Dimerization of two-dimensional mettalic lattices

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Abstract

With the aid of a tight-binding model of the electronic band structure on a *sq* (two-dimensional) lattice we investigate the range of parameters for which the lattice spontaneously distorts. Dimerization is found to occur only very close to half-filling, and never exceeds 2.2%. Even at precisely half-filling, the energy gap caused by the distortion does not extend all way around the fermi surface, hence there is no insulating phase in this model.

We consider spontaneous symmetry-breaking in a simplified model of two-dimensional metals.

This phenomenon was first studied by Pierls[1] in 1D, with the conclusion that for filling factor ν near to$1/2$ the homogenous phase is unstable with respect to the *dimerized* phase. At other filling factors,there could be found instability against incommensurate phases, tuned to $2k_F$. Much has been made of this in connection with the properties of one dimensional polyacetylene[2] . In 3D the role of distortion in the metal-insulator phase transition has been known for a long time.[3]However, in 2D the phenomenon has received scant attention despite the fact that van Hove similarities render the half filled two-dimensional band uniquely susceptible to distortion. The tetragonal-to-orthorhombic distortion observed in numerous high-temperature supeconductors, for which electronic conductivity is principally two-dimensional and anisotropic even within each plane,brings back to the fore what might otherwise be just an academic exercise.

Our model is a *sq* metal lattice on which electrons "hop" between nearest neighbors, and

which distorts as a consequence. We ignore the spin of the electron and the kinetic energy of the ions, both irrelevant to present arguments. Our purpose is to investigate conditions at $T = 0$ under which the lattice dimerizes, thereby spontaneously lowering both its symmetry and its energy. In our model the maximum distortion turns out to be some 2.2% ,which is quite in line with experimental observation. In the distorted phase we determine that the electronic dispersion is anisotropic,but always metallic for,surprisingly,when an energy gap appears it does not extend over the entire fermi surface.

Some sort of restoring forcers (parameter K) are needed to keep the bond length at some optimal value (all $t_{nm} = t_o$). Although the restoring force is ineffectual against rhombic and/or shear distortions, the omission is insignificant for present purposes. With hopping restricted to n.-n. sites, the simplest electronic Hamiltonian with which to demonstrate the Pierles' instability takes the form:

$$H = -\sum_{(n,m)} t_{mn} a_n^+ a_m + \frac{K}{2t_0^2} \sum_{(n,m)} (t_{nm} - t_0)^2 \tag{1}$$

with (n, m) labeling n.-n. pairs of sites. aside from the electronic filling factor ν there is just one dimensionless coupling constant, the ration $\gamma = K/t_0$. It is convenient to set $t_{nm} = t_0(1 - \xi_{nm})$with ξ_{nm} the fractional elongation of the bond connecting the neighboring atoms at $\mathbf{R}_n$ and $\mathbf{R}_m$, and rewrite (1) in dimensionless form:

$$H = -\sum_{(n,m)} (1 - \xi_{nm}) a_n^+ a_m + \frac{\gamma}{2} \sum_{(n,m)} \xi_{nm}^2. \tag{2}$$

This is essentially the "lattice" Hamiltonian studied by Su,Schrieffer and Heeger[2] in 1D, who assumed an additional condition: $\sum \xi_{nm} = 0$ - tantamount to assuming a fixed *ab initio* value for the average spacing. while the 2D analysis could also start here it is perhaps more instructive to examine the model in the absence of any constraints. We find that unless γ exceeds a critical value the model lattice collapses. Once γ is sufficiently large to prevent this collapse the maximum distortion is limited to a maximum of 2.2%, as mentioned earlier. The limitation would not have been apparent had we merely adopted (2) together with the SSH condition as the starting point.

Our first result: the trivial choice $\xi_{nm}$is *never* the ground state. Suppose $\xi_{nm} = -(c+y_{nm})$ with c a constant and y_{nm}an arbitrary distortion orthogonal to c(i.e: $c\sum y_{nm} = 0$). Then (2) takes the form:

$$H = 4 * \gamma N c^2 - \sum_{(n,m)} (1 + c + y_{nm}) a_n^+ a_m + \frac{\gamma}{2} \sum_{(n,m)} y_{nm}^2 \tag{3}$$

Optimizing with respect to c yields:

$$c = \frac{1}{2\gamma N} \sum_{(n,m)} < a_n^+ a_m > \tag{4}$$

which is a positive number $\simeq \nu/\gamma$ for $\nu \ll 1/2$ and $(1-\nu)/\gamma$ for $\nu \gg 1/2$. Thus in the absence of any additional constraints the partly-occupied lattice *always* shrinks from its pre-assigned value so as to maximize the electronic bonds. Equilibrium is determined by the magnitude of γ, which is what limits the shrinkage.

In the absence of any additional; distortion the maximum value of the r.h.s. of Eq(4) (for $\nu = 1/2$) can be calculated exactly, and is $(0.2026..)/\gamma$. If $\gamma < 0.2026$ the shrinkage of the bond length amounts to a nonsensical 100%. This sets the scale for the allowed values of γ. In a nonlinear model, say one which exhibits exponential dependence of the overlap parameter on the bond length, the results are qualitatively,if not quantitatively, similar.

Hence we assume $\gamma > 0.2026$ and c in the range: $0 < c < 1$. H can be rewritten in the form:

$$H = 4\gamma N c^2 - (1 + c) \sum_{(n,m)} (1 + \frac{y_{nm}}{1 + c}) a_n^+ a_m + \frac{\gamma}{2} (1 + c)^2 \sum_{(n,m)} (\frac{y_{nm}}{1 + c})^2 \tag{5}$$

allowing to define a *distortion Hamiltonian,*

$$H_{dist} = \frac{H - 4\gamma N c^2}{1 + c} = - \sum_{(n,m)} (1 + x_{nm}) a_n^+ a_m + \frac{\alpha}{2} \sum_{(n,m)} x_{nm}^2 \tag{6}$$

where $x_{nm} \equiv y_{nm}/(1 + c)$ and c fixed at its optimal value, Eq(4). *This* is the starting point of our study. The filling factor ν and stiffness coefficient $\alpha \equiv \gamma(1 + c)$ are the only parameters. Eq(6) is essentially similar to Eq(2), except for the stability requirement that $\gamma > 0.2026$. We examine the consequence below.

We next seek to optimize the total distortion energy by adjusting the $2N$ values of the distortion field x_{nm} subject only to $\sum x_{nm} = 0$. This defines a "bond problem"[5]. Two simple,homogeneous phases suggests themselves as prime candidates near $\nu = 1/2$:

1. **Rectangular:**all x_{nm}'s $= x$ along the horizontal axis,all x_{nm}'s $= -x$ along the vertical ;or *vice-versa.*

2. **Dimerized:** $x_{nm} = \pm x$ if $\mathbf{R}_{nm} = (\pm 1, 0)$ or $(0, \pm 1)$ and $\mathbf{R}_m = (2p, 2q)$, where p,q are integers.

Although there may exist other phases which lower energy even further,for example incommensurate phases with pitch precisely tuned to $2k_F$, we have been unable to identify any. What is more, the value of $2k_F$ is not known in the presence of distortion - it is only the total area below the Fermi surface which is fixed and the geometry of the perimeter itself. This soon become obvious when we plot contours of constant energy.

Phase 1 is obvious whereas phase 2 is somewhat unusual. It is therefore exhibited in Fig.1. The optimum x must be determined numerically. Our calculations reveal the rectangular phase always to be unstable against the dimerized phase, therefore phase 1 drops out and in the rest of the work we need consider only phase 2.

In phase 2 , the Bloch energies are $E(x \mid k) = \pm\sqrt{(\omega_k^2 + x^2\gamma_k^2}$, where $\omega_k = \cos k_x + \cos k_y$ and $\gamma_k = \sin k_x + \sin k_y$[6]. Note the resulting dispersion differs significantly from what would be obtained by using a *constant* matrix element to couple opposing flat portions of the Fermi surface. Fig.2 showing the contours of constant energy $E_\pm(x \mid k)$ at value $x = 0.5$, illuminates the electronic anisotropy caused by dimerization of this lattice. Note that the energy gap appears only along the $(1, 1)$ direction, not along the $(1, -1)$ axis. A similar plot at a more realistic $x = 0.02$ would exhibit qualitatively similar features. However, these could not be seen on the scale of this graph even lying in though the conduction properties at a Fermi surface near $E = 0$ would remain anisotropic.

The total distortion energy per site[7] is:

$$e_t = \frac{1}{N} \sum_{k \subset B.Z.} (E(x \mid k) - \mu) n(x \mid k) + \alpha x^2 + \mu\nu \tag{7}$$

where

$$n(x \mid k) = \frac{1}{e^{\beta(E(x|k)-\mu)}+1}$$

is the occupation number (Fermi function) and μ is the chemical potential required to achieve the specified filling factor. Fig.3 illustrates the band structure,again choosing an exaggerated value of distortion to render the features readily visible. note the total absence of an energy gap along XN while an important gap opens up at 90^0,along XM.

The *actual* value of x is obtained by optimizing the *free energy*. As a result ether $x = 0$ trivially, or else x is the solution of the following transcendental equation:

$$\frac{1}{N}\sum_{k\subset B.Z.}\frac{\gamma_k^2}{\sqrt{\omega_k^2+x^2\gamma_k^2}}n(x \mid k) = \alpha \tag{8}$$

At $T = 0$,$n(x \mid k)$ reduces to the unit step,i.e. $n = 1$ for $E - \mu < 0$ and $n = 0$ otherwise.

Remaining at $T = 0$, we find this equation has a nontrivial solution for ν lying in the range ν_c to $1 - \nu_c$. The critical filling factor ν_c is a function of α. As shown in Fig.4 the transition to a distorted phase is continues at ν_c for all $\alpha > 0.465$, e.i. it is second order. For $\alpha < 0.465$ it becomes discontinues (first order). This identifies $\alpha_c = 0.465$ as a *tricritical* point. We determine that it lies very close to instability point identified earlier. For $\alpha = \alpha_c$ and $\nu = 1/2$ the lattice compression parameter computed from Eq(4) is substantial: $c \approx 0.8$. Decreasing α by any significant amount would cause lattice collapse. as noted earlier. For this reason we believe the parameter range $\alpha < \alpha_c$ to be unphysical or on the verge of it, and restrict further consideration to the range $\alpha \geq \alpha_c$. Here the distortion x is a continues function of the two independent parameters and, by extension, of temperature T as well.

At *precisely* α_c the critical filling factor $\nu_c = 0.493$. The maximum distortion which occurs at half-filling, $\nu = 1/2$, is $x_{\max} = 0.012$. This translates to a physical fractional distortion in the amount: $y_{\max} = 0.012 \times (1 + c) = 0.022$,i.e. 2.2% as stated in introduction.

As α is increased, the maximum distortion decreases while the corresponding ν_c approaches $\nu = 1/2$. For example we see in Fig.4 that an increase of α from 0.465 to 0.487 causes $x_{\max}$ to decrease by 25%, from 0.012 to less than 0.009. Although seemingly small,

a $O(1\%)$ distortion is in fact typical of experimentally observed maximum deviation of the atomic positions from their ideal values in *all* materials, whether they be molecules,planar solids,or fully three-dimensional crystals.

In concluding, we remark that while the calculations have been limited to the ground state, at $T = 0$,simple mean-field theory can be used to extend results to finite temperature and yield familiar universal curves for $x(T)$. However, mean-field theory is notoriously unreliable in 2D. It is possible that topological defects enter into, and vastly complicate,the statistical mechanics at finite T and the phases of lowest free energy are highly textured, in contrast to the ground state. To proceed it is necessary to determine the symmetry class of the Hamiltonian. However,it is not clear whether H is discrete (two possible directions of distortion enter into the picture) or continues (as in the shape of the Fermi surface). Finite T properties in 2D hinge on such "details". We intend to reexamine this issue in the future.

REFERENCES

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[5] typically more structered than a "site problem"

[6] this choice is one of two; the other equivalent (but orthogonal) phase has $\gamma_k = \sin k_x - \sin k_y$. Thus if these were the only two possible phases one would expect *twinning* - just as found in some high-temperature superconductors.[4]

[7] as there are 2 bonds *per* site, one divides here by $2N$

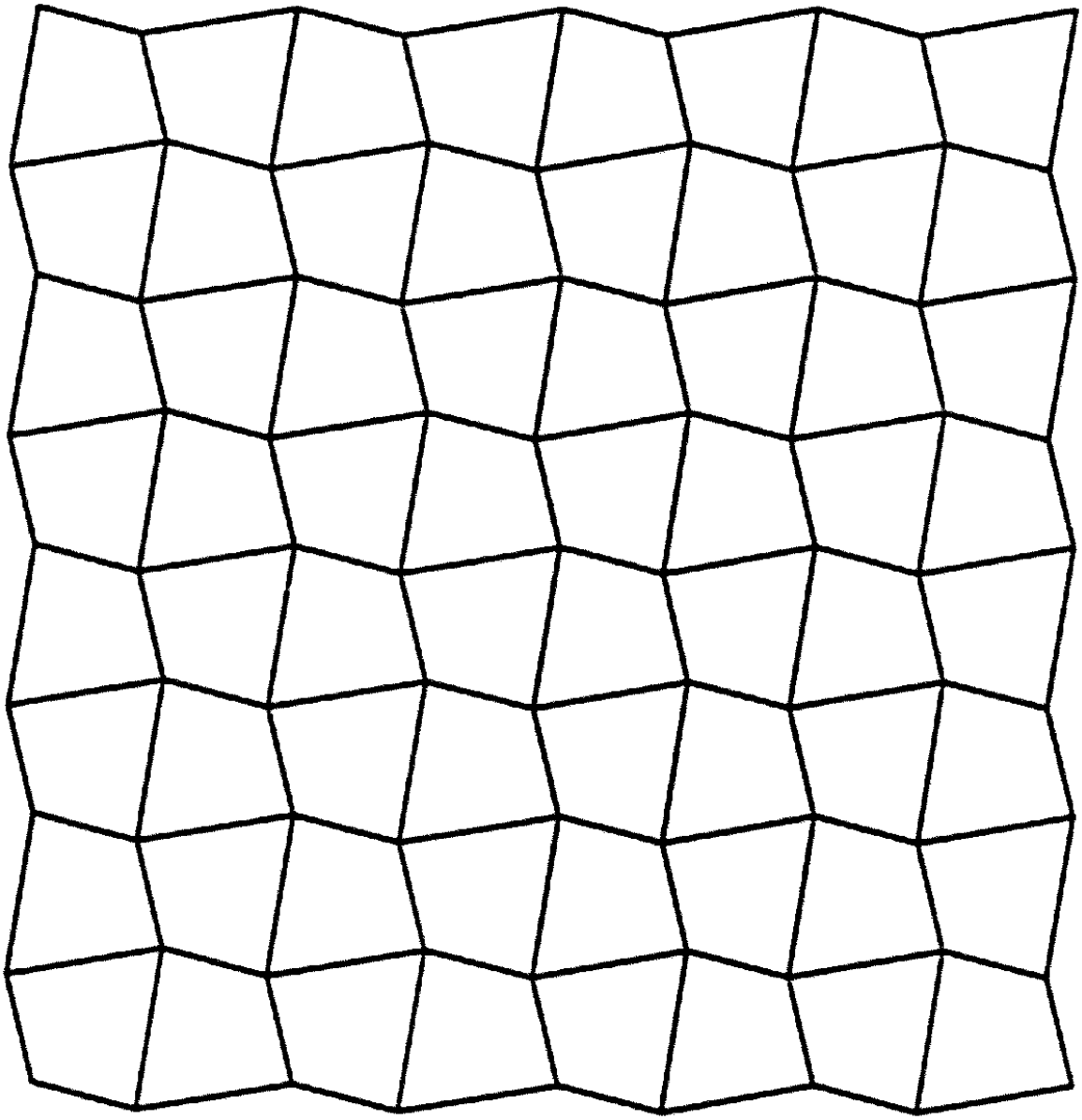

FIG. 1. Schematically shows the geometry of a dimerized lattice.

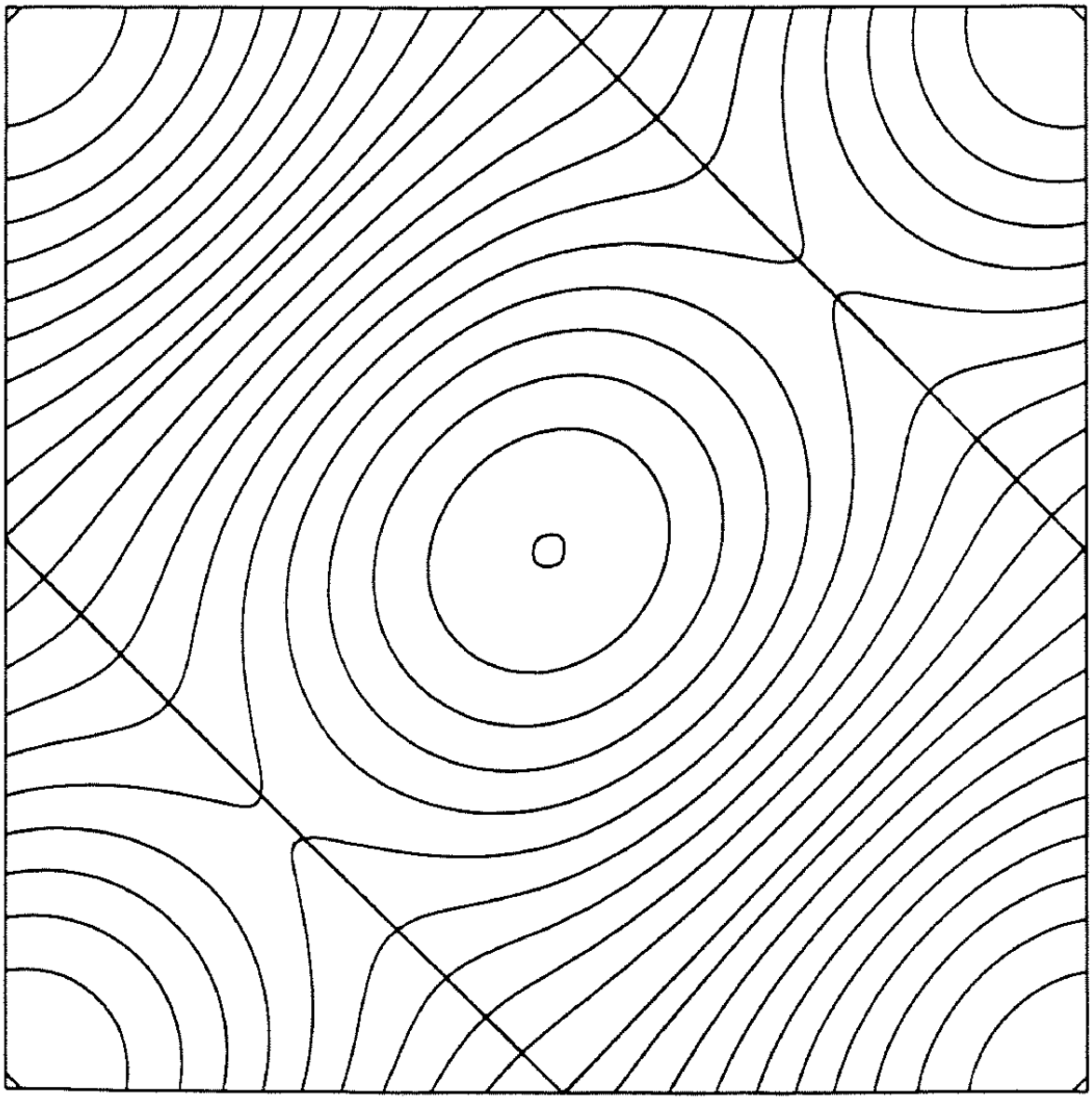

FIG. 2. Contours of constant energy,showing anisotropy. (This picture is for 50% distortion to emphasize the anisotropy).

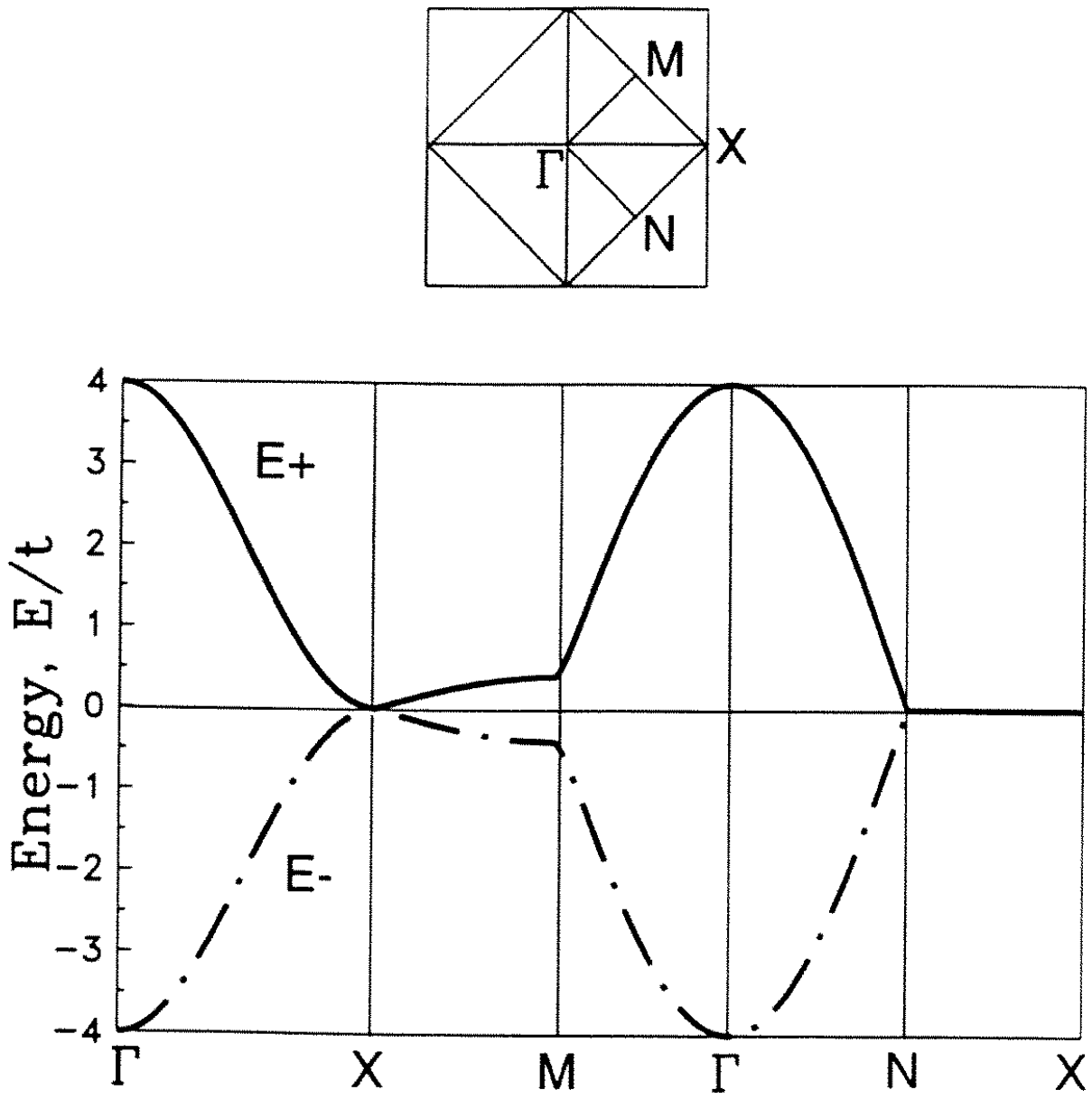

FIG. 3. Some symmetry points in Brillouin Zone, and the band structure ($E_{\pm}$) along the varios axis connecting them. The energies are computed for a value of distortion parameter $x = 0.1$. Note the anisotropic energy gap which is zero along XY, and nonzero along XM.

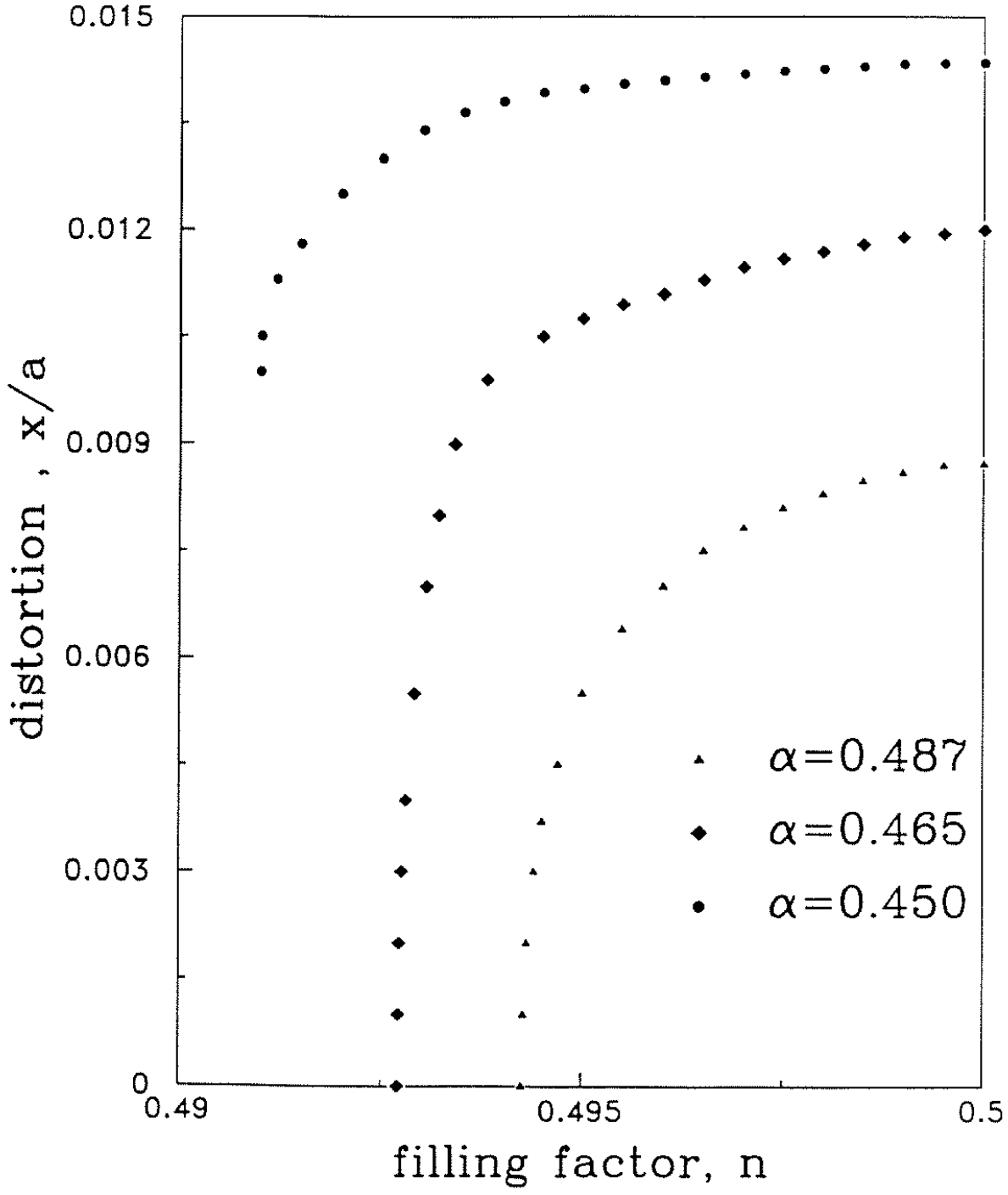

FIG. 4. Distortion parameter x as a function of filling factor ν for various values of the elastic parameter α, at $T = 0$. The points shown have been found by numerical solution of Eq(8). The cross-over from continous (as for $\alpha = 0.487$) to reentrant behavior (as for $\alpha = 0.450$) occurs at $\alpha_c = 0.465$.