# Charge ordering and elastic constants in Fe₃₋ₓZnₓO₄

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**Abstract.** We present the temperature dependence of elastic modes of $Fe_{3-x}Zn_xO_4$ with $x = 0$, $x = 0.02$ and $x = 0.032$. The $c_{44}$ shear modes show a pronounced softening which can be normalized to a common behavior for all these substances. We can explain the softening with a bilinear coupling of the elastic strain to an order parameter linked to charge ordering processes. The other elastic modes ($c_{11}$, $c_{12}$ and the bulk modulus) do not show any softening. We present a symmetry analysis for the charge ordering model.

**PACS.** 71.30.+h Metal-insulator transitions and other electronic transitions – 62.65.+k Acoustical properties of solids – 75.40.Cx Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.)

## 1 Introduction

Magnetite ($Fe_3O_4$) undergoes a metal-insulator transition at $T_v \approx 124$ K [1]. Upon substituting with Zn ($Fe_{3-x}Zn_xO_4$) the strongly first order transition becomes continuous for $x > 0.012$, or even, as suggested by some authors [22] the long range order is missing, and above $x > 0.036$ no anomaly is encountered [2,3]. The nature of this transition was suggested to be connected to a charge ordering [1] although the details of this mechanism and of the structure seems not to be settled yet [4]. Magnetite undergoes a paramagnetic-ferrimagnetic transition at a much higher temperature $T_c = 858$ K. This ferrimagnetic order is due to an antiferromagnetic coupling between the A-sites (tetrahedral $Fe^{3+}$ $S = 5/2$) and the B-sites (octahedral $Fe^{3+}$, $Fe^{2+}$ $S = 2$) in the cubic inverse spinel structure [5]. The magnetite formula can be written as $Fe_3O_4 = Fe_{tet}^{3+}[Fe^{2+}Fe^{3+}]_{oct}O_4$. Upon substitution the Zn ions occupy only the tetrahedral sites [6]: $[Fe_{3-x}Zn_xO_4]$ $= [Fe_{1-x}^{3+}Zn_x^{2+}]_{tet}[Fe_{1+x}^{3+}Fe_{1-x}^{2+}]_{oct}O_4$.

The charge ordering at $T_v$ is due to the $Fe^{2+} - Fe^{3+}$ ordering on the octahedral sites. In this structure the B-sites can be seen as forming a network of 4 separated tetragons within a unit cell (Fig. 1). The four tetrahedrons form therefore a separate unit. The simplest view of the charge ordering on these tetrahedrons would be the one originally proposed by Verwey: $Fe^{2+}$ ($Fe^{3+}$) cations alone occupy alternating [110] chains as indicated by the dotted lines in Figure 1 [1,4,7].However, this pattern was not verified by the precise neutron studies [20].
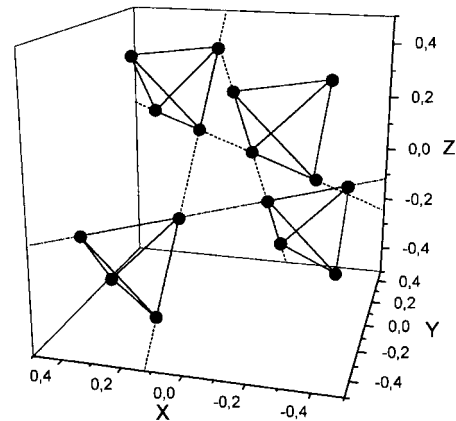
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**Fig. 1.** Fe-ions on octahedral sites. They form 4 tetrahedra in the unit cell. Origin at (0, 0, 0) and with axis $\pm a/2$. Dotted lines connecting the tetrahedra along the different [110]-directions.

Recently charge ordering with an accompanying one dimensional band Jahn-Teller effect was proposed for the structural transition of the anti-$Th_3P_4$ structure material $Yb_4As_3$ at 292 K [8]. Subsequently a strong softening of the $c_{44}$ elastic constant was observed for $T > T_c$ [9]. A Landau theory description gave a bilinear coupling of the $\varepsilon_{\Gamma 5}$ strain and the charge ordering order parameter thus explaining the softening of the $c_{44}$ mode by such a symmetry analysis [9]. In magnetite having the same high temperature symmetry for the tetrahedrons as in $Yb_4As_3$ and a similar strong softening for $c_{44}$ a similar symmetry

**Table 1.** $T_v$ and elastic constants at 270 K.

|  | $x = 0$ | $x = 0.02$ | $x = 0.032$ |
|---|---|---|---|
| $T_v$ [K] | 124 | 94 | 83 |
| $c_{11}$ [$10^{11}$ erg/cm$^3$] | 27.2 | 25.3 | 26.0 |
| $c_{12}$ [$10^{11}$ erg/cm$^3$] | 17.8 | 14.3 | 14.6 |
| $c_{44}$ [$10^{11}$ erg/cm$^3$] | 6.1 | 8.4 | 6.5 |

analysis should be possible in order to identify the order parameter and the coupling to the symmetry strains.

In this paper we present elastic constant data for the system $Fe_{3-x}Zn_xO_4$ for $0 < x < 0.032$, with particular attention to the high temperature phase $T > T_v$. We will show that the softening of the $c_{44}$-mode as a function of temperature can be explained naturally with a strain-charge ordering coupling. Because of domain wall stress effects especially for the first order transition at $T_v$ we cannot draw any conclusion about the elasticity in the charge ordered monoclinic phase nor can we make definite statements about the charge ordering in this phase.

## 2 Elastic constants

We measured elastic constants and attenuation using a phase comparison and a phase sensitive (quadrature) method [10,11]. As transducers we used piezoelectric foils for the longitudinal modes and quartz plates for shear waves. The single crystals of $Fe_{3-x}Zn_xO_4$ were grown by the cold crucible technique (skull melting) [12] at Purdue University. The crystals were then subjected to subsolidus annealing under $CO/CO_2$ gas mixtures to establish appropriate metal/oxygen ratio [13].

In Figure 2 we show the elastic constants $c_{11}$, $(c_{11} - c_{12})/2$ and $c_{44}$ for magnetite ($Fe_3O_4$) as a function of temperature. Reorientation of the magnetization around 130 K affects the sound propagation very strongly [14]. In order to avoid such magnetic domain effects we applied a magnetic field of 0.5 T for the various modes as before [14]. We notice a strong softening (about 10%) of the $c_{44}$ mode from room temperature down to $T_v = 124$ K. The other modes show a weak temperature dependence for $T > T_v$. On the other hand all modes exhibit strong positive steps at the transition temperature $T_v$. These results for $Fe_3O_4$ are in good agreement with previous measurements [14] except for the absolute values of the $c_{ij}$. These absolute values are given in Table 1 together with other data from our investigation.

In Figures 3-5 we show the temperature dependence of the various elastic modes for the $Fe_{3-x}Zn_xO_4$ system. Again the most interesting mode is the $c_{44}$-mode which shows an increasing softening with rising $x$. For the highest concentration $x = 0.032$, $c_{44}$ exhibits a total softening of 34% (Fig. 3). The positive step function at $T = T_v$ has also disappeared for $x = 0.032$ indicating that the transition is now close to second order. As shown in Figure 4 also the $c_{11}$-mode steps at $T_v$ are significantly reduced with increasing Zn content $x$ until for $x = 0.032$ the transition is essentially of second order. Finally for the $(c_{11} - c_{12})/2$-mode the anomaly at $T_v$ is smallest and the temperature
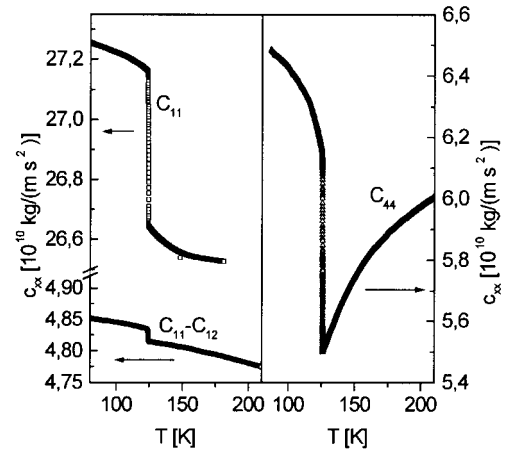


**Fig. 2.** Temperature dependence of the elastic constants for $Fe_3O_4$. A magnetic field of 0.5 T was applied to remove the domains. This implies for all the elastic constant data in Figures 2-6.
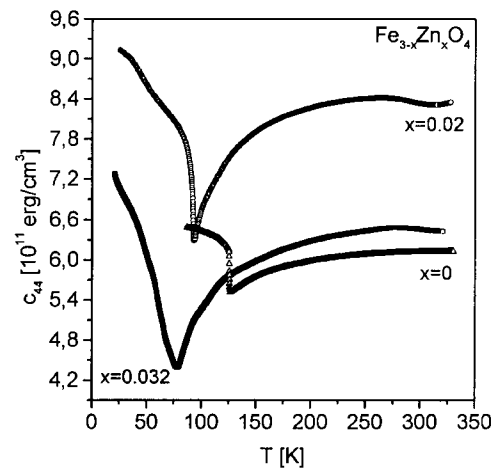


**Fig. 3.** Temperature dependence of the $c_{44}$-modes for $Fe_{3-x}Zn_xO_4$ for $x = 0$, 0.02, 0.032.

dependence for $T > T_v$ is weakest of all different modes (see Fig. 2).

Figure 5 shows the elastic anisotropy $A = 2c_{44}/(c_{11} - c_{12})$ and the Poisson ratio $\nu = c_{12}/(c_{11} + c_{12})$ as a function of temperature. The anisotropy exhibits the expected softening due to $c_{44}$, but the material is rather isotropic elastically (*i.e.* $A \approx 1$). The Poisson ratio shows a rather weak temperature dependence for $T > T_v$. This quantity describes the extent of possible valence fluctuations [15]. Apparently the charge fluctuations of $Fe^{2+}$-$Fe^{3+}$ observed for $T > T_v$ do not alter this ratio but they affect very strongly the $c_{44}$-mode as shown below. The Poisson ratio $\nu$ may be little affected because only the Fe-ions on octahedral sites exhibit valence hopping and because $Fe_3O_4$ is an inhomogeneously mixed-valence compound in contrast to the homogeneously mixed compounds in 4f systems [16].
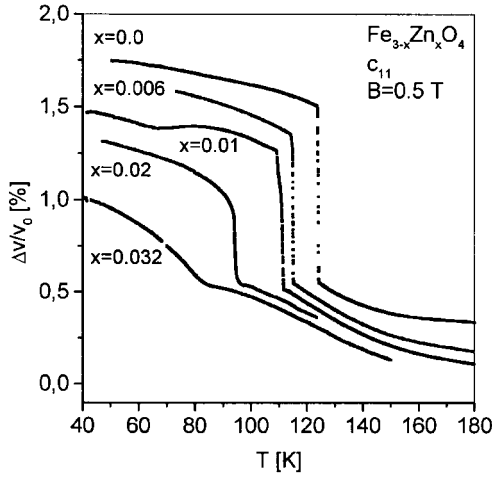
**Fig. 4.** Relative sound velocity for the $c_{11}$-mode for $x = 0$, 0.006, 0.01, 0.02, 0.032 as a function of temperature.
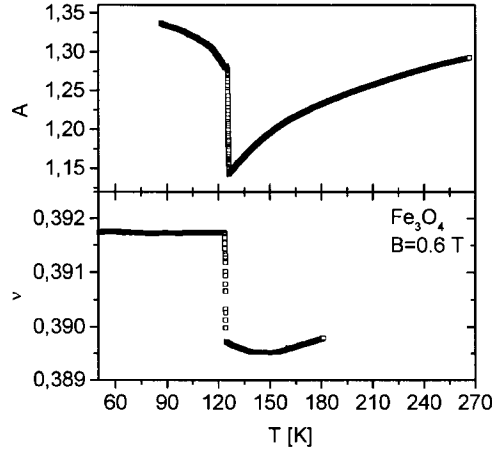


**Fig. 5.** Poisson ratio $\nu$ and elastic anisotropy A for $Fe_3O_4$ as a function of temperature.

## 3 Electron-phonon coupling: symmetry considerations

The space group of the cubic magnetite structure is $O_h^7$ (Fd3m) and a cubic unit cell contains 8 formula units. The octahedral B sites form 4 tetrahedra as shown in Figure 1. In order to determine the electron-phonon coupling we consider just one such tetrahedron with $T_d$ symmetry. The three others are gained by translation vectors. The character table for this symmetry is given in Table 2. We denote the charge densities for the $Fe^{2+}$, $Fe^{3+}$ ions in such a tetrahedron by $\rho_i$ ($i = 1$-4). The average valence of these charges is 2.5. These charges have coordinates $(-1,-1,-1)$, $(-1,1,1)$, $(1,-1,1)$, $(1,1,-1)$ for $\rho_1$ $\rho_2$ $\rho_3$ $\rho_4$ respectively. In the following we use the method of calculations presented in reference [9]. Application of the 24 symmetry operations of $T_d$ on the $\rho_i$ gives a reducible $4\times4$ matrix representation. This can be decomposed into a sum of the irreducible representations. The character of the reducible representation $\chi_{tet}$ is also given in Table 2. It decomposes into the two irreducible representations $\Gamma_1 + \Gamma_5$.

**Table 2.** Character table for $T_d$.

|  | $E$ | $8C_3$ | $6\sigma_d$ | $6S_4$ | $3C_2$ |
|---|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 |
| $\Gamma_2$ | 1 | 1 | $-1$ | $-1$ | 1 |
| $\Gamma_3$ | 2 | $-1$ | 0 | 0 | 2 |
| $\Gamma_4$ | 3 | 0 | $-1$ | 1 | $-1$ |
| $\Gamma_5$ | 3 | 0 | 1 | $-1$ | $-1$ |
| $\chi_{tet}^{(red)}$ | 4 | 1 | 2 | 0 | 0 |

Since the direct product $\Gamma_5 \times \Gamma_5$ contains $\Gamma_1$ there are charge fluctuation modes of these symmetries, $\eta(\Gamma_5)$, that couple bilinearly to the elastic strains $\varepsilon_{xy}$, $\varepsilon_{yz}$, $\varepsilon_{zx}$ of the $c_{44}$-mode ($\Gamma_5$) bilinearly and furthermore there is a coupling to the volume strain $\varepsilon_v$ of the bulk modulus $c_B(\Gamma_1)$. This coupling to $c_B$ has no effect on the charge ordering.

In the $Fe_{3-x}Zn_xO_4$ system the important strain coupling is to the $c_{44}$ mode as discussed before (Figs. 2, 3, 4). As shown above we can have a bilinear coupling between strain $\varepsilon(\Gamma_5)$ and charge fluctuation mode $\eta(\Gamma_5)$: $F_{int} = g_\Gamma \varepsilon_\Gamma \eta_\Gamma$. Taking the usual Landau expansion with order parameter $\eta$ and this strain-order parameter coupling one gets for the soft $c_{44}$ mode [9,17]

$$c_{44} = c_{44}^o(T - T_c)/(T - \Theta). \qquad (1)$$

Here $\Theta$ enters the usual Landau term $\alpha = \alpha'(T - \Theta)$ and denotes the charge ordering transition without strain interactions, and $T_c$ is the transition temperature if the transition is of second order: $T_c = \theta + g^2/2\alpha'c^o$. The difference $T_c - \Theta$ is a measure for the strain-order parameter coupling.

Formula (1) fits our experimental results very nicely as shown in Figure 6. Here we plot the $c_{44}$ elastic constants for all 3 specimens ($x = 0$, 0.02, 0.032) as a plot of normalized $c_{44}(T)/c_{44}(270\,K)$ *versus* temperature. The values for $c_{44}(270\,K)$ are given in Table 1. For $T > T_v$ and in the region of overlap the results of the various $c_{44}$ modes almost coincide. In addition the excellent Landau fit with equation (1) shows that this approach is justified. From the fit we obtain $T_c = 66$ K and $\Theta = 56$ K. The $c_{44}$-modes do not soften completely however. The abrupt stop of this softening at $T_v$ is due to first order terms or other interactions not considered in our analysis for $T > T_v$. Note also that the low temperature structure is monoclinic.

We have not yet discussed the order parameter for the Landau analysis. This we will do again for the case of a single tetrahedron considered above. Using the projection operator technique we get for the charge fluctuation modes the following expressions [18]:

$$\rho_{\Gamma1} = \rho_1 + \rho_2 + \rho_3 + \rho_4$$
$$\rho_{\Gamma5}^{yz} = \rho_1 + \rho_2 - \rho_3 - \rho_4$$
$$\rho_{\Gamma5}^{zx} = \rho_1 - \rho_2 + \rho_3 - \rho_4$$
$$\rho_{\Gamma5}^{xy} = \rho_1 - \rho_2 - \rho_3 + \rho_4. \qquad (2)$$

For the Landau theory we obtain the change in the charge density $\Delta\rho$

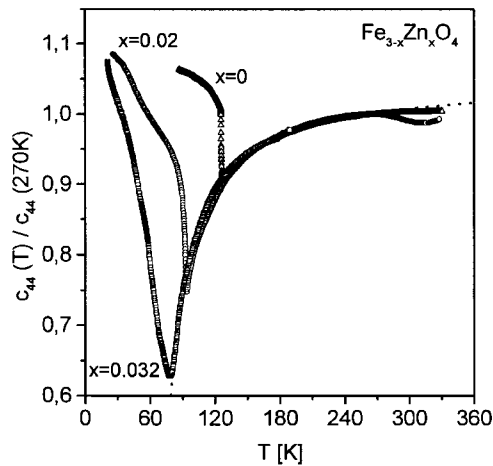$$\Delta\rho = \eta_{yz}\rho_{yz} + \eta_{zx}\rho_{zx} + \eta_{xy}\rho_{xy}. \qquad (3)$$

**Fig. 6.** Normalized soft modes $c_{44}(T)/c_{44}$ (270 K) for the $Fe_{3-x}Zn_xO_4$ crystals together with a fit to equation (1) (dotted line).

Here the coefficients $\eta_{yz}$, $\eta_{zx}$, $\eta_{xy}$ in equation (3) are the orderparameter to describe the charge ordering of the B-sites. They are zero ($\Delta\rho = 0$) in the high temperature phase above $T_v$. They enter also the strain-order parameter coupling given above. From equations (2, 3) we can determine possible charge distributions for $T < T_v$. $\rho_{\Gamma 1}$ would correspond to an average valence of $+2.5$ at each ion site in the tetrahedron. For $\rho_{\Gamma 5}$ there are different possibilities depending on whether just one component of the order parameter say $\eta_{xy} \neq 0$ and $\eta_{yz} = \eta_{zx} = 0$ or whether two components are $\neq 0$ or whether all three are $\neq 0$. Since the low temperature structure in magnetite is not completely known yet we will not discuss all these possibilities except to note that for an orthorhombic subgroup $C_{2v}$ of $T_d$ we have the first mentioned case $\eta_{xy} \neq 0$. The orthorhombic structure $C_{2v}$ would be the low temperature structure if one neglects the monoclinic tilt angle $\beta$ [5]. This order parameter would lead to a charge distribution of $Fe^{+2}$ along the [110] direction and $Fe^{3+}$ along the other [011] of Figure 1. This gives a charge ordering anticipated before [1].

In summary we can say that the charge ordering mechanism can account for the softening of the $c_{44}$ mode in this system. The absence of complete softening is due to first order mechanisms not considered here. The absence of any softening in $c_{11}$ can be put on the small coupling constant $g_{\Gamma 1}$ of the corresponding strain-order parameter coupling. The absence of any softening in the $(c_{11} - c_{12})/2$ mode can be explained by the absence of any bilinear strain order-parameter coupling for the tetrahedron.

## 4 Conclusions

We have presented the results of an experimental study of elastic constants in $Fe_{3-x}Zn_xO_4$ systems. We have found that the shear wave $c_{44}$ shows strong softening in the cubic phase and we have explained this fact with a charge ordering mechanism. In addition we propose a physical picture of the possible charge ordering in the low temperature phase. In this investigation the monoclinic phase was not considered explicitly. Our experiment can only account for order parameter at the $\Gamma$ point. Other experiments (inelastic neutron scattering) can identify a $k \neq 0$ order parameter with $\Delta$ symmetry [20].

There were attempts in the literature to explain the Verwey transition with a cooperative Jahn-Teller mechanism [19] acting on the $Fe^{2+}$-ion. Apart from the fact that the charge ordering had still to be explained the effect of spin orbit coupling had to be considered on the same footing as the cooperative Jahn-Teller mechanism especially for octahedron deformation $c/a > 1$ [21]. Therefore we do not pursue this further.

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