F I Z I K A V O L U M E 10 S U P P L E M E N T 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics
of Condensed Matter, Kruševac, September, 18-22, 1978

ON THE TUNNELING EFFECTS IN THE STRUCTURAL PHASE TRANSITIONS

S. Stamenković*, N.M. Plakida†, V.L. Aksenov† and T. Sikloš††

*The Institute of Nuclear Sciences "Boris Kidrič" - Vinča
Laboratory of Theoretical Physics, Beograd, SFRJ

†Joint Institute for Nuclear Research, Dubna, SSSR

††Central Research Institute for Physics, Budapest, Hungary

Abstract. The effective Hamiltonian which desribes both the tunneling and phonon vibrations of active atoms is formulated on the basis of the self-consistent pseudospin-phonon formalism. Limiting cases of displacive and order-disorder transitions are considered.

1. INTRODUCTION

The recent studies of ruther simple models[1-4] have shown that both displacive and order-disorder type excitations have the essential role in the dynamics of structural phase transitions (ST). It is also well known that tunneling effects lead to collective excitations which may have a soft mode character[5] or cause the appearance of a central peak[4]. Since the tunneling energy (of the order of the quantum ground state splitting) is usually much smaller than a characteristic phonon energy the role of such excitations can be predominant at low temperatures ($\Omega \sim k_B T$). On the other hand, in addition to a renormalization of the pseudospin-energy parameters the higher phonon excitations can lead to the phase transition of the displacive type (through a phonon soft mode)

The purpose of the present work is to take into account self-consistently the excitations of both type (displacive and order-disorder) - as coupled both with the tunneling and the higher phonon states of active atoms - in the framework of the previous general model[1] and the variational approach of Bogolybov[6].

2. THE HAMILTONIAN

Starting from quite a general Hamiltonian

$$H = \sum_i \left[\frac{p_i^2}{2m} + U(s_i)\right] + \frac{1}{2}\sum_{i\neq j} V(s_i, s_j) , \tag{1}$$

where s_i is a local normal coordinate[7,8], active in a given ST, being represented as a slow tunneling motion coordinate (r_i) and a fast phonon displacement (u_i)

$$s_i = r_i + u_i , \quad \langle u_i \rangle = 0 . \tag{2}$$

We assume that the system can be described by a trial Hamiltonian in the form

$$H_o = H_{ph}(\{u_i\}) + H_s(\{r_i\}) ; \tag{3}$$

$$H_{ph}(\{u_i\}) = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{ij} \phi_{ij} u_i u_j , \tag{4}$$

$$H_s(\{r_i\}) = \sum_i \left(\frac{p_i^2}{2m} + \tilde{U}(r_i)\right) + \frac{1}{2}\sum_{i\neq j} C_{ij}(r_i - r_j)^2 , \tag{5}$$

$\phi_{ij}, \tilde{U}(r_i), C_{ij}$ - being the variational parameters.

For the strongly anharmonic motion described by Eq. (5) it is convenient to introduce the pseudospin representation with respect to symmetric and antisymmetric single-particle states

$$\left(\frac{p_i^2}{2m} + \tilde{U}(r_i)\right)\psi_{s,a}(r_i) = \varepsilon_{s,a}\psi_{s,a}(r_i) , \tag{6}$$

so that $H_s(\{r_i\})$ is cast in the well known form of De Gennes[9]

$$H_s = -\Omega\sum_i \sigma_i^z - \frac{1}{2}\sum_{i\neq j} J_{ij}\sigma_i^x\sigma_j^x + E_o , \tag{7}$$

where Ω, J_{ij} and E_0 are simple functions of $\varepsilon_\alpha, C_{ij}$ and the matrix element $\langle\alpha|r_i|\beta\rangle$ $(\alpha,\beta = s,a)$ calculated with the wave functions in Eq. (6).

The variational parameters ϕ_{ij}, $\tilde{U}(r_i)$ and C_{ij} are determined from the variational approach[6], namely from the condition of stationarity of the free energy,

$$F = F_0 + \langle H - H_0\rangle_0 ; \quad F_0 = T \ln Sp\{e^{-H_0/T}\},$$
$$\langle H - H_0\rangle_0 = Sp\{e^{(F_0-H_0)/T}(H-H_0)\}, \tag{8}$$

with respect to variations over these parameters or, equivalently, over the corresponding correlation functions $(\langle u_i u_j\rangle_0)$. Further, the closed system of self-consistent equations for all parameters entering in Eqs. (4), (5), (7) is obtained thus describing the mutual influence of phonon and pseudospin subsystems.

3. PHASE TRANSITIONS IN THE FERROELECTRIC MODEL

Having written the single-particle double-well potential in the convenient form[2]

$$U(s_i) = -\frac{A}{2}s_i^2 + \frac{B}{4}s_i^4 , \tag{9}$$

where parameters A and B define the distance $(2s_0 = 2(A/B)^{1/2})$ and the height of the potential barrier $(U_0 = A^2/4B)$ between the potential minima, and the pair-potential (in Eq. (1)) in the harmonic approximation,

$$V(s_i,s_j) = \frac{1}{2}\varphi_{ij}(s_i - s_j)^2 , \tag{10}$$

the variational approach gives the self-consistent expressions for the parametters ϕ_{ij}, $\tilde{U}(r_i)$ (renormalizing the parameter $A \Rightarrow \tilde{A} = A - 3B\langle u_i^2\rangle$) and $C_{ij} = \frac{1}{2}\varphi_{ij}$, while

for the pseudospin parameters in Eq. (7) one obtains:

$$\Omega = \frac{1}{2}(\varepsilon_a - \varepsilon_s) + \frac{1}{2}(r_{aa}^2 - r_{ss}^2)\, C_0 \,, \qquad J_{ij} = r_{sa}^2 \varphi_{ij} \,. \tag{11}$$

The correlation-displacement function relevant for the nature of ST are determined by the following equations:

$$\langle u_i^2 \rangle_0 = \frac{1}{Nm} \sum_k \frac{1}{2\omega_k} \operatorname{cth} \frac{\omega_k}{2k_B T} \,, \tag{12}$$

$$\langle r_i^2 \rangle = \frac{1}{2}\left[(r_{ss}^2 + r_{aa}^2) + (r_{ss}^2 - r_{aa}^2) \langle \sigma_i^x \rangle \right], \tag{13}$$

where the phonon frequency is given by the equation

$$m\omega_k^2 = \Delta + \varphi_0 - \varphi_k \;;\; \varphi_k = \sum_j \varphi_{ij} e^{ik(x_i - x_j)}, \tag{14}$$

$$\Delta = -A + 3(\langle u_i^2 \rangle_0 + \langle r_i^2 \rangle_0) B \,. \tag{15}$$

The phase transition is described by the solution of the self-consistent system of equations which, owing to Eq. (6), can be obtained only numerically. Therefore only a qualitative analysis for the limiting cases is possible.

a) Order-disorder transition

Analogously to the previous analysis[1], in the temperature region when

$$\varphi_0 \ll \tilde{A} = A - 3B\langle u_i^2 \rangle \,, \tag{16}$$

the order-disorder transition is possible in the pseudospin subsystem through mediation of the order parameter $\langle \sigma^z \rangle$. In the molecular field approximation for the transition temperature one finds

$$T_c = J_0 \frac{2q}{\ln \frac{1+q}{1-q}} \;;\; q = \Omega / J_0 < 1. \tag{17}$$

The estimation obtained in the case of weak tunneling ($\Omega \ll J_0$) corresponds to the results of the unified model[1,3] for f_0 (i.e. φ_0 here) $\ll 1$, namely,

$$T_c \sim J_0 \sim \varphi_0 \tilde{r}_0^2 \sim \varphi_0 \frac{\tilde{A}}{B} \ll \tilde{U}_0 \ . \qquad (18)$$

Note that the phonon excitations do not play the essential role in this case, since $\langle u_i^2 \rangle \ll \tilde{r}_0^2$.

b) Displacive transition

When the temperature is raised the atomic fluctuations $\langle u_i^2 \rangle$ can not be neglected and the character of the coupling could be changed, i.e.

$$\varphi_0 \gg \tilde{A} \qquad (19)$$

(even for $\varphi_0 \ll A$!) thus leading to the displacive phase transition ($\Delta(T_0) \to 0$ and $\tilde{r}_0^2(T_0) \to 0$). In the classical limit

$$\tilde{A}(T_0) = 0 ; \quad \langle u_i^2 \rangle = \frac{1}{3} \frac{A}{B} , \qquad (20)$$

and the transition temperature is estimated as follows

$$T_0 \sim \frac{1}{3} \varphi_0 \frac{A}{B} \ . \qquad (21)$$

A similar result have been obtained[1,3] for $\varphi_0 \gg 1$.

4. CONCLUSIONS

The taking into account of tunneling effects in the case of structural phase transtion is based on the assumption that there are two types of excitations: fluctuations (or "jumps") between the equilibrium positions and fast phonon oscillations which could be separated in a self-consistent approach. As it is well known the energy

spectrum of a particle in a double-well potential has quite a complex shape (see for example refs. 4,10). So the separation of the two types of excitations can be done merely as an approximative scheme which has an interpolating character. Nevertheless, the suggested description is a natural generalization of the traditional introduction of atomic equilibrium states into the Hamiltonian of ruther anharmonic character. A similar generalization is used in the dinamical theory of fluids and other diffusion processes.

Concluding this paper we point out that a phase transition in an intermediate case (for $\varphi_0 \simeq 1$) has a mixed character which can thoroughly be elaborated only by means of numerical calculations. In the frame of the present model one expects a more complex renormalization of the pseudospin parameters[9] in deuterated compounds. In addition, the condition $T_c < T_0$ holds in general.

Acknowledgements: The authors wich to acknowledge a short but stimulating discussion with Dr B. Žekš from Ljubljana.

REFERENCES: 1/ S.Stamenković et al. Phys. Rev. B14, 5080 /1976/; 2/ N.S. Gillis, in: Dynamical Properties of Solids, ed. G.K. Horton, A.A Maradudin, v.2, p.107-150, North-Holland, Amsterdam, 1975; 3/ V.L. Aksenov et al. FTT 18, 2921 /1976/; 4/ H. Beck, J. Phys. C: Solid St. Phys. 9, 33 /1976/; 5/ R.Blinc, B.Žekš, Ferroelectrics and Antiferroelectrics: The Lattice Dynamics, ed. Mir, Moscow, 1975; 6/ N.M.Plakida,in: Statistical Physics and Quantum Theory of Fields, ed. by N.N. Bogolyubov, Nauka, Moscow,1973, pp.205-240; 7/ H. Thomas, in: Structural Phase Transition and Soft Modes, ed. by F. Samuelson et al., Universitet for laget, Oslo, 1971; 8/ M.A.Moore, H.Williams, J.Phys. C5, 3168 /1972/; 9/ P.G. De Gennes, Solid St. Comm. 1, 132 /1963/; 10/ I.V.Stasyuk, Preprint ITF-75-108P,Kiev,1975.