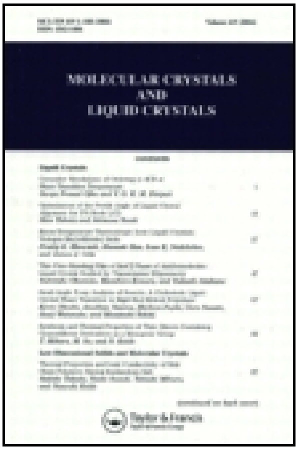

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Transitions in the Hubbard Model for a Half Filled Band

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To cite this article: Harry Th. Jonkman & Jan Kommandeur (1982): Phase Transitions in the Hubbard Model for a Half Filled Band, Molecular Crystals and Liquid Crystals, 85:1, 49-55

To link to this article: http://dx.doi.org/10.1080/00268948208073630

Mol. Cryst. Liq. Cryst., 1982, Vol. 85, pp. 49-55
0026-8941/82/8501-0049$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

PHASE TRANSITIONS IN THE HUBBARD MODEL FOR A HALF FILLED BAND

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Submitted for publication: 21 August 1981

ABSTRACT

The phase-transitions for a half-filled band can be numerically calculated from the Hubbard Hamiltonian with an exponential inter-site dependence of the transfer integral. Even for four sites with four electrons the results compare very well with experiments on spin susceptibilities and the intensities of charge-transfer absorptions.

In a previous paper in this series (1) we showed, how the $4k_F$ and the $2k_F$-transitions of a quarter-filled band could be obtained from the Hubbard Hamiltonian with an exponential dependence on intersite distance of the transfer-integral as applied to the very simple system of four sites (on a ring) and two electrons.

The rather surprisingly good results of this model encouraged us to extend the calculation to half-filled bands i.e. in this case to a ring of four sites with four electrons. The Hamiltonian of the electronic system is:

$$H = -\sum_{\substack{l\neq m \\ \sigma}} t_{lm}\, c^{+}_{l,\sigma}\, c_{m,\sigma} + U\sum_{l} n_{l,\sigma} n_{l,-\sigma}$$

where the symbols have their usual meaning. The intersite electron-phonon coupling is obtained by writing

$$t_{lm}(R_{lm}) \sim R^{3}_{lm} \exp\,(-CR_{lm})$$

where R_{lm} is the inter-site distance and $C = Z'/2a_o$, where Z' is the effective nuclear charge and a_o the Bohr radius. C thus measures the steepness of the inter-site transfer interaction. Neglecting lattice entropy the lattice energy is written as

$$F_{lat}(\xi) = B\sum_{l\neq m} R^{-n}_{lm} \approx \tfrac{1}{2}\alpha\xi^{2}$$

where B is a constant for the Born repulsion, n is a measure for the steepness of it, and ξ is the dimensionless distortion or order parameter. From the electronic states E_i the partition function is calculated:

$$Z = \sum_{i} g_i \exp(-\,E_i(\xi)/kT)$$

which is numerically evaluated as a function of ξ. $\xi = |\Delta R|\,R_o$, where ΔR is the shortening or lengthening of the original inter-site distances R_o. The free energy of the system is formed from

$$F = -kT\ln Z + F_{lat}$$

and its minimum is found as a function of ξ. The parameters were again (1): $CR_o = 10$, $n = 12$ and $\alpha = 160\ t_o$ (t_o is the value of the undistorted transfer integral).

A phase transition is always obtained. Its behavior as a function of U is given in fig. 1.

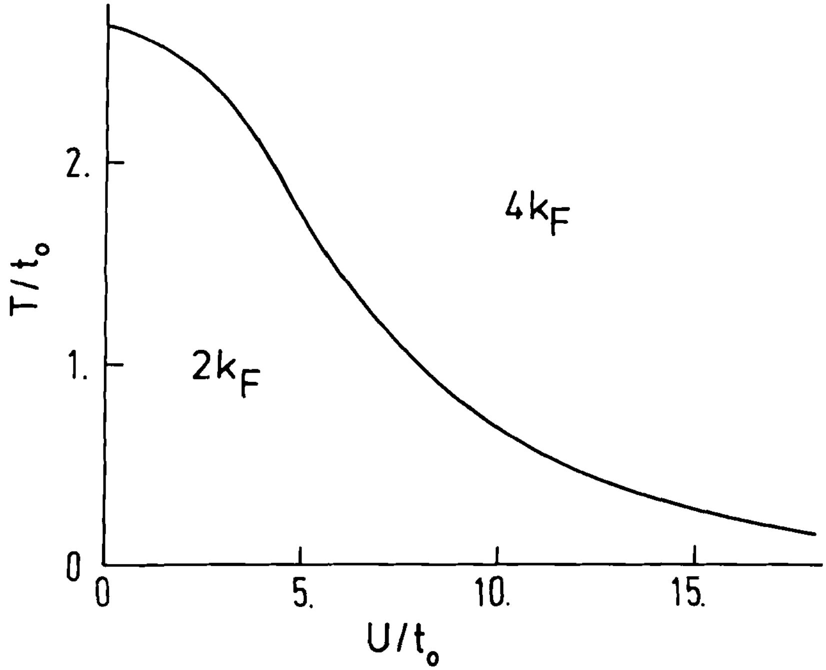

FIGURE 1. The Peierls Transition temperature as a function of the on-site electron-electron repulsion.

It describes the transition from an electronic (at low U) to a spin Peierls transition at high U. The phase transition temperature goes down, since at high U the spin Peierls transition is caused by the exchange energy

$J \approx 2t_o^2/U$, which decreases as U increases.

The most surprising result was the rather good agreement with experiment. In fig. 2 we give a fit obtained for a spin susceptibility of Würster's Blue Perchlorate as a function of temperature, a long-standing problem (2), which now appears to have found its solution. Also in table I we give the results for a number of equally good fits of the spin susceptibility of a number of half-filled TCNQ-salts. The decrease in t_o with the increase of the ionic radius of the counter-ion is clearly observed. The decrease in U probably derives from the increase in the polarizability of the counter ions.

TABLE I. Fitted parameters for some half-filled band systems.

	U/t_o	CR_o	U(eV)	t_o(eV)	T_c (°K)	$T_{c,exp}$ (°K)
TMPD ClO_4	40.0	9.0	1.00	0.025	190	196
NaTCNQ	6.0	6.5	2.27	0.38	305	345
K TCNQ	6.0	6.6	1.72	0.29	367	396
Rb TCNQ(II)	4.0	6.0	1.08	0.27	238	220
Cs TCNQ	4.0	6.0	0.88	0.21	195	217
Rb TCNQ(I)	3.0	5.8	0.76	0.25	282	310

Another problem with the half-filled bands has been the strong increase of the long-wavelength charge-transfer absorption (3). Our calculations show that this is entirely due to the increase of the transfer integral between the dimers upon dimerization. Figure 3 shows a comparison between experiment and calculation. The strong

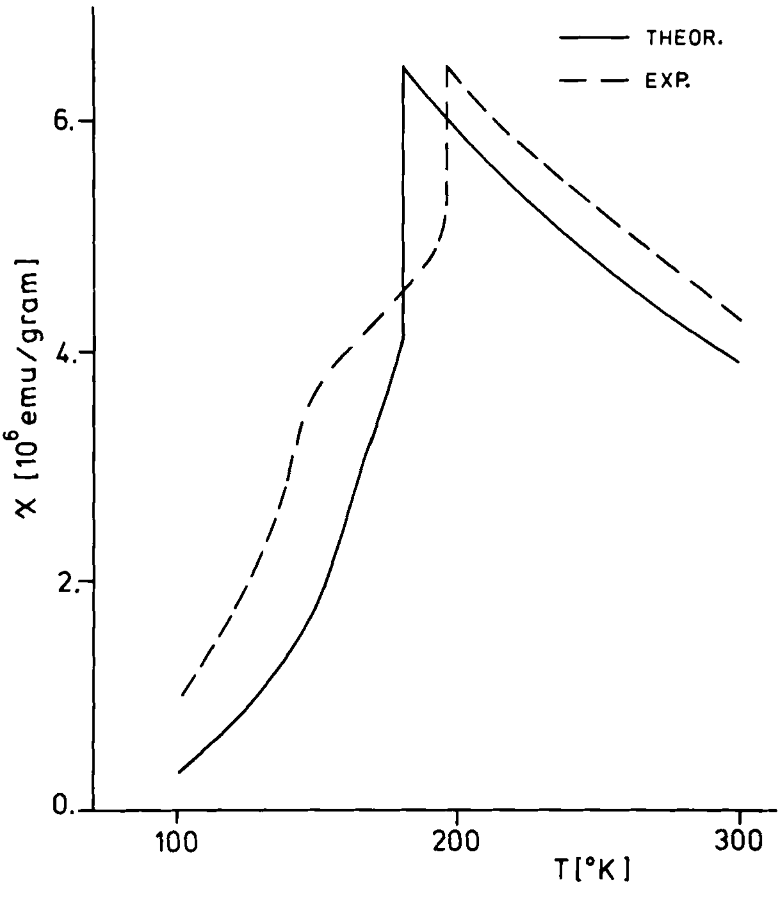

FIGURE 2. Calculated and experimental spin-susceptibility of Würster's Blue Perchlorate as a function of temperature. The parameters used for the fit are given in the text and $U/t_o = 6$.

increase in the I-R absorption of symmetrical molecular vibrational modes; as observed by Pecile and co-workers (4) for instance in K^+chloranil can be calculated as well.

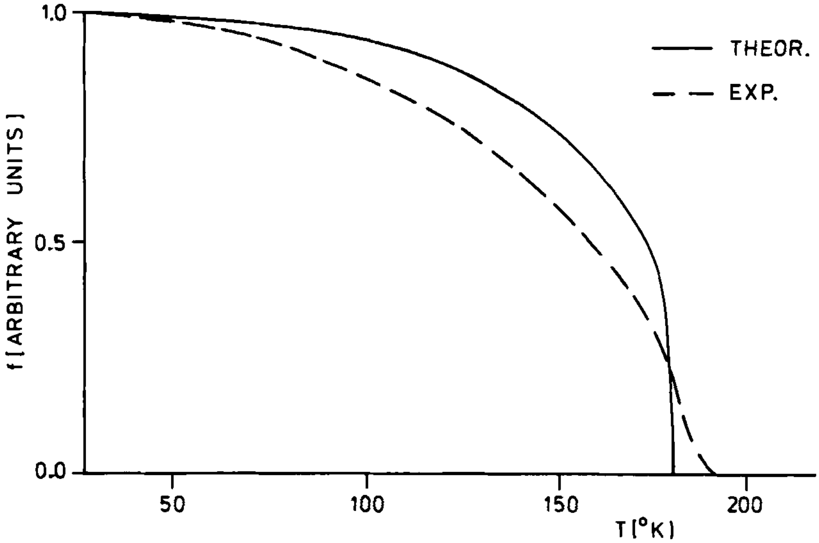

FIGURE 3. Comparison of the calculated and experimental strength of the charge-transfer absorption in Würster's Blue Perchlorate as a function of temperature. The parameters used were the same as used in fig. 1 for the spin-susceptibility.

Finally, a magnetic field can be introduced into the calculation. Then, in addition to the usual $2k_F$-phase, a $(2k_F + k_F)$ phase is obtained, similar to the new phases recently reported by Bloch et al.(5).

It can be concluded that, surprisingly enough, calculations with the Hubbard Model with an exponentially varying transfer integral on small rings yield results that favorably compare with experiment for reasonable values of the parameters used. To investigate the effects of enlarging the ring, we are presently endeavoring to calculate the behavior of eight sites with four electrons.

REFERENCES

1. Proceedings of the International Conference on Low Dimensional Synthetic Metals, Copenhagen 1980.
2. Gerard T. Pott, Chris F. van Bruggen and Jan Kommandeur, J. Chem. Phys. 47, 408 (1967).
3. T. Sakata and S. Nagakura, Bull. Chem. Soc. Japan 42, 1497 (1969).
4. R. Bozio, A. Girlando and C. Pecile, Chem. Phys. 21, 257 - 263 (1977).
5. D. Bloch, J. Voiron, J.W. Bray, I.S. Jacobs, J.C. Bonner and J. Kommandeur, Phys. Lett. 82A, 21 (1981).