

ISOTOPE EFFECT AND CATION SELF-DIFFUSION IN METAL-DEFICIENT OXIDES (*)

W. K. CHEN

Argonne National Laboratory, Argonne, Illinois, USA

and N. L. PETERSON

Institut für theoretische und angewandte Physik der Universität Stuttgart,
Stuttgart, Germany, On leave from Argonne National Laboratory, Argonne, Illinois, USA

Résumé. — Il est admis généralement que les défauts principaux dans les oxydes déficients en métal, NiO, CoO et $\langle \text{FeO} \rangle$ sont des lacunes cationiques. Dans la formule générale M_{1-x}O , x est environ égal à 0,001-0,01 dans NiO et CoO et 0,05-0,13 dans $\langle \text{FeO} \rangle$. Des mesures antérieures, la diffusion simultanée des traceurs ^{57}Ni et ^{60}Ni dans NiO et ^{55}Co et ^{60}Co dans CoO ont donné des valeurs de $f \Delta K$ indépendantes de la température et égales à $0,61 \pm 0,02$ et $0,58 \pm 0,01$ respectivement. Ces valeurs expérimentales de $f \Delta K$ imposent que l'autodiffusion du cation dans NiO et CoO soit due à un mécanisme par lacunes isolées. La structure du défaut dans $\langle \text{FeO} \rangle$ est beaucoup plus complexe que dans NiO et CoO en raison de son large écart à la stoechiométrie. Des mesures récentes montrent que la diffusivité isotherme de ^{59}Fe est peu sensible à la valeur de x dans Fe_{1-x}O . L'effet de masse dans la diffusion simultanée de ^{52}Fe et ^{59}Fe dans $\langle \text{FeO} \rangle$ donne des valeurs de $f \Delta K$ comparables, quoiqu'un peu plus faibles, à celles obtenues dans NiO et CoO. Des effets éventuels d'agglomération de lacunes sur la diffusivité du cation dans $\langle \text{FeO} \rangle$ sont discutés.

Abstract. — The predominant point defect in metal-deficient oxides, NiO, CoO and $\langle \text{FeO} \rangle$, is generally recognized to be a cation vacancy. In a general formula M_{1-x}O , x is about 0.001, 0.01, and 0.05-0.13 for NiO, CoO, and $\langle \text{FeO} \rangle$, respectively. In previous measurements, the simultaneous diffusion of the tracers ^{57}Ni and ^{60}Ni in NiO and ^{55}Co and ^{60}Co in CoO give values of $f \Delta K$ that are independent of temperature and equal to 0.61 ± 0.02 and 0.58 ± 0.01 , respectively. These experimental values of $f \Delta K$ require that cation self-diffusion in NiO and CoO occur by a single-vacancy mechanism. The defect structure in $\langle \text{FeO} \rangle$ is much more complex than that in NiO and CoO because of its extended deviation from stoichiometry. Recent measurements show that the isothermal diffusivity of ^{59}Fe is rather insensitive to the value of x in Fe_{1-x}O . The mass effect for simultaneous diffusion of ^{52}Fe and ^{59}Fe in $\langle \text{FeO} \rangle$ gives values of $f \Delta K$ that are similar to, but somewhat smaller than, those obtained for NiO and CoO. Possible effects of vacancy clustering on cation self-diffusivity in $\langle \text{FeO} \rangle$ are discussed.

1. **Introduction.** — Unlike alkali halides, many metal oxides are stable over a range of compositions. An excess of cations or anions in an oxide creates non-stoichiometric point defects in the crystal lattice. Thus the concentration of lattice defects in an oxide, has, in many cases, been controlled by equilibrating the oxide to the partial pressure of a constituent. From the dependence of the diffusion coefficient on the ambient partial pressure of one of the constituents (usually oxygen), a model can be formulated. The model, in turn, can be used to deduce the defect structure in the lattice and, in turn, the diffusion mechanism.

Another approach to the study of the diffusion mechanism is the measurement of the isotopic mass effect on diffusion. This approach has been used successfully for diffusion in metals and some alkali

halides [1] but has only recently been attempted in metal oxides [2]-[5]. The present paper reports a recent study of the isotope effect for cation diffusion in $\langle \text{FeO} \rangle$. The results will be discussed in conjunction with those previously obtained in CoO and NiO. The oxides, NiO, CoO and $\langle \text{FeO} \rangle$, are cation-deficient oxides that exhibit p-type semiconduction at high temperatures in a proper oxygen partial pressure. In a general formula M_{1-x}O , the value of x is about 0.001, 0.01 and 0.05-0.13 for NiO, CoO and $\langle \text{FeO} \rangle$, respectively. Previous studies have considered the dominant non-stoichiometric defect in these oxides to be a cation vacancy. The crystal structure of these oxides is of the NaCl type.

2. **Correlation factors and isotopic mass effect.** — For random atomic jumps in a cubic crystal, the diffusion coefficient D is given by

$$D = \frac{1}{6} \Gamma r^2, \quad (1)$$

(*) Work performed under the auspices of the US Atomic Energy Commission.

where Γ is the atomic jump frequency, and r is the jump distance. If the jump direction of a given atom depends on the direction of a previous jump, then

$$D = \frac{1}{6} \Gamma r^2 f, \quad (2)$$

where the correlation factor f takes into account the correlation between the directions of successive atomic jumps. For self-diffusion in a cubic lattice, f is a numerical factor determined only by the crystal lattice and the diffusion mechanism, and it has been calculated for several diffusion mechanisms in a number of crystal structures [6], [7]. Thus, direct measurement of f may enable a unique determination of the mechanism of diffusion.

For tracer diffusion in solids, f can be obtained from an accurate measurement of the relative diffusion rates of two isotopes of the same element. The isotope effect in diffusion has been expressed by Schoen [8], and later by Tharmalingam and Lidiard [9], as

$$\frac{(1 - D_\beta/D_\alpha)}{(1 - \Gamma_\beta/\Gamma_\alpha)} = f, \quad (3)$$

where the subscripts α and β pertain to the isotopes with masses m_α and m_β , respectively. In those cases in which only one atom undergoes an atomic displacement during the jump process and its jumping motion is not coupled with the surrounding atoms, the ratio of the jump frequencies may be approximated by the simple relation

$$\frac{\Gamma_\beta}{\Gamma_\alpha} = \left(\frac{m_\alpha}{m_\beta}\right)^{1/2}. \quad (4)$$

However, if the motion of the jumping atom is coupled with the surrounding atoms, the ratio of the jump frequencies, as given by Mullen [10], is

$$1 - \frac{\Gamma_\beta}{\Gamma_\alpha} = \Delta K \left[1 - \left(\frac{m_\alpha}{m_\beta}\right)^{1/2} \right]. \quad (5)$$

Here ΔK is the fraction of the total translational kinetic energy at the saddle point, associated with motion in the direction of the diffusional jump, that belongs to the jumping atom. From eq. (3) and (5), the general expression for the isotopic mass effect in diffusion becomes

$$\frac{1 - (D_\beta/D_\alpha)}{1 - (m_\alpha/m_\beta)^{1/2}} = f \Delta K. \quad (6)$$

For diffusion mechanism that involve more than one atom in the jump process, Vineyard [11] has shown that the quantity $(m_\alpha/m_\beta)^{1/2}$ in eq. (6) should be replaced by

$$\left[\frac{(n-1)m + m_\alpha}{(n-1)m + m_\beta} \right]^{1/2}, \quad (7)$$

where n is the number of atoms participating in the jump process, and m is the average mass of the nontracer atoms.

From the above expressions, one can determine $f \Delta K$ by measuring the relative diffusion coefficients of two isotopes of the same element. The measured value of $f \Delta K$ and the allowed values of f and ΔK may permit an unambiguous determination of the diffusion mechanism and thus provide a unique value of ΔK .

3. Experimental. — All experiments on $\langle \text{FeO} \rangle$ were performed on high-purity single crystals. The crystals were grown by the Verneuil process in a controlled oxygen partial pressure. The ^{59}Fe isotope was purchased from New England Nuclear Corporation, Boston, Mass., in the form of FeCl_3 in 0.5 N HCl. The ^{52}Fe isotope was produced by 36 MeV ^3He bombardment of ^{52}Cr by the nuclear reaction $^{52}\text{Cr}(^3\text{He}, 3n)^{52}\text{Fe}$ in the Argonne National Laboratory cyclotron. The ^{52}Fe isotope was chemically separated from the chromium target by ion exchange. The final product was in the form of FeCl_3 in 0.5 N HCl.

The diffusion samples of approximately 10 by 10 by 5 mm were cut from crystal boules and were ground parallel and flat. The finished samples were preannealed in a given oxygen partial pressure at the diffusion temperature. The preannealing time was at least twice as long as the diffusion annealing time to ensure that the oxide samples were in thermodynamic equilibrium at a given temperature and oxygen partial pressure. The radioactive tracers were deposited on a sample surface by drying a drop of a solution containing either ^{59}Fe or a mixture of ^{52}Fe and ^{59}Fe in a sulfate form.

The samples were diffusion annealed in a given oxygen partial pressure at a given temperature. A partial pressure of oxygen was obtained from a CO_2 -CO gas mixture and was monitored with a gas partitioner.

After the diffusion anneal, the edges of the samples were ground to eliminate edge effects. The penetration of radioactive tracers was determined by a serial sectioning technique. The radioactivity in each section was counted using a well-type NaI(Tl) crystal scintillation counter. For these experimental boundary conditions, the distribution of specific activity C of a radioactive tracer may be expressed in the usual exponential form [12]

$$C = M/(\pi Dt)^{1/2} \exp(-X^2/4Dt), \quad (8)$$

where X is the penetration distance, D is the diffusion coefficient, M is the activity per unit area deposited at $t = 0$ in the plane $X = 0$, and t is the diffusion annealing time.

For the isotope-effect measurements, the ^{52}Fe and ^{59}Fe isotopes were diffused simultaneously in the crystal. The ratio of specific activities (C_{52}/C_{59}) as a function of penetration (i. e., C_{59}) can be shown from eq. (8) to be

$$\ln(C_{52}/C_{59}) = \text{const.} - [1 - (D_{59}/D_{52})] \ln C_{59}, \quad (9)$$

where the subscripts 52 and 59 pertain to ^{52}Fe and ^{59}Fe . Thus, a plot of $\ln(C_{52}/C_{59})$ versus $\ln C_{59}$ permits a determination of the relative diffusion coefficient $1 - (D_{59}/D_{52})$. In this manner, errors arising from the diffusion annealing time, temperature, stoichiometric composition, and sectioning are eliminated. The ratio of the specific activities (C_{52}/C_{59}) was determined at various positions in the sample to within 0.1% by a half-life separation of the γ activities of ^{52}Fe (half-life = 8.285 ± 0.009 h) and ^{59}Fe (half-life = 45 days).

4. Results and discussions. — Penetration plots for a typical run from each temperature in this experiment are presented in figure 1. Since all penetration

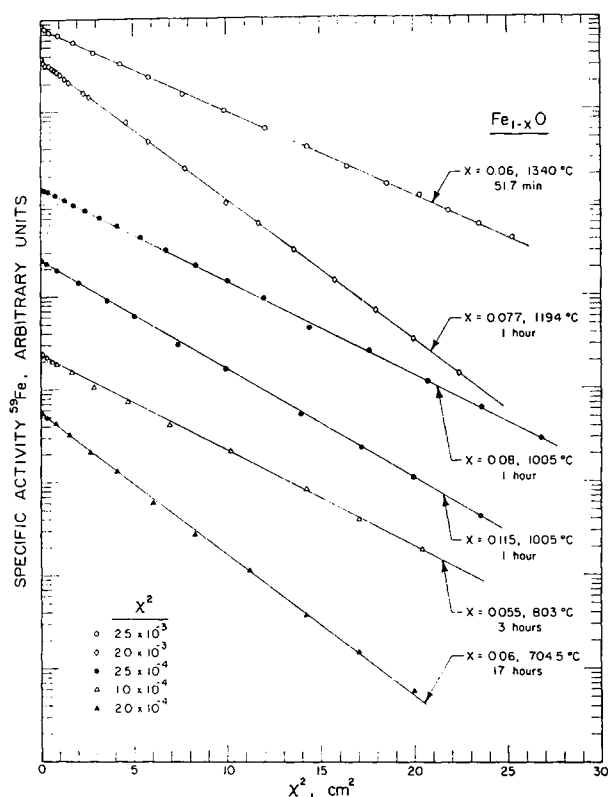


FIG. 1. — Log of specific activity of ^{59}Fe vs penetration distance squared for the diffusion of ^{59}Fe in Fe_{1-x}O .

plots are straight lines over two to three decades in activity, the calculated diffusion coefficients represent bulk diffusion.

The temperature dependence of the diffusion coefficient for $\text{Fe}_{0.94}\text{O}$ in the temperature range 700–1340 °C can be expressed as

$$D = (8.6 \pm 0.5) \times 10^{-3} \exp\left(-\frac{29350 \pm 300}{RT}\right) \text{cm}^2/\text{s}, \quad (10)$$

which is in fair agreement with that previously obtained by Himmel *et al.* [13] for $\text{Fe}_{0.907}\text{O}$ between 700 and 1000 °C.

Figure 2 illustrates the diffusivity of ^{59}Fe in Fe_{1-x}O as a function of deviation from stoichiometry at given temperatures. In contrast to the previously reported results [2], [13]–[14], figure 2 shows that the

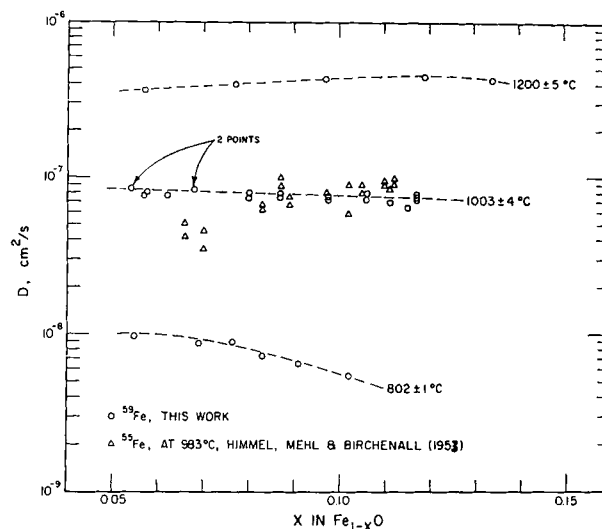


FIG. 2. — Diffusion coefficient of ^{59}Fe in Fe_{1-x}O as a function of deviation from stoichiometry. Plotted as $\log D$ vs X .

diffusivity decreases with an increase in x at 802 °C, is rather insensitive to any change in x at 1003 °C, and increases slightly with an increase in x at 1200 °C. This general trend was supported by a recent study of the Mössbauer line broadening for ^{57}Fe in Fe_{1-x}O by Anand and Mullen [15].

Figure 3 presents the plots of $\ln(C_{52}/C_{59})$ versus

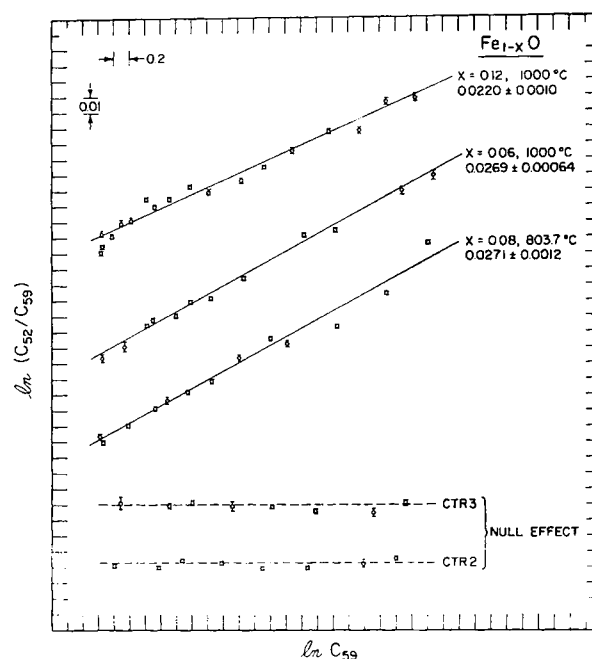


FIG. 3. — Plots of $\ln(C_{52}/C_{59})$ vs $\ln C_{59}$ for the cation self-diffusion in Fe_{1-x}O ; $\ln(C_{52}/C_{59})$ increases from the bottom to the top, and $\ln C_{59}$ decreases from the left to the right.

TABLE I
Isotope effect for cation self-diffusion in non-stoichiometric oxides

Oxide	x	Temperature °C	$f\Delta K$	Isotopes
Ni_{1-x}O	< 0.001	1 200-1 680	0.613 ± 0.021	$^{57}\text{Ni}/^{66}\text{Ni}$
Co_{1-x}O	< 0.01	1 080-1 410	0.582 ± 0.009	$^{55}\text{Co}/^{60}\text{Co}$
Fe_{1-x}O	0.057	1 000	0.440 ± 0.010	$^{52}\text{Fe}/^{59}\text{Fe}$
	0.111	1 000	0.360 ± 0.016	
	0.077	803.7	0.443 ± 0.019	

In C_{59} for the simultaneous diffusion of ^{52}Fe and ^{59}Fe in Fe_{1-x}O . The values of $f\Delta K$ obtained from these measurements are listed in table I. In previous studies [3], [4], measurements of the simultaneous diffusion of ^{57}Ni and ^{66}Ni in NiO and ^{55}Co and ^{60}Co in CoO gave values of $f\Delta K$ (Table I) that are independent of temperature. The values of $f\Delta K$ for NiO and CoO are consistent with cation self-diffusion by a single-vacancy mechanism (i. e., $f = 0.78$) with $\Delta K = 0.78$ and 0.75 , respectively, for NiO and CoO.

In view of the large defect concentration (i. e., $x \approx 0.05 - 0.13$ in Fe_{1-x}O), a simple linear relationship between the cation diffusivity D and the deviation from stoichiometry that exists in NiO and CoO would not be anticipated at all temperatures in Fe_{1-x}O . Simple calculations show that the random probabilities of a vacancy with none, one, or two other vacancies as nearest neighbors are 0.54, 0.24 and 0.11, respectively, in a face-centred-cubic (fcc) lattice with a vacancy fraction of 0.05. From neutron diffraction studies, Roth [16] suggests a model of Fe_{1-x}O that contains defect complexes consisting of two cation vacancies in octahedral sites and an interstitial cation in a tetrahedral site of the fcc oxygen sublattice. Further studies by Koch and Cohen [17] of superstructure diffraction peaks from Fe_{1-x}O suggest the existence of periodically spaced clusters of vacancies in quenched specimens. Thus, a simple defect model that does not include defect clustering would appear to be inappropriate for this oxide.

Although a quantitative understanding of the diffu-

sion results is not available at this time, a plausible interpretation may be developed in terms of defect clustering. The interpretation of the data in figure 2 may be that iron ions migrate by free mobile vacancies (or divacancies) which coexist with higher order defect clusters. As the deviation from stoichiometry is increased, a larger number of the vacancies are in the form of immobile defect clusters. Thus the diffusion coefficient will decrease with an increase in non-stoichiometric defects at lower temperatures, but may increase with increasing defect concentration at higher temperatures where the defect binding energy is less important relative to kT . The smaller value of $f\Delta K$ in Fe_{1-x}O relative to NiO and CoO and the decrease in $f\Delta K$ with increasing defect concentration at 1 000 °C suggest that the correlation factor may decrease with increasing defect concentration. This suggests that divacancies (and possibly trivacancies) are contributing to diffusion in Fe_{1-x}O . (The term ΔK may be the same in Fe_{1-x}O as in NiO and CoO because the saddle point atoms are oxygen atoms on a complete sublattice in all three materials.) The linear Arrhenius plot for $\text{Fe}_{0.94}\text{O}$ requires a proper balance between binding energies and migration energies of the various vacancy groups. If the migration energy for the divacancies is smaller than the migration energy for the monovacancies in Fe_{1-x}O as in fcc metals, the divacancy contribution will be more important at low temperatures than at high temperatures in a material containing a constant number of defects like $\text{Fe}_{0.94}\text{O}$.

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DISCUSSION

R. A. SWALIN. — It has been postulated on the basis of EMF studies that three subfields exist in the Fe_{1-x}O phase. These presumably are not discrete phases (if they exist at all) but represent regions of different types of defect structures. Did you examine your diffusion anomalies in the context of these presumed regions? It would seem to me that careful diffusion research of the type you have done could be useful in proving or disproving whether these regions exist in Fe_{1-x}O .

N. L. PETERSON. — The curves of the diffusion coefficients as a function of composition shown in figure 2 traverse more than one of the proposed subfields in the Fe_{1-x}O phase. We see no abrupt change in slope at our curves (Fig. 2).

F. BÉNIÈRE. — How are calculated the error bars

shown on the isotope effect plots? Are they smaller than the statistical fluctuations?

N. L. PETERSON. — The error bars on the data points in figure 3 are simply one standard deviation of the least squares error in the fitting of the counting data from a given section to the equation:

$$C_T = C_\alpha \exp(-\lambda_\alpha t) + C_\beta \exp(-\lambda_\beta t).$$

In this equation C_T is the total activity of the section as a function of time t from some arbitrary time zero. C_α and C_β are the concentrations of isotopes α and β at time zero, and λ_α and λ_β are the decay constants of isotopes α and β . The error bars are somewhat larger than the 0.1 % error resulting from counting statistics. The possible systematic errors resulting from slight changes in counting geometry from one section to the next are not included in the error bars for a given section.