ISOTOPE EFFECT FOR CATION DIFFUSION IN CoO

by

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Isotope Effect for Cation Diffusion in CoO*

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Abstract

The simultaneous diffusion of ^{55}Co and ^{60}Co has been measured in CoO as a function of equilibrium oxygen pressure in the range $10^{-9} < p_{\text{O}_2} < 1$ atm at 1200°C. The slope of the $\log D_{\text{Co}}^*$ vs $\log p_{\text{O}_2}$ plot changes from a value of about 1/4 at high p_{O_2} to about 1/5 at low p_{O_2} in agreement with the extensive measurements of Dieckmann. The isotope effect is independent of p_{O_2} , which suggests that diffusion by defect clusters, interstitial Co ions and impurity-induced defects is not important in the present measurements. Conductivity, diffusion, stoichiometry, and isotope-effect results are consistent with diffusion by neutral, singly charged, and doubly charged vacancies; the relative contributions from the various vacancies varies with p_{O_2} .

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1. Introduction. - Cobalt monoxide is an off-stoichiometric, NaCl-structured oxide exhibiting p-type semiconduction at high temperatures with oxygen pressures near 1 atm. The extensive measurements of the deviation from stoichiometry δ , as a function of p_{O_2} [1-6] show an excess of oxygen ions relative to cobalt ions. The rapid cation tracer diffusion [1,7-9] relative to the anion tracer diffusion [10] ($D_{Co}^*/D_O^* \sim 5 \times 10^4$ at 1200°C) strongly suggests that the excess oxygen ions are accommodated by the formation of cation vacancies rather than anion interstitials.

It is apparent from the above that the principal point defects to be considered in CoO are cation vacancies and electron holes. Various charges are possible for the cation vacancies. The formation of neutral vacancies can be expressed as follows:

Singly charged vacancies can be formed by the dissociation of neutral vacancies:

Further dissociation of electron holes yields doubly charged vacancies:

If only one type of cation vacancy is present in CoO, and the defect concentration is sufficiently low that defect-defect interactions can be neglected, then the application of the law of mass action to eqs. (1) - (3) allows one to relate the defect concentration to the oxygen partial pressure:

$$[V_{Co}^x] \propto (p_{O_2})^{1/2} \quad (4)$$

$$[V_{Co}'] \propto (p_{O_2})^{1/4} \quad (5)$$

$$[V_{Co}''] \propto (p_{O_2})^{1/6} \quad (6)$$

The bracketed quantities are the fraction of point-defect species per mole of cation lattice sites. If the mobility of the various cation-vacancy types is the same and independent of p_{O_2} , then a measurement of the cation tracer diffusivity as a function of p_{O_2} may be related to the deviation from stoichiometry δ and provide a determination of the dominant vacancy type from its p_{O_2} dependence.

Most measurements of δ [1-3,5,6], electrical conductivity [3,11-13] and cation tracer diffusion [1,7.8] are concentrated at high p_{O_2} values and may be fitted to eq. (5), indicating a dominance of singly charged cation vacancies. Several measurements of δ [4], electrical conductivity [2,5,14], and cation tracer diffusion [9] cover a large range of p_{O_2} . These measurements show a curved plot vs $\log p_{O_2}$, indicating that more than one type of defect is present in CoO.

Dieckmann [9] has made an extensive analysis of the literature data on the p_{O_2} dependence of δ and electrical conductivity, and of his own results on cation tracer diffusion. In addition to neutral, singly charged and doubly charged vacancies [eqs. (1) - (3)], he also included Frenkel point-defect equilibrium and Schottky point-defect equilibrium in his analysis. Dieckmann was able to obtain an acceptable fit of this simple five-defect "ideal solution" model to the existing data. He concludes that the concentrations of cobalt interstitials and oxygen vacancies are negligible; the dominant defects are vacancies on the cation sublattice and electron holes, and the vacancies can be formally treated as neutral, singly, or doubly charged. The curvature in the plots of $\log D_{Co}^*$ vs $\log p_{O_2}$ (and similar plots for δ and electrical conductivity as a function of p_{O_2}) can be quantitatively interpreted in terms of a change in relative contributions of differently charged vacancies with varying p_{O_2} as shown by Dieckmann [9]. Other possible interpretations of the data include (a) impurity-induced (extrinsic) defects at low p_{O_2} and (b) defect clustering at high p_{O_2} .

One measurement that may distinguish between the possible interpretations of the data is the p_{O_2} dependence of the correlations factor f for cation diffusion: (a) If the interpretation of Dieckmann is correct, f for cation diffusion should be independent of p_{O_2} (if the vacancies do not interact with each other). (b) If there is a small concentration of trivalent impurity ions in the CoO, these ions would introduce extrinsic vacancies that would make a larger relative contribution at low p_{O_2} than at high p_{O_2} . Cobalt diffusion by bound impurity-vacancy pairs will occur with a much smaller f than for cation diffusion by free vacancies. Thus, f for cation diffusion would decrease with decreasing p_{O_2} . (c) Defect-clustering effects may be important at high p_{O_2} where the total vacancy concentration may reach 1%. As an example, calculations by Catlow et al. [15] for MnO show that at $\delta = 10^{-4}$ (corresponding to low p_{O_2} in CoO), all the defects are isolated vacancies; at $\delta = 10^{-2}$ (corresponding to high p_{O_2} in CoO), 87% of the vacancies are in clusters of four vacancies or larger. If the calculations for MnO are at all relevant for CoO, defect clustering may be expected to play a major role in cobalt monoxide. Measurements on $Fe_{1-\delta}O$ suggest that f decreases when defect clustering becomes important [16]. Thus one expects f to decrease with increasing p_{O_2} if defect clustering is important in CoO.

In this paper we present results on the p_{O_2} dependence of f using isotope-effect techniques in order to select the appropriate interpretation of the diffusion and conductivity outlined in the above paragraph. Values of D_{Co}^* as a function of p_{O_2} are a by-product of the isotope-effect experiments and may be used to check the recent values of Dieckmann.

For tracer diffusion in solids, information concerning the value of f may be obtained from the relative diffusion rates of two isotopes of the same element [17]. The general expression for the isotopic mass effect in diffusion is [18]

$$E \equiv \left(\frac{D_\alpha}{D_\beta} - 1 \right) / \left[\left(\frac{m_\beta}{m_\alpha} \right)^{1/2} - 1 \right] = f\Delta K, \quad (7)$$

where the subscripts α and β pertain to isotopes with masses m_α and m_β , respectively. The term 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. The measured value of E and the allowed values of f and ΔK may permit an unambiguous determination of the diffusion mechanism. Although ΔK may have different values for different mechanisms, ΔK is thought to be independent of p_{O_2} for a given mechanism at constant temperature.

2. Experimental Results and Discussion - The tracer-sectioning technique was employed for the measurements of ^{60}Co diffusion in CoO single crystals. The various values of p_{O_2} were established by a CO_2 - CO or Ar - O_2 gas mixture or pure O_2 flowing through the furnace. The samples were diffusion annealed at 1200°C and at the same p_{O_2} as was used for an extensive preanneal. For the isotope-effect measurements, ^{55}Co and ^{60}Co were diffused simultaneously in the CoO crystals. The ratio of the specific activities of the two isotopes, necessary for the determination of $(D_\alpha/D_\beta)-1$, was determined at various positions in the sample to within 0.1% by a half-life separation of the γ activity of ^{55}Co and ^{60}Co . Details of the experimental technique may be found in Ref. 7.

Diffusion and isotope-effect measurements were made at six values of p_{O_2} at 1200°C . The values of $\log D_{\text{Co}}^*$ are plotted vs $\log p_{O_2}$ in Fig. 1; the earlier results of Dieckmann [9] and the present authors [7] are also shown. The solid line is a result of Dieckmann's empirical fit of the defect model to the nonstoichiometric data, the electrical conductivity data and his diffusion data [9]. The present results are in acceptable agreement with Dieckmann's empirical model. Lines with a slope of $1/4$ and $1/6$, corresponding to diffusion by singly ionized and doubly ionized vacancies [eqs (5) and (6)], respectively, are also shown.

The values of $f\Delta K$ are also plotted vs $\log p_{O_2}$ in Fig. 1. A value of $f\Delta K = 0.58$ (within 3%), independent of temperature and oxygen partial pressure, is probably the best value for CoO. This value of $f\Delta K$ is consistent with diffusion by noninteracting vacancies and $\Delta K = 0.75$ as previously discussed [7].

Of the four possible causes of curvature in the $\log D_{Co}^*$ vs $\log p_{O_2}$ plot discussed in the Introduction, only the change in relative contribution of differently charged vacancies with varying p_{O_2} is consistent with the present, p_{O_2} -independent value of $f\Delta K$. The other possible causes of curvature are expected to produce a p_{O_2} -dependent value of $f\Delta K$ that would be observable within the present experimental error. As an example, if impurity-induced (extrinsic) defects or interstitials at low p_{O_2} are responsible for the curvature in the $\log D_{Co}^*$ vs $\log p_{O_2}$ plot, we can estimate the corresponding p_{O_2} dependence of $f\Delta K$ on the assumption that diffusion at $p_{O_2} = 1$ atm is entirely due to singly charged unassociated vacancies. We may assume that a 15% change in E with p_{O_2} is easily detected. The curvature in the $\log D_{Co}^*$ vs $\log p_{O_2}$ plot then requires that $0.65 > E_{ext} > 0.45$ for the extrinsic or interstitial defects in order for the required p_{O_2} dependence of E to go undetected. However, E_{ext} would be expected to be less than $E_{int}/2$ ($E_{int} = 0.55$, the value at high p_{O_2}) for a dumbbell interstitial [19], an interstitialcy [20], or an impurity-vacancy pair [21] mechanism or near unity for a freely migrating interstitial [22], none of which are within the range of 0.45 to 0.65 that would be consistent with the experimental observations. More qualitative arguments suggest that defect clustering, to the extent suggested by theory for MnO [15], is also inconsistent with the observed p_{O_2} dependence of E .

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Fig. 1. - The value of D_{Co}^* and $f\Delta K$ as a function of the oxygen partial pressure for cation self-diffusion in CoO at $1200^\circ C$. The results of Dieckmann [9] and Chen, Peterson and Reeves [7] are also shown.

Fig. 1.