13}$ rad sec^{-1}, assuming the mass of this mode to be twice that of the vanadium atom. The value of D corresponds to a small anharmonicity, namely, $C\eta^2=D\eta^4$ for a value of η which corresponds to an 18% shortening of the vanadium-vanadium distance along a chain.

This calculation scheme has been implemented and the results are displayed in Fig. 2 which shows the variation of the free energy F as a function of the two variational parameters, calculated at the transition temperature T_c. This diagram evidences (i) the first-order nature of the transition, i.e., the fact that two free-energy minima separated by a line of maxima become equal and (ii) that the transition affects

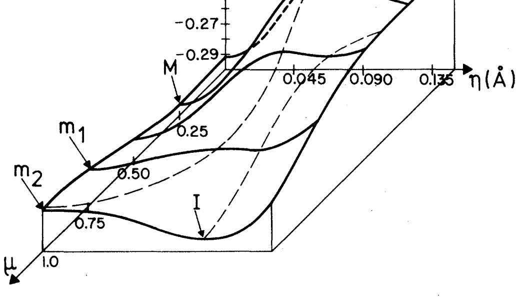

FIG. 2. Free energy per vanadium atom as a function of the distortion η and the local-moment amplitude μ, calculated at the transition temperature T_c. M and I correspond to the equistable metallic and insulating phases coexisting at the first-order transition. m_1 and m_2 are the coordinates of unstable states referred to in the text.

both the lattice distortion η and the average amplitude of the local moments μ which (discontinuously) change from $\eta = 0.105$ Å and $\mu = \bar{n}_{\parallel} = 0.99$ in the low-temperature phase to $\eta = 0$ and $\mu = 0.27$ (i.e., $\mu < \bar{n}_{\parallel} = 0.78$) in the high-temperature one. Moreover, as displayed in Fig. 3, at $T < T_c$ the distorted local minimum is always the absolute one and its η coordinate continuously varies with T, whereas μ is always equal to $\bar{n}_{\parallel} \sim 1$, at $T > T_c$, the undistorted minimum becomes the absolute one and μ continuously decreases with increasing T, as discussed in Sec. V below. This calculation suggests that the average moment amplitude μ vanishes at a temperature $T_{\mu} \sim 800$ K. The associated changes in the $d_{\parallel}$-band shape and in the $d_{\parallel}$- and π^*-band positions are displayed in Fig. 4 which shows the density of states of each equilibrium state at $T = T_c$: the low-temperature phase is an insulating one with a density-of-states gap between the lower Hubbard $d_{\parallel}$ band and the π^* one. The temperature dependence of this gap is displayed in Fig. 5. At first glance, this density of states gap $E_{G,\mathrm{DOS}}$ should be compared to the thermal gap deduced from transport experiments.[31] There is, however, some uncertainty about the relevant value of $E_{G,\mathrm{th}}$ whether one chooses (i) the activation energy of the conductivity σ at $T < T_c$, namely, $E_{G,\mathrm{th}} \sim 0.25$ eV, (ii) the value of $d\ln\sigma/d(1/k_BT)$ at $T = T_c$, $E_{G,\mathrm{th}} \sim 0.8$ eV, or (iii) the conductivity jump at the transition, $E_{G,\mathrm{th}} \sim 0.5$ eV. The best estimate seems to be the third one, owing to the fact that the mobilities in both phases have been experimentally shown to be comparable,[32] and this value is also in agreement with the (nonunambiguous) determination of the optical gap.[33] We thus find a gap $E_{G,\mathrm{DOS}} = 0.22$ eV at $T = T_c$, about twice smaller than the experimental value. It is unlikely that either a reasonable change of $U_{\parallel}$ or of the shape of the undistorted $\rho_0^{\parallel}$, may increase $E_{G,\mathrm{DOS}}$ by a factor of 2. This discrepancy may appear as a weakness of our model, even if one keeps in mind the experimental uncertainty on $E_{G,\mathrm{th}}$. However, our thermodynamic approach, relying on the single-site CPA, is better suited to give the ground-state energy, related to the first moments of the density of states, rather

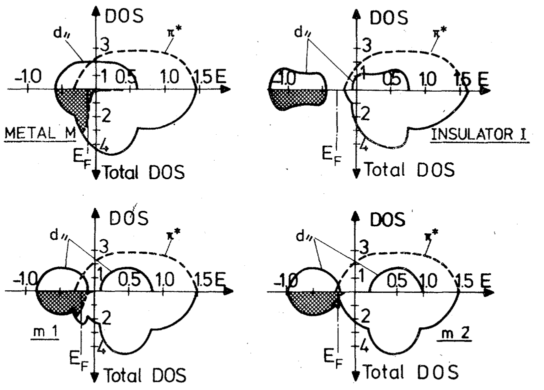

FIG. 4. Electronic density of states calculated at the transition temperature for the metal M and the insulator I phases, and for the intermediate states m_1 and m_2. Hatched areas correspond to occupied states.

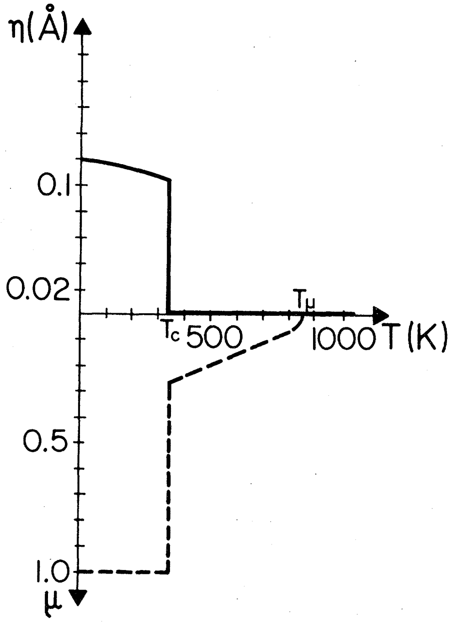

FIG. 3. Temperature variation of the amplitudes of the distortion η and of the local magnetic moment μ.

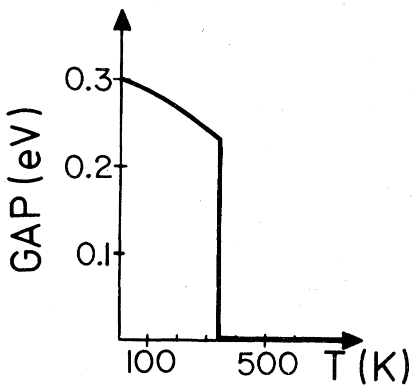

FIG. 5. Thermal variation of the gap in the electronic density of states.

than the density-of-states gap related to its fine structure; moreover it is well known that the conductivity activation energy may be larger than the density-of-states gap, in case of Anderson localization (see the discussion in Ref. 10).

The calculation also yields the latent heat which is $L = 564$ cal per VO_2 mole, compared to the experimental one 1024 cal per VO_2 mole.[34] This calculated value may be considered as the sum of an electronic contribution, $L_{el} = 0.437L$ and a spin-order one $L_{spin} = 0.536L$, the phonon contribution not being included in our calculation. It is worth pointing out that our calculated L amounts to 55% of the experimental value and corresponds to different (rough) estimates[35] or the electronic plus spin) contribution, the remaining part being the phonon one. In our view, the importance of the phonon term does not come about from the softening of a single mode but rather from a general weakening of force constants in the metallic phase, as suggested by a number of experiments.[36]

It is by now well established that the lattice dynamics are dominated by the structure of the dielectric constant,[37] i.e., by the screening of interionic Coulomb interactions. The dielectric constant change at the insulator to metal transition, which in particular affects the $q = 0$ screening, modifies the lattice dynamics. It points to a general softening of the lattice and thus to a lowering of the Debye temperature and to an increase of phonon energy. Our scheme is thus qualitatively in agreement with experiments although we are not able to account quantitatively for this effect.

For the sake of simplicity, we may separate our discussion of the phase transition process in two stages. In the first place, we see that, for a single-band system (e.g., for $d_{\parallel}$ alone), the electron-phonon interaction renormalizes the electron-electron one and vice versa. Although both interactions contribute to lower the internal energy, it appears that at a given $U_{\parallel}$, the critical value of μ which opens a Hubbard gap is an increasing function of η. The electronic energy gain for a given distortion η, $E(\mu,0) - E(\mu,\eta)$, is a decreasing function of μ. For a single-band system, the combination of electron-phonon and electron-electron interactions would lead to two distinct second-order phase transitions, namely, a ferroelastic transition and a metal-insulator one. In the second place, the presence of a π^* band, coupled to the $d_{\parallel}$ one by both the deformation and the Hartree-Fock potentials, leads to a single first-order transition associated to both the opening of a finite gap and the onset of a finite distortion. One may get some insight on the transition mechanism by considering (Fig. 4) not only the density-of-states diagrams M and I which correspond to the two equilibrium states at T_c but also the diagrams m_1 and m_2 (see their coordinates in Fig. 2). The m_1 diagram shows that the opening of a Hubbard gap does not necessarily imply an insulating behavior and the m_2 diagram shows that, as soon as the π^* band is nearly empty, the system gains an additional energy by distorting itself, this distortion being stabilized by the lattice energy. This analysis clearly shows that, although η is the (Landau) order parameter of the transition, its thermal variation is but a consequence of a subtle coupling with electron correlations [i.e, with a mechanism which is not described by a (Landau) order parameter]. Thus the leading instability, the one which may lead to large amplitude fluctuations, is that of the average moment μ, occurring at T_{μ} (~ 800 K), whereas the onset of a distortion at T_c is not expected to induce large-amplitude fluctuations of η, i.e., to induce any soft mode associated to the R point of the Brillouin zone. Indeed the $F(\eta,\mu)$ diagram at T_c (Fig. 2) exhibits a very small curvature along the μ axis, but a significant one along the η axis. It is worth noticing that similar conclusions have been obtained for the so-called "triggered" phase transitions[38] from a formal discussion of a phenomenological Landau expansion; we show in Appendix C the correspondence between our microscopic model and the phenomenological one.

V. MAGNETIC PROPERTIES

As in other cases of correlation induced metal-insulator transitions (e.g., V_2O_3), the magnetic properties of the system and their variation at the transition are important features of the problem. In actual fact, the average amplitude of the local moments μ enters our model as a basic parameter. However its calculated variation cannot be compared directly to the experimental data but to what may be inferred from the variation of the magnetic susceptibility χ.

One may expect that the thermodynamic approach which has provided us with the ground-state energy of the system, would lend itself to estimate the response to an external field. Under application of a magnetic field h, the symmetry between the two equivalent alloys experienced by the spin-up and the spin-down electrons is broken, the statical distribution becoming

$$\mathcal{P}(\{\mu_i\}) = \prod_i [(\tfrac{1}{2} + \delta c)\delta(\mu_i - \mu - \delta\mu) + (\tfrac{1}{2} - \delta c)\delta(\mu_i + \mu - \delta\mu)] \ . \tag{5.1}$$

Besides the Zeeman energy, the free-energy change results both from a concentration variation δc and from the difference $\delta\mu$ in moment amplitudes:

$$F = F_0 + \Delta F(T, \delta c, \delta\mu, h) \ .$$

Minimizing F with respect to δc and $\delta\mu$ and keeping terms up to the second order in h, allows us to identify the magnetic susceptibility χ from

$$\Delta F^{(2)} = -\tfrac{1}{2}\chi h^2 \ .$$

This program may be implemented in the case of the simple Hubbard model, for $\bar{n}=1$, using the perturbative method developed by Ducastelle and Gautier.[26] These calculations will be reported elsewhere; they show that (i) in the insulating limit, for $U/W >> 1$ and $\mu \simeq 1$, the susceptibility is only due to δc and tends towards a Curie-Weiss form

$$\chi = \frac{\mu_B^2}{k_B(T+T_c)} \ ,$$

with

$$k_B T_c = \frac{W^2}{4U} \ , \tag{5.2}$$

i.e., the Anderson superexchange, and that (ii) at the metallic limit $\mu << 1$, χ mainly derives from $\delta\mu$ and exhibits an enhanced Pauli behavior

$$\chi = \frac{\mu_B^2 \rho(E_F)}{1-\frac{1}{2}U\rho(E_F)} \ , \tag{5.3}$$

the density of states at the Fermi level $\rho(E_F)$ being estimated in the presence of the equilibrium value of μ. These results are important because they show that one passes continuously from the Curie-Weiss to the Pauli limit and, in particular, that at the metallic limit, the susceptibility is *not* merely the addition of a Pauli contribution due to the electrons considered as itinerant and of a Curie contribution due to the localized moments built up by the same electrons, as conjectured in Ref. 10.

This calculation program would be exceedingly difficult to implement for the VO_2 problem, owing to the presence of the electron-phonon coupling and to the multiband character of the electronic structure. However, the study of the insulating limit of the Hubbard model confirms the relevance, for the magnetic properties of the M_1 phase of VO_2, of the equivalent Ising chain introduced in Sec. III E; let us notice that the $J_{s(l)}$ of the Ising model derives from a superexchange scheme.

For the M_1 phase of VO_2, the spin contribution having been included in the total free energy F which is minimized with respect to η and μ, we know at any temperature the equilibrium value of these parameters and thus the actual values of J_s and J_l which enter the Ising-like interaction H_{exch} [Eq. (3.24)]. Following the same calculation technique, namely the transfer-matrix method[29] (see Appendix B), we are able to estimate (i) the nearest-neighbor spin-correlation functions

$$\langle \epsilon_i \epsilon_{i+1} \rangle_{l(s)} = -\tanh \frac{J_{l(s)}\mu^2}{k_B T} \ , \tag{5.4}$$

where the $J_{l(s)}$ have been given in Eq. (3.25), $l(s)$ standing for a long (short) bond along the vanadium chain in the distorted phase, and (ii) the spin susceptibility of the vanadium atom

$$\chi_{\text{atom}} = \frac{\mu_B \mu^2}{k_B T} \exp\left[\frac{J_s + J_l}{k_B T}\mu^2\right] \Big/ \cosh\left[\frac{J_s + J_l}{k_B T}\mu^2\right] \ . \tag{5.5}$$

The temperature dependence of the correlation function is displayed in Fig. 6, which shows that the intradimer (short bond) spin correlation is as large as 0.993 close to the transition, i.e., that the spin dimerization actually corresponds to a molecule, thus accounting for the essentially vanishing spin susceptibility. The point we wish to emphasize is that, although the existence of the insulating phase derives from the onset of well-developed magnetic moments on the vanadium sites, this local moment formation, owing to the electron-phonon pairing of vanadium ions, does not result in a Curie-like susceptibility in this phase; whereas, in the M_2 phase, the undimerized chain of vanadium does exhibit the paramagnetic behavior of localized moments.[3]

In the R (metallic) phase of VO_2 where both $d_\parallel$ and π^* electrons contribute to the magnetic susceptibility one may estimate the $d_\parallel$ contribution as an enhanced Pauli susceptibility given by Eq. (5.3); such an estimate gives a divergent susceptibility. The origin of this negative result has to be attributed to three deficiencies in our description of the metallic phase, namely (i) a local moment amplitude, $\mu \sim 0.3$ at T_c, which does not correspond to experiment,[39] (ii) a small curvature of the free energy versus μ curve in the whole temperature range $T > T_c$, which indi-

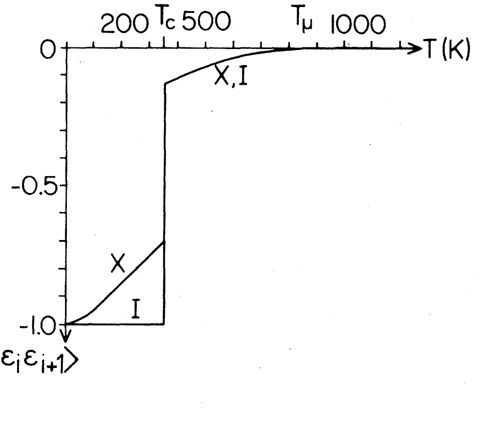

FIG. 6. Thermal variation of the nearest-neighbor spin correlation function $\langle \epsilon_i \epsilon_{i+1} \rangle$ along intradimer (I) and extradimer (X) bounds.

cates large fluctuations of the moment amplitude around the equilibrium value, and (iii) a transition at $T_\mu \sim 800$ K between a correlated metal and a normal one which is likely to be an artifact of the model. This points to the necessity to reconsider the approximations we used to deal with the functional integral, in order to estimate the linear response of the metallic phase which, being calculated perturbatively from the ground state, demands a more accurate specification of the latter. First, within the steepest-descent method, one would approximate the degeneracy factor $g(\{\mu_i\})$ in Eq. (3.8) by a g_P defined from a class of variational probability distributions different from Eq. (3.9), for instance

$$P_\sigma(\{\mu_i\}) = \prod_i \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{1}{2}\frac{\mu_i^2}{\sigma^2}\right] ,$$

the width σ of the distribution being variational and the CPA average $\langle Z_0(\{\mu_i\})\rangle$ being accordingly modified. Second, one would go beyond the steepest-descent approximation by accounting up to the first order for the fluctuations of the variational parameters in the free energy and in the associated susceptibility calculations, that is the Brueckner approximation.[40] Finally, one would have to relax the static approximation which is certainly valid in the limit $\mu \sim 1$ but breaks down for vanishing μ when the lifetime of the local moments becomes close to the time an electron spends on a given site; let us point out that scattering by time-dependent spin fluctuations modifies the density of states as scattering by static moment does. In Ref. 13(b), we have begun to improve the magnetic susceptibility calculation along this line, and we found a $\chi_\parallel$ susceptibility enhanced by a factor of 8 which compares with the factor of 6 needed to fit the experimental data at T_c (with our choice of band parameters). However a comprehensive discussion of these three improvements for the metallic phase of VO_2 would lead us far beyond the scope of the present paper. We postpone the study of the ground state and of the magnetic susceptibility of the metallic phase of the one-band Hubbard model to a future publication.

VI. CONCLUSION

To summarize, we have unified a number of theoretical schemes and partial treatments which had been put forward in the literature, in order to build up a model of the VO_2 transition model which incorporates all the mechanisms previously thought relevant and which quantitatively describes the transition. Our treatment, we believe, puts an end to a long-standing controversy by carrying the theoretical arguments parallel to the experimental ones,[12] which establish that electron-electron correlations are the driving mechanism of the VO_2 transition, the onset of a lattice distortion being but a consequence of this primary mechanism.

Our treatment clarifies some points which deserve comment. First, electron-electron interactions and electron-lattice interactions are not merely additive but combine themselves in a subtle way as seen from the fact that, given the value of μ, the correlation gap in the $d_\parallel$ band is smaller in presence of a Peierls distortion than that it would be in an undistorted system. Secondly, the multiband structure does not merely introduce a marginal intricacy in the problem, because the presence of both $d_\parallel$ and π^* electrons, mutually interacting through electrostatic interactions and coupled via the deformation potential, make the transition a first-order one with a rather high transition temperature, while a pure $d_\parallel$ electron correlation mechanism would have led to a second-order transition, at a lower temperature. We stress that our model does not rely on a too-peculiar feature of the electronic structure and/or of the phonon spectrum; it makes use but of a minimal number of parameters, each of them taking accepted values discussed in the literature and the qualitative features of our results are preserved even for significant changes in these parameter values.

Improvements may be introduced to the model. They are not expected to qualitatively alter our scheme of the transition, and the gain in the accuracy of the description has to be put in balance with the weight of additional computational complexity. A first improvement would be to account for the short-range order (i.e., antiferromagnetic order) along the line of the Economou *et al.*[10] discussion, the major advantage of this procedure being to automatically incorporate antiferromagnetic order without resorting to any equivalent exchange interaction. In the second place, one may introduce a better description of the metallic ground state and incorporate in the free energy the effect of amplitude fluctuations of both the local moment and the crystallographic distortion, as outlined in Sec. V. Beyond the specific problem of the VO_2 system, namely, the identification of the proper mechanism of the phase transition, we have demonstrated that the ESW-Cyrot formalism may actually by implemented in a complex situation, giving a quantitative description which is in fair agreement with experiment. Finally, our analysis makes a large use of the specific phrasing of phase transitions (e.g., order parameters). This in particular has enabled us to disentangle the electron-electron and electron-lattice aspects of the transition. However, the use of this phrasing emphasizes that, should the electronic-structure change introduced by the Hubbard mechanism be an electronic phase transition, the proper order parameter and the associated symmetry breaking are still to be identified. Such an order-parameter specification, in terms of an irreducible representation of a given symmetry group (a criterion which is not fulfilled by a *bona fide* order parameter like the mean amplitude of the local moment or the value of the density-of-states gap), would provide us with both a better understanding of the physics of the phenomenon and a more reliable thermodynamical treatment.

APPENDIX A: SCALING OF THE ELECTRON-ELECTRON INTERACTION CONSTANTS

In Sec. III A we defined the electron-electron interaction Hamiltonian $H_{e\text{-}e}$ which depends on four constants: $U_{\parallel}$, interaction energy between two electrons $d_{\parallel}$ on the same site; U_*, interaction energy between two electrons π^* of the same orbital, on the same site; W_{**}, interaction energy between two electrons π^* of different orbitals on the same site; and and $W_{*\parallel}$, interaction energy between one electron $d_{\parallel}$ and one electron π^* on the same site.

These coefficients are two-electron matrix elements of the general form:

$$W_{\alpha\beta}=\int \phi_\alpha(\vec{r}_1)\phi_\alpha^*(\vec{r}_2)\frac{1}{|\vec{r}_1-\vec{r}_2|}$$

$$\times\,\phi_\beta(\vec{r}_2)\phi_\beta^*(r_2)\,d^3r_1\,d^3r_2\ ,$$

where ϕ_α and ϕ_β are Wannier wave functions centered on the same site. In a well-chosen reference frame, the $d_{\parallel}$-wave function behaves like a d_{xy} orbital with radius $R_{\parallel}$, the π^{*1}, π^{*2} wave functions being d_{xz} and d_{yz} orbitals with radius R_* greater than $R_{\parallel}$.

For the sake of simplicity we shall choose d orbitals with Gaussian radial wave functions, for instance:

$$|xy\rangle=\frac{(2\alpha_1)^{7/4}}{\pi^{3/4}}xy\exp[-\alpha_1(x^2+y^2+z^2)]\ ,$$

with

$$\alpha_1=\frac{1}{R_{\parallel}^2}\ .$$

One is thus reduced to computing

$$U_\alpha\sim\int\frac{x^2y^2X^2Y^2\exp[-\alpha(x^2+y^2+z^2+X^2+Y^2+Z^2)]}{[(x-X)^2+(y-Y^2)+(z-Z)^2]^{1/2}}\,dx\,dy\,dz\,dX\,dY\,dZ\ ,$$

and

$$W_{\alpha_1\alpha_2}\sim\int\frac{x^2y^2X^2Z^2\exp[-\alpha_1(x^2+y^2+z^2)-\alpha_2(X^2+Y^2+Z^2)]}{[(x-X)^2+(y-Y)^2+(z-Z)^2]^{1/2}}\,dx\,dy\,dz\,dX\,dY\,dZ\ .$$

Using the substitution[41]

$$\frac{1}{r_{ij}}=\frac{1}{\pi^{1/2}}\int_{-\infty}^{+\infty}e^{-r_{ij}^2t^2}\,dt\ ,$$

one obtains after a simple but tedious calculation:

$$U_\alpha=\frac{2^3}{\pi^{1/2}}\alpha^{1/2}\int_{-\infty}^{+\infty}\frac{(4+4\sigma^2+3\sigma^4)^2}{(4+4\sigma^2)^{11/2}}\,d\sigma\ ,$$

and

$$W_{\alpha_1\alpha_2}=\frac{2^3}{\pi^{1/2}}\alpha_1^{1/2}\rho^{7/2}\int_{-\infty}^{+\infty}\frac{[4\rho+2(1+\rho)\sigma^2+\sigma^4][4\rho+2(1+\rho)\sigma^2+3\sigma^4]}{[4\rho+2(1+\rho)\sigma^2]^{11/2}}\,d\sigma\ ,$$

with $\rho=\alpha_2/\alpha_1$. Computation of the ratio of these two integrals, $W_{\alpha_1\alpha_2}/U_{\alpha_1}$, shows that, for $R_2/R_1>2$ one gets approximatively

$$\frac{W_{21}}{U_1}=1.06\frac{R_1}{R_2}\ ,$$

$$\frac{W_{11}}{U_1}=0.897,\quad\text{and}\quad\frac{U_2}{U_1}=\frac{R_1}{R_2}\ .$$

Thus one obtains the scaling relations:

$$U_*=\frac{R_{\parallel}}{R_*}U_{\parallel},\quad W_{*\parallel}=1.106U_{\parallel}\frac{R_{\parallel}}{R_*}\ ,$$

and

$$W_{**}=0.897U_*=0.897U_{\parallel}\frac{R_{\parallel}}{R_*}\ .$$

For our model we choose $R_{*}=2R_{\parallel}$ (the Wannier π^* orbitals have a greater extension than the $d_{\parallel}$ ones, as they are hybridized with the p orbitals of the oxygen atoms), and choosing $U_{\parallel}=0.110$ eV, we obtain $U_{*}=0.55$, $W_{*\parallel}=0.61$, and $W_{**}=0.49$ eV.

APPENDIX B: TRANSFER-MATRIX METHOD

In our microscopic model, we simulate the exchange free energy using an equivalent Ising-like chain with two alternate exchange interactions. Although the transfer-matrix method used in our calculations to compute exact thermodynamic quantities is well known,[29] we find it useful to recall it.

Let us consider the following Ising-like chain Hamiltonian:

$$H(\{\mu_i\})=\sum_n (J_s\mu_{2n-1}\mu_{2n}+J_l\mu_{2n}\mu_{2n+1})-\sum_n \mu_B h\,\mu_n \ ,$$

where (i) J_s and J_l are nearest-neighbor exchange interactions associated with short and long bonds, (ii) the local momentum μ_i can take values $+\mu$ (↑ configuration) or $-\mu$ (↓ configuration), and (iii) μ_B and h are the Bohr magneton and the applied magnetic field, respectively.

We suppose that the chain, being in fact a ring, contains $2N$ sites, the $2N$th one being a neighbor of the first one through a long bond. The partition fucntion Z is written $Z=\sum_{\{\mu_i\}}e^{-\beta H\{\mu_i\}}$, where $\sum_{\{\mu_i\}}$ stands for the sum running over all the different momentum configurations. $H\{\mu_i\}$ can be decomposed into

$$H\{\mu_i\}=\sum_{n=1}^{2N}H_n(\mu_n,\mu_{n+1}) \ ,$$

with

$$H_n(\mu_n,\mu_{n+1})=J_n\mu_n\mu_{n+1}-\mu_B h\,\mu_n \ ,$$

where J_n stands for J_l or J_s whether n is even or odd. Thus

$$\exp(-\beta H\{\mu_i\})=\prod_{n=1}^{2N}\exp[-\beta H_n(\mu_n,\mu_{n+1})] \ .$$

Let us define the so-called transfer matrices T_n:

$$T_n=\begin{vmatrix} z_n(+\mu,+\mu),z_n(+\mu,-\mu)\\ z_n(-\mu,+\mu),z_n(-\mu,-\mu)\end{vmatrix} \ ,$$

with

$$\begin{aligned} z(\mu_n,\mu_{n+1})&=\exp[-\beta H_n(\mu_n,\mu_{n+1})]\\ &=\langle\mu_n|T_n|\mu_{n+1}\rangle \ . \end{aligned}$$

We are obviously dealing with only two different transfer matrices $T_l=T_{2n}$ and $T_s=T_{2n+1}$.

The partition function is written

$$\begin{aligned} Z=\sum_{\{\mu_i\}}&=z_1(\mu_1,\mu_2)z_2(\mu_1,\mu_3)\cdots z_{2N}(\mu_{2N},\mu_1)\\ &=\sum_{\{\mu_i\}}\langle\mu_1|T_1|\mu_2\rangle\langle\mu_2|T_2|\mu_3\rangle\cdots\langle\mu_{2N}|T_{2N}|\mu_1\rangle\\ &=\sum_{\mu_1}\langle\mu_1|T_1T_2\cdots T_{2N}|\mu_1\rangle=\mathrm{tr}\left(\prod_{n=1}^{2N}T_n\right)\\ &=\mathrm{tr}[(T_sT_l)^N]=\Theta_+^N+\Theta_-^N \ , \end{aligned}$$

where Θ_+ and Θ_- are the eigenvalues of $T=T_sT_l$, Θ_+ being chosen as having the larger modulus. The total free energy is

$$\begin{aligned} F=k_BT\ln Z&=-k_BT\ln(\Theta_+^N+\Theta_-^N)\\ &=-k_BT\{\ln\Theta_+^N+\ln[1+(\Theta_-/\Theta_+)^N]\} \ , \end{aligned}$$

and at the thermodynamic limit, the free energy per site Φ becomes

$$\Phi=\lim_{N\to\infty}F/2N=-\tfrac{1}{2}k_BT\ln\Theta_+ \ . \tag{B1}$$

The mean magnetization M is

$$M=-\frac{d\Phi}{dh}=k_BT\frac{d\Theta_+}{dh}\Big/\Theta_+ \tag{B2}$$

and the associated magnetic susceptibility χ becomes

$$\chi=\left.\frac{dM}{dh}\right|_{h=0}=\tfrac{1}{2}k_BT\frac{d}{dh}\left.\left(\frac{d\Theta_+}{dh}\Big/\Theta_+\right)\right|_{h=0} \ . \tag{B3}$$

Explicit evaluations of Eqs. (B1) and (B3) give formulas (3.26) and (5.5).

The spin-spin correlation function can be computed using a similar method. For instance, in the $2N$ ring:

$$\begin{aligned} \langle\epsilon_1\epsilon_2\rangle_N=\frac{\langle\mu_1\mu_2\rangle_N}{\mu^2}&=\frac{1}{Z}\sum_{\{\mu_i\}}\frac{\mu_1\mu_2}{\mu^2}e^{-\beta H\{\mu_i\}}\\ &=\frac{1}{Z}\sum_{\{\mu_i\}}\frac{\mu_1}{\mu}\langle\mu_1|T_1|\mu_2\rangle\frac{\mu_2}{\mu}\langle\mu_2|T_2|\mu_3\rangle\\ &\qquad\times\langle\mu_3|T_3|\mu_4\rangle\cdots\langle\mu_{2N}|T_{2N}|\mu_1\rangle\\ &=\frac{1}{Z}\mathrm{tr}(MT_1MT_2T_3\cdots T_{2N}) \ , \end{aligned}$$

with

$$M=\begin{vmatrix}+1 & 0\\ 0 & -1\end{vmatrix} \ .$$

Let us define the matrices $K_s=MT_sMT_l$ and

$K_l = MT_lMT_s$; we obtain

$$\langle \epsilon_1\epsilon_2 \rangle_{l,s^N} = \frac{1}{Z}\mathrm{tr}(K_{l,s}T^{N-1}) \ .$$

If $|+\rangle$ and $|-\rangle$ are the eigenvectors of T (i.e., $T = |+\rangle\Theta_+\langle+|+|-\rangle\Theta_-\langle-|$), we obtain

$$\langle \epsilon_1\epsilon_2 \rangle_{l,s^N} = \frac{\langle+|K_{l,s}|+\rangle\Theta_+^{N-1} + \langle-|K_{l,s}|-\rangle\Theta_-^{N-1}}{\Theta_+^N + \Theta_-^N} \ ,$$

which leads, in the thermodynamic limit to

$$\langle \epsilon_1\epsilon_2 \rangle_{l,s^N} = \langle+|K_{l,s}|+\rangle/\Theta_+ \ , \tag{B4}$$

whose explicit evaluation gives formula (5.4).

This method, which emphasizes the importance of the anisotropy of the coupling along the chain ($J_l \neq J_s$), allows us to properly account for the influence of electron-lattice (Peierls interaction) on the spin dimerization; another approach to this problem is given in Person *et al.*[42]

APPENDIX C: LANDAU EXPANSION OF THE FREE ENERGY

The total free energy obtained from the thermodynamics of our microscopic model can be expanded in powers of the two variational parameters η and μ. As can be seen from the shape of the free-energy surface (see Fig. 2), the simplest expansion is

$$F = \tfrac{1}{2}a(T - T_\mu)\mu^2 + \tfrac{1}{4}b\mu^4 + \tfrac{1}{2}\alpha\eta^2 - \tfrac{1}{4}\beta\eta^4 + \tfrac{1}{6}\gamma\eta^6 - \tfrac{1}{2}g\eta^2\mu^2 \ , \tag{C1}$$

where the coefficients a, b, α, β, γ, and g are positive and temperature independent, and where T_μ is the temperature at which local moments appear ($T_\mu \sim 800$ K).

The form of free-energy expansion has been carefully studied by Holakowski[38] who has showed that, provided $4(\frac{1}{3}\alpha\gamma)^{1/2} > \beta + g^2/b$, two phase transitions occur.

The high-temperature one at $T = T_\mu$ is second order and corresponds to the building up of the local-moment amplitude μ in an undistorted phase ($\eta = 0$). The other one, occurring at the lower temperature,

$$T_c = T_\mu - \frac{3}{16}\frac{b}{ag\gamma}\left\{[4(\tfrac{1}{3}\alpha\gamma)^{1/2}]^2 - \left(\beta + \frac{g^2}{b}\right)^2\right\} \ ,$$

is a first-order one and describes the onset of a finite distortion η together with a jump of μ. The thermal variation of η and μ are thus similar to those found from our microscopic model (see Fig. 3). As can be seen in Eq. (C1) the leading instability is associated to μ, the fluctuations of which are diverging at T_μ. On the contrary, the frequency of the lattice mode associated to η is constant for $T > T_\mu$. slightly decreasing as the temperature decreases from T_μ to T_c, due to the growing of μ, but does not vanish at T_c: the structural phase transition at T_c is not due to a lattice instability but is triggered by the electronic instability taking place at T_μ.

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[1] D. Alder and H. Brooks, Phys. Rev. 155, 826 (1967).
[2] J. Goodenough, Solid State Chem. 3, 490 (1971).
[3] J. P. Pouget, H. Launois, T. M. Rice, P. Dernier, A. Gossard, G. Villeneuve, and P. Hagenmuller, Phys. Rev. B 10, 1801 (1974).
[4] (a) J. Hubbard, Proc. R. Soc. London Ser. A 276, 283 (1963); (b) 281, 401 (1964).
[5] A. Zylbersztejn and N. F. Mott, Phys. Rev. B 11, 4383 (1975).
[6] M. Gupta, A. J. Freeman, and D. E. Ellis, Phys. Rev. B 16, 3338 (1977).
[7] W. E. Evenson, J. R. Schrieffer, and S. Q. Wang, J. Appl. Phys. 41, 1199 (1970).
[8] M. Cyrot, J. Phys. (Paris) 33, 125 (1972).
[9] M. Cyrot and P. Lacour-Gayet, Solid State Commun. 11, 1767 (1972).
[10] E. N. Economou, C. T. White, and R. R. de Marco, Phys. Rev. B 18, 3946 (1978); C. T. White and E. N. Economou, Phys. Rev. B 18, 3959 (1978).
[11] J. R. Brews, Phys. Rev. B 6, 2557 (1970).
[12] J. P. Pouget and H. Launois, J. Phys. (Paris) 37, C4-49 (1976).
[13] (a) D. Paquet and P. Leroux-Hugon, J. Magn. Magn. Mater. 15–18, 999 (1980); (b) P. Leroux-Hugon and D. Paquet, J. Phys. (Paris) 41, C5-67 (1980); (c) D. Paquet and P. Leroux-Hugon, Ferroelectrics 26, 681 (1980).
[14] G. Villeneuve, M. Drillon, and P. Hagenmuller, Mater. Res. Bull. 8, 1111 (1973).
[15] M. Marezio, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B 5, 2541 (1972).
[16] J. P. Pouget, H. Launois, J. P. D'Haenens, P. Merenda, and T. M. Rice, Phys. Rev. Lett. 35, 873 (1975).
[17] C. Sommers, R. DeGroot, D. Kaplan, A. Zylbersztejn, J. Phys. (Paris) 36, L-157 (1975).
[18] E. Carruthers, L. Kleinman, and H. I. Zhang, Phys. Rev. B 7, 3753 (1973).
[19] J. P. Pouget (private communication).
[20] D. B. McWhan, M. Marezio, J. P. Remeika, and P. D. Dernier, Phys. Rev. B 10, 490 (1974).

[21] C. Sommers and S. Doniach, Solid State Commun. 28, 133 (1978).

[22] S. K. Sinha and B. N. Harmon, Phys. Rev. Lett. 35, 1515 (1975).

[23] P. Lacour-Gayet, Ph.D. thesis (Orsay, 1974) (unpublished).

[24] J. Hubbard, Phys. Rev. B 19, 2626 (1979).

[25] (a) P. Soven, Phys. Rev. 156, 809 (1967); (b) B. Velicky, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[26] F. Ducastelle and F. Gautier, J. Phys. F 6, 2039 (1976).

[27] C. T. White and E. N. Economou, Phys. Rev. B 15, 3742 (1977).

[28] P. Lacour-Gayet and M. Cyrot, J. Phys. C 7, 400 (1974).

[29] C. J. Thomson, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, London, 1972), Vol. 1.

[30] J. G. Traylor, H. G. Smith, R. M. Nicklow, and M. K. Wilkinson, Phys. Rev. B 3, 3457 (1971).

[31] C. N. Verglund and H. J. Guggenheim, Phys. Rev. 185, 1022 (1969).

[32] W. Rosevear and W. Paul, Phys. Rev. B 7, 2109 (1973).

[33] P. Merenda, D. Kaplan, and C. Sommers, J. Phys. (Paris) 37, C4-59 (1976).

[34] O. A. Cook, J. Am. Chem. Soc. 69, 331 (1947).

[35] F. Pintchovski, W. S. Glaunsinger, and A. Navrotsky, J. Phys. Chem. Solids 39, 941 (1978).

[36] See discussions in Refs. 5, 6, and 12.

[37] R. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B 1, 910 (1970).

[38] J. Holakowski, Phys. Status Solidi 56, 615 (1973).

[39] P. J. Brown and D. R. A. Zielbeck, J. Phys. C 11, 2791 (1978).

[40] J. Hubbard, Phys. Rev. Lett. 3, 77 (1959).

[41] J. C. Browne and R. D. Poshusta, J. Chem. Phys. 36, 1933 (1962).

[42] K. A. Person, A. Holz, and K. H. Bennemann, Phys. Rev. B 13, 433 (1976).