substance: Fe_3O_4
property: crystal structure, lattice parameters, low temperature phase

Magnetite shows a highly unusual transition at 119 K– the Verwey transition. Above this temperature, the material shows the properties of a poor metal, but below T_V a distortion to a semiconducting phase of much lower symmetry is found.

crystal structure: monoclinic, space group C_s^4 – Cc, very close to D_{2h}^{11} – Pmca or C_{2v}^2 – $Pmc2_1$ [77Y, 82I].

At 119K, Fe_3O_4 undergoes a first-order crystallographic transition to a structure of lower symmetry. The unit cell parametes vary in an unusual fashion (Fig. 1). The low-temperature phase has been studied by X-ray diffraction [77Y, 77I], NMR [78M1, 78M2, 81Y], neutron diffraction [75S, 75I, 75F, 76S], Moessbauer spectroscopy [70H, 71R] and magnetoelectric effect [79S, 79K, 78M3].
Initially, Verwey [41V, 47V] predicted an orthorhombic LT symmetry as a result of ordering of Fe^{2+} and Fe^{3+} on the B-sites, (Fig. 2). Early neutron work [58H] supported this model, but later studies [68S, 75S] revealed the true symmetry to be much lower.

lattice parameters

a	11.888 Å	*T* = 84 K	77Y
	11.868(2) Å	*T* = 10 K	82I
b	11.847 Å	*T* = 84 K	77Y
	11.851(2) Å	*T* = 10 K	82I
c	16.773 Å	*T* = 84 K	77Y
	16.752 Å	*T* = 10 K	82I
β	89.76º	*T* = 84 K	77Y
	90.20(3)º	*T* = 10 K	82I

Such a low symmetry suggests an alternation of Fe^{3+} and Fe^{2+} ions in the [1 1 0] direction as in the *ab* model of Fig. 2. Neutron diffration data have been used to suggest that the transition involves the condensation of a particular optical mode $\Delta_5^{(1)}$ (Fig. 3) [79L, 75I]. Even more complex structures have been proposed as a result of NMR experiments [78M1]. Three-dimensional neutron scattering data [82I] have been refined in the two primitive orthorhombic space-groups Pmca and $Pmc2_1$. The resulting ionic displacements and Fe–O distances are shown in Fig. 4. The charge-density distribution in the LT phase has not been finally determined; discrepancies exist in the interpretations of Moessbauer and NMR data [78M1] relative to the neutron data [82I], probably as a result of the different time scales of the measurements.

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Fig. 1.

Fe_3O_4. Details of lattice expansion at low temperatures. Coefficient β in $L(T) = L_0(1+\beta(T))$ (L_0 = length at –180ºC) vs. temperature. Measurements in three crystallographic directions [50D].

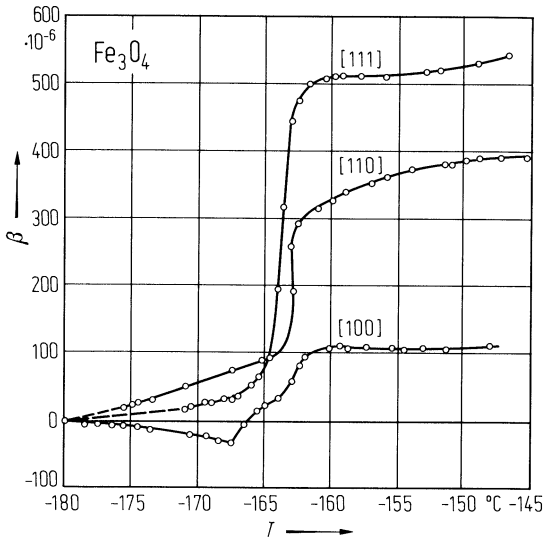

Fig. 2.

Fe_3O_4. Comparison of the Verwey and *ab* models of ion ordering below the Verwey temperature [75S]. $x \parallel [100]_{cub}$,; $y \parallel [010]_{cub}$; $z \parallel [001]_{cub}$. Fe^{2+} and Fe^{3+} are arranged on octahedral (B) sites. Z in units of the lattice parameter.

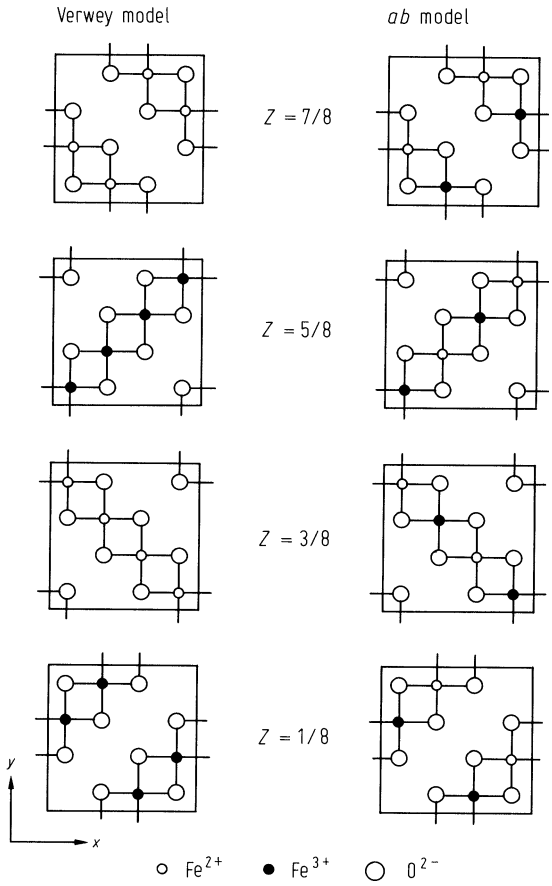

Fig. 3.

Fe_3O_4. (a) The $\Delta_5^{(1)}$ mode, (b) resultant *ab* order [79L, 75I]. The axes [100] etc. refer to the cubic system and O_a, O_b, *c* define the orthorhombic axes. *ab* order: combined $\Delta_5^{(1)}$ order (due to electron phonon interaction) and *b* line order (ordering along *b* axis induced by the Coulomb interaction between next nearest neightbours). For one primitive cell the four B sites are denoted by 1...4 - For more detailed description of *a* line and *b* line order, see [79L] and references therein.

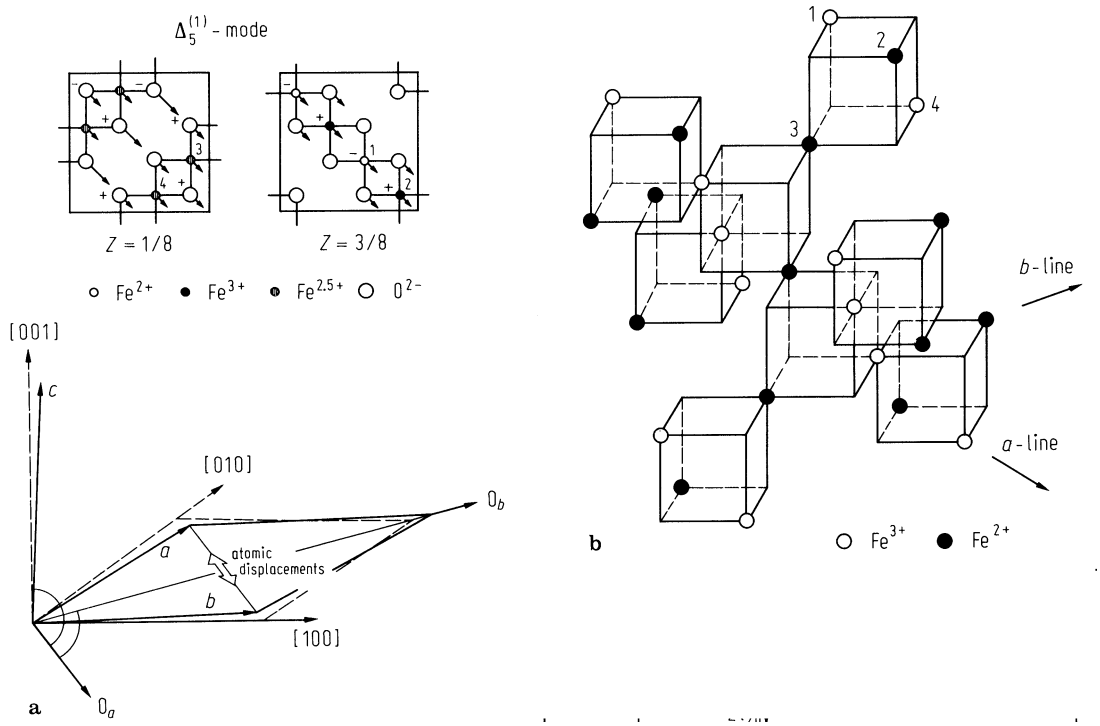

Fig. 4.

Fe_3O_4. Atomic displacements from the cubic high temperature phase determined from neutron diffraction studies (a) refined in $Pmc2_1$ (b) refined in Pmca. Displacements in *x* and *y* are shown by arrows and *z* displacements are also indicated. All displacements are in fractional coordinates $\cdot 10^3$. O^{2-} ions are shown as open circles, B-site Fe-ions as full circles and A-site Fe ions as dashed circles [82I].