—Technical Paper—

A Chemla-Type Electrotransport Experiment in Magnetite, $\text{Fe}_{3-\delta}\text{O}_4$

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We have performed a Chemla-type electrotransport experiment on magnetite, Fe_3O_4 , from which the tracer diffusion coefficient of iron and its effective charge can be determined simultaneously. The experiment was conducted with radiotracer ^{59}Fe by measuring the spread and drift of the tracer source in a constant electric field at a temperature of 1200°C and an oxygen activity of $\log(a_{\text{O}_2}) = -4$. The tracer diffusion coefficient and the effective charge of Fe in magnetite were determined from the tracer profiles using both the residual activity and the tracer sectioning method. While the tracer diffusion coefficient agrees well with the values reported in literature, the effective charge number of Fe was found to be $+2$, in contrast to the average, formal charge number $8/3$ of Fe in magnetite. This result can be explained either due to the interaction between ionic and electronic charge carriers which has been observed in other semiconducting oxides or due to a much higher mobility of Fe^{2+} compared to Fe^{3+} .

Key Words : Chemla-type Electrotransport, Tracer Diffusion, Effective Charge Number, Magnetite

1 Introduction

Magnetite is the basic material system of spinel ferrites which are very important for the application of magnetic materials.¹⁾ So there have been many studies of the defect structure and related transport properties of this system, especially by Dieckmann and coworkers.²⁻⁹⁾ They performed systematic studies of the defect structure and transport properties of magnetite through their series of papers, showing that at low oxygen activities cation interstitials and at high oxygen activities cation vacancies dominate.

In spite of these studies, however, there is still not much known about the interactions between ions and electrons in magnetite. Those interactions can be studied by considering the so-called effective charge of Fe, which appears in electrotransport experiments and which differs from the formal charge due to cross effects in the transport coefficients.¹⁰⁾ Formerly, there were some reports about the cross effect between charge carriers in semiconducting, nonstoichiometric oxides like CoO .¹⁰⁻¹⁶⁾ According to those studies, the effective charge of the cation is $z_{\text{Co}}^{\text{eff}} \approx +1$ at 1000°C in air, for example, and different from its formal charge, $z_{\text{Co}} = +2$, due to the interaction between ionic and electronic charge carriers. This cross effect was examined by several different experimental methods and explained either by the long range coulombic interaction or the association between cation vacancies and electron holes. In magnetite, recently performed electrochemical experiments¹⁷⁾ indicated also that the effective charge of Fe is different from its average formal charge ($8/3$).

The aim of our investigation is to determine whether

the effective charge of Fe is likely to be different from its average formal charge ($8/3$) or not, by performing a Chemla electrotransport experiment, which has already been used to evaluate the effective charge of Co in former studies.^{18,19)} In the Chemla-type electrotransport experiment a crystal sandwich is used and the broadening and drift of a radiotracer source of the cations is measured in an external electric field. In the following sections first a formal treatment is given and then the results of our experiments are discussed in detail.

2 Formal Treatment

According to irreversible thermodynamics,²⁰⁾ the fluxes of the moving species, Fe^{2+} , Fe^{3+} and electrons e' ($i = 1, 2, 3$) depend linearly on the gradients of the corresponding electrochemical potentials η_i :

$$\dot{j}_i = - \sum_{k=1}^3 L_{ik} \nabla \eta_k \quad i = 1, 2, 3 \quad (1)$$

where L_{ik} are the transport coefficients. With the reduction reaction of each cation, $\text{Fe}^{n+} + ne' = \text{Fe}$ ($n = 2, 3$), the iron flux, $\dot{j}_{\text{Fe}} = \dot{j}_1 + \dot{j}_2$, can be expressed as:

$$\dot{j}_{\text{Fe}} = - \left(\sum_{i=1}^2 \sum_{k=1}^2 L_{ik} \right) \cdot \nabla \mu_{\text{Fe}} + \left(\sum_{i=1}^2 \sum_{k=1}^3 L_{ik} \cdot z_k \right) \cdot \nabla \eta_3 \quad (2)$$

where μ_{Fe} is the chemical potential of the neutral metal. The first term in eq.(2) represents the diffusion flux of iron due to a chemical potential gradient²¹⁾ (ambipolar diffusion), and can be written as

$$j_{Fe}^{diff} = -L_{FeFe} \cdot \nabla \mu_{Fe} \quad (L_{FeFe} = L_{11} + L_{12} + L_{21} + L_{22}) \quad (3)$$

where L_{FeFe} is the transport coefficient of iron. The transport coefficients are connected to the diffusion coefficient of iron, D_{Fe} , and the individual diffusion coefficients of Fe^{2+} and Fe^{3+} , D_1 and D_2 , via:

$$L_{FeFe} = \frac{D_{Fe} \cdot c_{Fe}}{RT} = \frac{D_1 \cdot c_1 + D_2 \cdot c_2}{RT} = (L_{11} + L_{12}) + (L_{21} + L_{22}) \quad (4)$$

In a chemically homogeneous crystal, $\nabla \mu_{Fe} = 0$, exposed to an external electric field, E , we have $\nabla \eta_3 = F \cdot E$ and the second term in eq.(2) is the iron drift flux, j_{Fe}^{drift} , in the electrotransport experiment. We can now define the effective charge of iron, z_{Fe}^{eff} , during its motion in the electric field via the following relation:

$$j_{Fe}^{drift} = L_{FeFe} \cdot z_{Fe}^{eff} \cdot F \cdot E \quad (5)$$

Since the iron drift flux causes a shift Δx of the tracer profile, $j_{Fe}^{drift} = v_{drift} \cdot c_{Fe} = c_{Fe} \cdot \Delta x / t_{drift}$, we can easily calculate the effective charge of iron as a function of measurable quantities:

$$z_{Fe}^{eff} = \frac{\Delta x \cdot RT \cdot f}{t_{drift} D_{Fe}^* \cdot F \cdot E} \quad (6)$$

where D_{Fe}^* is the iron tracer diffusion coefficient and f the tracer correlation factor ($D_{Fe}^* = D_{Fe} \cdot f$). In the vacancy regime of magnetite where our experiments have been performed the correlation factor is $f = 0.546$.⁷⁾

Furthermore, z_{Fe}^{eff} can be expressed in terms of the diffusion coefficients D_1 and D_2 and the transport coefficients L_{13} and L_{23} by combining the expressions for the drift fluxes in eqs. (2) and (5):

$$z_{Fe}^{eff} = \frac{D_1 \cdot c_1 \cdot z_1 + D_2 \cdot c_2 \cdot z_2}{D_1 \cdot c_1 + D_2 \cdot c_2} - \frac{L_{13} + L_{23}}{L_{FeFe}} \quad (7)$$

If we finally introduce the so-called charge of transport of iron, $\alpha_{Fe}^* = (L_{13} + L_{23}) / L_{FeFe}$, we obtain:

$$z_{Fe}^{eff} = \frac{D_1 \cdot c_1 \cdot z_1 + D_2 \cdot c_2 \cdot z_2}{D_1 \cdot c_1 + D_2 \cdot c_2} - \alpha_{Fe}^* \quad (8)$$

Thus, the effective charge of iron consists of two parts. The first part is an average of the formal charges of the ions with weighting factors $D_i c_i$ ($i = 1, 2$), while the second part is due to the cross coefficients L_{13} and L_{23} which reflect interactions between ions and electrons. In a formal analysis in ref. (22) it was shown that the effective charge (or the transport coefficients) for the ions can be determined by observing the motion of tracers of the ions.

3 Experiments

Detailed descriptions of the Chemla-type electrotransport experiments were given in ref. (18,19). The advantage of this method is that we can measure the diffusion coefficient and effective charge of ions simultaneously in

a single experimental run. Compared with former studies,^{18,19)} we applied in our study the residual activity method and the tracer sectioning method simultaneously to the analysis of the shifted diffusion profile of an Fe-isotope. In former studies, only the residual activity method was applied, from which the drift distance of the tracer profile could only be determined after corrections for self-absorption.¹⁹⁾ In the sectioning method, however, the Gaussian tracer profile is determined directly, from which the shift distance of the tracer profile can be determined more accurately.

In this study, we used two disk shaped ($\phi = 2$ mm) single crystalline Fe_3O_4 -samples²³⁾ in order to avoid any effects of grain boundary diffusion. We performed precise polishing of two samples down to 1 μm with diamond paste. Before making the crystal couple, a drop of radioactive tracer solution (^{59}Fe) which acts as a thin film tracer source was placed onto the polished surface of one crystal with a micropipet (Eppendorf) and dried carefully under an infrared lamp. At the same time we applied a small amount of Pt paste onto the surface of the other as inert markers. After applying the diffusion source, we made a diffusion couple and performed the heat treatment at 1200°C in nitrogen atmosphere (vacancy regime for magnetite). After short duration for the healing of two samples, a constant electric field is applied to the crystal couple for a prefixed time. The whole experimental setup is given in Fig.1.

After the heat treatment, we performed sample grinding with a grinding machine by which the grinding thickness could be controlled down to a few μm . We used a ground section of the sample for the tracer sectioning method and the remaining bulk sample for the residual activity method. For the detection of the γ -activity, we used a γ -ray detector (high purity Ge-detector with high energy resolution, EG & G GEM-25185P) and a multichannel analyzer. We analyzed two characteristic peaks of ^{59}Fe at 1099.25 keV and 1291.6 keV. After compiling the activity information of two energy states from each sectioning step, we could get the penetration profiles of the tracer. Further details of our experimental method can be found in ref. (24).

Fig. 1 Schematic diagram of the experimental setup. The gaussian curve shows the shift of a tracer concentration profile in the electric field.

Fig. 2 Typical residual activity profile of ^{59}Fe . Fig. 3 Typical tracer sectioning profile of ^{59}Fe .

4 Evaluation of the Diffusion Coefficient and Effective Charge

Typical activity profiles from both methods are given in Figs. 2 and 3. In the pictures, the dashed line denotes the initial position of the tracer and the solid line indicates the new centroid position of the profile after the experiment. For the tracer sectioning method we can use the thin-film solution of diffusion (see also ref. (19))

$$c_{\text{Fe}}^*(x, t_{\text{diff}}, t_{\text{drift}}) = \frac{M^*}{\sqrt{\pi D_{\text{Fe}}^* t_{\text{diff}}}} \exp \left(-\frac{(x - v_{\text{drift}} \cdot t_{\text{drift}})^2}{4 D_{\text{Fe}}^* t_{\text{diff}}} \right) \quad (9)$$

where D_{Fe}^* is the tracer diffusion coefficient, x the penetration distance, M^* the initial tracer amount per area, v_{drift} represents the tracer drift velocity, and t_{diff} and t_{drift} are the time duration of diffusion anneal and time dura-

tion for which the electric field was applied, respectively. The corresponding residual activity, A_R , is obtained by integration of the concentration profile in eq. (9) and given by:

$$A_R(x, t_{\text{diff}}, t_{\text{drift}}) = K \exp(\alpha x) \left\{ 1 - \text{erf} \left[\frac{\alpha \sqrt{D_{\text{Fe}}^* t_{\text{diff}}} + (x - v_{\text{drift}} \cdot t_{\text{drift}})}{2 \sqrt{D_{\text{Fe}}^* t_{\text{drift}}}} \right] \right\} \quad (10)$$

where α is the self absorption coefficient and K a constant.⁽¹⁹⁾ In eqs. (9) and (10), $v_{\text{drift}} t_{\text{drift}}$ is the drift distance of the tracer which is measured by the shift distance, Δx , of the diffusion profile relative to its initial position. Thus we can get the iron tracer diffusion coefficient, D_{Fe}^* , and the shift distance of the profile, Δx , from a nonlinear least squares fitting of the profiles.

5 Experimental Results and Discussion

We performed two independent experiments with different times t_{drift} in order to check the reproducibility of our results. The experimental conditions and results of the fitting are summarized in Table 1. The iron tracer diffusion coefficients, D_{Fe}^* , and the shift distances, Δx , from two different γ -peaks of ^{59}Fe , two independent analyzing methods and two independent experiments agree well within experimental error. The iron tracer diffusion coefficient is also in good agreement with the reported value.⁽²⁾ These agreements strongly indicate the proper performance of our experiments. With these fitting results, we can evaluate the effective charge of Fe using eq. (6). We find an effective charge of Fe around +2 (see Table 1) which is significantly smaller than its average formal charge 8/3.

To discuss this experimental finding we compare the results with the theoretical expression for the effective charge of Fe in eq. (8). Since the concentrations and formal charges of the ions are fixed ($c_1:c_2 = 1:2$, $z_1 = 2$, $z_2 = 3$) the effective charge depends on the diffusion coefficients of the ions, D_1 and D_2 , and the charge of transport, α_{Fe}^* . Now we can extend our consideration to three limiting cases, (i) $D_1 = D_2$, (ii) $D_1 \gg D_2$ and (iii) $D_1 < D_2$.

In the first case, the diffusion coefficients of the iron ions are the same regardless of the valence state, $D_1 = D_2$. In this case the effective charge of Fe becomes:

Table 1 Experimental conditions and results.

Experimental conditions	γ -peak pos./keV	Method	D_{Fe}^* ($\mu\text{m}^2/\text{sec}$)	Δx (μm)	$z_{\text{Fe}}^{\text{eff}}$
$\text{Log}(P(\text{O}_2)/\text{bar}) = -3.96$ $T_{\text{diff}} = 36600 \text{ sec}$ $T_{\text{drift}} = 36000 \text{ sec}$	1099.3	res.	0.98 ± 0.03	47 ± 3	1.9 ± 0.2
		sec.	0.98 ± 0.03	45 ± 3	1.8 ± 0.2
	1291.6	res.	0.98 ± 0.02	47 ± 2	1.9 ± 0.2
		sec.	0.98 ± 0.03	44 ± 3	1.8 ± 0.2
$\text{Log}(P(\text{O}_2)/\text{bar}) = -4.01$ $T_{\text{diff}} = 58500 \text{ sec}$ $T_{\text{drift}} = 57600 \text{ sec}$	1099.3	res.	0.99 ± 0.03	69 ± 4	2.1 ± 0.2
		sec.	1.02 ± 0.02	66 ± 3	1.9 ± 0.2
	1291.6	res.	0.99 ± 0.03	69 ± 4	2.1 ± 0.2
		sec.	1.02 ± 0.02	66 ± 3	1.9 ± 0.2

$$\text{case (i)} \quad z_{\text{Fe}}^{\text{eff}} = \frac{8}{3} - \alpha_{\text{Fe}}^* \quad (9)$$

Eq. (9) means that if there is no cross effect, then the effective charge of Fe is 8/3, which agrees with the average formal charge. But if there is any interference between ionic and electronic charge carriers, the effective charge becomes smaller due to α_{Fe}^* . In the other cases, the effective charge of Fe is given as

$$\text{case (ii)} \quad z_{\text{Fe}}^{\text{eff}} = 2 - \alpha_{\text{Fe}}^* \quad (10)$$

$$\text{case (iii)} \quad z_{\text{Fe}}^{\text{eff}} = 3 - \alpha_{\text{Fe}}^* \quad (11)$$

Our experimental result, $z_{\text{Fe}}^{\text{eff}} \cong 2$, can be explained by all three cases. In cases (i) and (iii) there would be an appreciable cross effect, $\alpha_{\text{Fe}}^* \cong 1.6$ and $\alpha_{\text{Fe}}^* \cong 1$, respectively. In case (ii), however, where Fe^{3+} is much less mobile than Fe^{2+} , no cross effect is necessary.

A priori we cannot decide which case is more probable to explain the observed effective charge of iron. We can only expect that among the three cases, (i) and (ii) are more probable to occur because it is known that in magnetite three-valent ions diffuse slower than di-valent ions.⁴⁾ Assuming that this behavior is also valid for Fe^{2+} and Fe^{3+} we may conclude that case (ii) is valid for magnetite. However, due to the electrode arrangement and since we could not exclude polarization at the electrode we can't neglect the possibility of underestimating the effective charge of iron. Thus further considerations and future experiments with real four point arrangement of the electrode are necessary to decide whether there is a cross effect between ions and electrons in magnetite.

6 Conclusion

Chemla-type electrotransport experiments have been performed on magnetite, Fe_3O_4 , at 1200°C and $\log(a_{\text{O}_2}) = -4$ (vacancy regime) to evaluate the effective charge of Fe. We have applied the residual activity method and the tracer sectioning method simultaneously to measure the tracer diffusion profiles. According to our results, the effective charge of Fe in magnetite is around +2 which is smaller than the average formal charge 8/3. A formal analysis of the transport problem shows that this result can be explained in two different ways: (i) there might be an interference between charge carriers which has been adopted similarly in CoO .¹⁵⁾ (ii) if the diffusivity of Fe^{3+} is much smaller than the diffusivity of Fe^{2+} no cross effect is necessary and the effective charge is identical to the formal charge of Fe^{2+} .

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