Phonon order parameters in the Verwey phase transition

Przemysław Piekarz, Krzysztof Parlinski and Andrzej M. Oleś

Institute of Nuclear Physics, Polish Academy of Sciences, ul. Radzikowskiego 152, Kraków, Poland

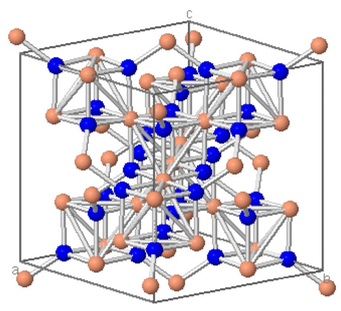
The mechanism of the phase transition in magnetite (Fe_3O_4) at T_V = 122 K, discovered by Verwey [1], has remained a big puzzle in the condensed matter physics for almost 70 years. Developments in experimental and theoretical methods during last years revealed subtle changes in the crystal and electronic structure below T_V [2,3]. A simple charge ordering picture in which metal-insulator transition is induced by electrostatic interactions was replaced by a highly complex scenario in which lattice, charge, spin and orbital degrees of freedom are involved. In the previous work [4], we have obtained the phonon spectrum of magnetite using the *ab initio* computational technique [5]. We have identified two primary order parameters at $\mathbf{k}_X = (0,0,1)$ and $\mathbf{k}_\Delta = (0,0,1/2)$ with the X_3 and Δ_5 symmetry, respectively, which both play important role in the VT: (i) the Δ_5 mode is responsible for the doubling of the unit cell along the *c* direction in the monoclinic phase, while (ii) the X_3 phonon induces the metal-insulator transition by its coupling to the electronic states near the Fermi energy [4]. Due to the electron-phonon interaction the above order parameters are combinations of the electron (charge-orbital) and lattice components. This explains why the phonon soft mode has not been observed. Instead, low-energy critical fluctuations of order parameters were found by the diffuse neutron scattering [7]. The condensation of the order parameters below T_V explains the crystal symmetry change as well as the charge-orbital ordering [2,3].

The group theory predicts also secondary order parameters, which do not effect the symmetry below T_V but modify the properties of magnetite close to a transition point. At the Γ point, the T_{2g} mode can be classified as the secondary order parameter and its coupling to the shear strain explains the softening of the C_{44} elastic constant [8].

Mechanism of the Verwey transition: group theory analysis and *ab initio* studies

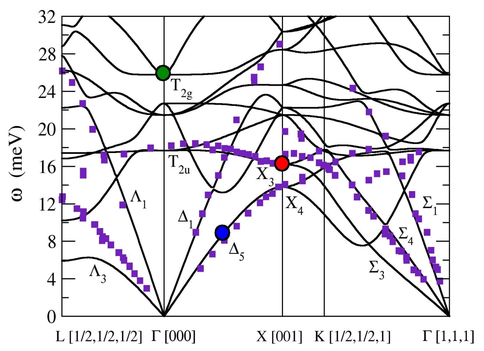
High - symmetry phase *Fd3m*

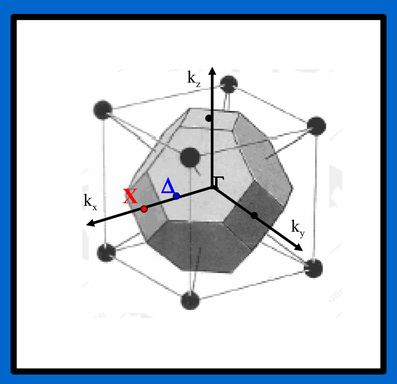
T > T_V



Phonon dispersion curves

Neutron scattering data taken from Ref. [6]





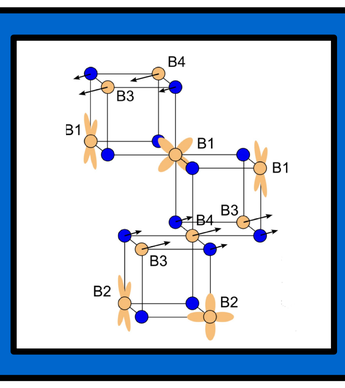
Two primary order parameters: X_3 and Δ_5

Fd3m* => X_3, k=(0,0,1) => *Pmna

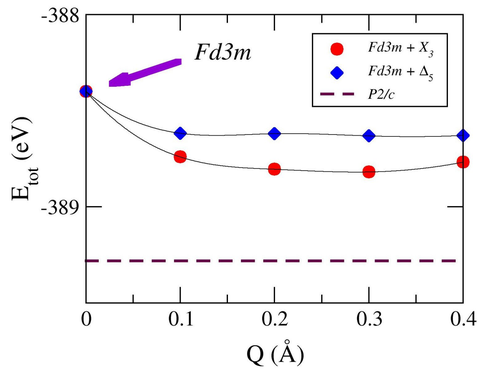
Fd3m* => Δ_5, k=(0,0,1/2) => *Pbcm

Diffuse scattering at k = (4,0,1/2) $T>T_V$ Ref. [7]

Doubling of the unit cell along c direction
=> Bragg reflections at *(h,k,l+1/2)* $T<T_V$

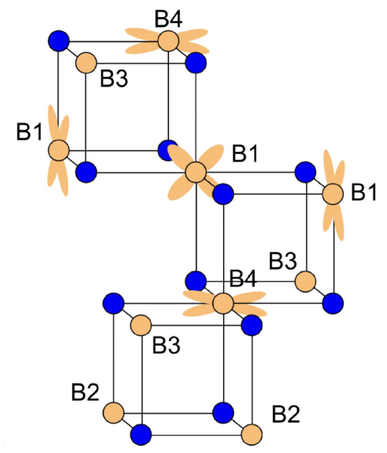


The total energy is lowered when the cubic symmetry is distorted by the X_3 or Δ_5 mode



Low - symmetry phase *P2/c* $T < T_V$

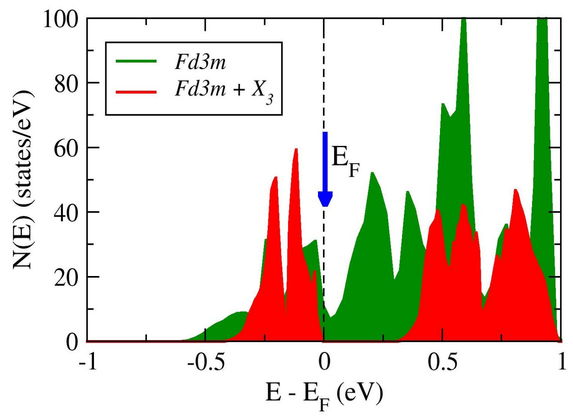
Pmna* ∧ *Pbcm* = *P2/c

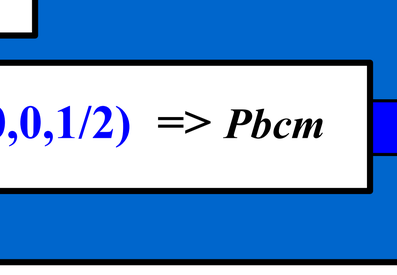


Charge - orbital ordering in the *P2/c* monoclinic phase

Openning of the gap at E_F in the t_{2g} spin-down states

=> Metal - insulator transition





Landau free energy functional expanded into the invariants of the components of the order parameters: $X_3(g)$, $\Delta_5(q)$, and $T_{2g}(\varepsilon)$

$$F = F_0 + \alpha_1 g^2 + \beta_1 g^4 + \gamma_1 g^6 + \alpha_2 q^2 + \beta_2 q^4 + \gamma_2 q^6 + c^o_{44}\varepsilon^2 + \delta_1 g^2 q^2 + \delta_2 g^2 \varepsilon$$

$$\delta F/\delta q = 0 \Rightarrow q^2 = -(\delta_1 g^2 + \alpha_2)/\beta_2$$

$$c_{44} = c^o_{44}(T - T_0)/(T - \theta) \Rightarrow \text{softening of the shear elastic constant Ref. [8]}$$

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