

# Cation Self-Diffusion and Impurity Diffusion of Mn and Zn in CoO: (I) A Comparison of the Residual Activity and the Tracer Sectioning Method

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Self diffusion coefficients of  $^{57}\text{Co}$  and impurity diffusion coefficients of  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$  in single crystalline CoO have been measured by applying different radioactive isotopes simultaneously. To compare the residual activity method and the tracer sectioning method we analyzed our tracer diffusion experiments by using both methods simultaneously. According to our experimental results, the diffusion coefficients obtained from both methods are identical within experimental error, demonstrating the reliability of our experimental procedures. The diffusion coefficients of all the isotopes obtained during these test experiments for the methodology are similar in magnitude and show similar dependences on oxygen partial pressure. These first observations indicate that impurity diffusion of Mn and Zn occur via a vacancy mechanism as known for self diffusion of cobalt.

**Key words :** Radioactive Tracer diffusion, Tracer Sectioning Method, Residual Activity Method, Self Diffusion, Impurity Diffusion

## I. Introduction

There have been many studies<sup>1-12)</sup> of the defect structure and transport properties in CoO, i.e. on the types, concentrations and mobilities of defects, e.g. by analyzing self- and impurity diffusion in this oxide. Due to this knowledge, CoO has often been used<sup>13-21)</sup> as a model system to verify theoretical concepts for the transport properties of transition metal oxides. Nevertheless, still many unsolved problems remain in this system, especially related with the defect interactions. Thus pure or doped CoO is still being used as one main system for experimental and theoretical studies.<sup>13-21)</sup> Many experimental methods have been developed and used to characterize the transport properties of materials<sup>1-12, 13-21)</sup> up to now. Among these methods, the tracer diffusion technique with radioactive tracers is known<sup>10, 20, 21)</sup> as a very useful one to investigate the role of impurity ions in the host matrix. This is possible because the high specific activity of radioactive tracers enables us to perform diffusion experiments at very low concentrations of diffusing species which do not disturb the intrinsic defect nature of the matrix. Two methods are known to analyze a tracer diffusion experiment, the tracer sectioning method and the residual activity method. In the tracer sectioning method the activity of thin slices which are ground off the sample are counted yielding directly the tracer penetration profile. In the residual activity method the activity of the remaining sample (after grind-

ing off a slice) is counted from which the penetration profile can be obtained by a derivation with respect to position. In the former method very small activities have to be counted while in the latter method counting is no problem due to the high residual activities, but corrections for self absorption and geometrical effects during counting are necessary. Normally, both methods have not been used simultaneously and the results have not been cross-checked. Therefore we focus in this paper on a comparison of both methods by applying both of them simultaneously to study self and impurity diffusion in CoO.  $^{57}\text{Co}$ ,  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$  (Du Pont) all of which are  $\gamma$  emitters were selected for the self- and impurity diffusion study respectively. They are representatives of the host cation (Co), an aliovalent impurity (Mn) and a homovalent impurity (Zn) with a known tetrahedral site preference.

## II. Experimental Setup

To count the activities in both the tracer sectioning and the residual activity method a very sensitive radiation detecting system (EG & G GEM-25185P) was used with a high purity germanium single crystal cooled by liquid nitrogen. Due to its high atomic valence and large cross sectional area for photon absorption<sup>22)</sup> germanium is the proper material for detecting gamma radiation. The schematic diagram of the whole detecting system is given in Fig. 1.

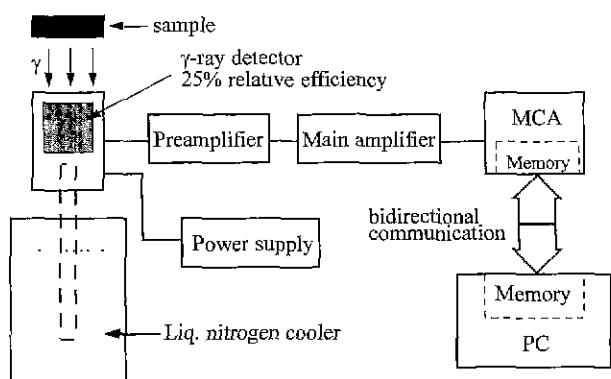


Fig. 1. Schematic diagram of the experimental setup for radiation detection.

For the heat treatment of the samples, a high temperature electric furnace was used which can be heated up to 1500°C by a spiral type SiC-heating element. The temperature of the furnace is controlled by a multistep programmable controller (Eurotherm 902P). A closed water cooling system for the furnace was used in order to ensure the safety against radioactive contamination. The oxygen partial pressure in the furnace was controlled by mixing air and N<sub>2</sub> with high accuracy gas flowmeters (Matheson Co.). The oxygen partial pressure was measured with a concentration cell type oxygen sensor (YSZ). To analyze the penetration profiles of the diffusing tracer ions very accurately, we designed a special sample-grinding system by which the grinding thickness could be controlled down to a few μm.

### III. Experimental Procedure

In order to avoid grain boundary diffusion and to obtain real bulk diffusion coefficients we used single crystalline samples of CoO. First we performed a precise grinding of the sample (6×6 mm in cross sectional area) with a diamond wheel and then polished both sides of the sample down to 1 μm with diamond paste. We could get very flat and parallel surfaces with a roughness less than 1 μm. In order to annihilate any residual stress in the samples which might be formed during sample preparation and to establish the equilibrium defect structure, the samples were pre-equilibrated under the same experimental conditions used later in the tracer diffusion experiments. The pre-equilibration time was at least double the time of the diffusion time in order to give enough time for the sample to be equilibrated. After heat treatment, we checked the flatness of the sample surfaces again. Then the thin film tracer source was applied by placing drops of solution containing the radioactive tracer onto one surface of the sample and careful drying. In this way, we applied three isotopes, <sup>57</sup>Co, <sup>54</sup>Mn and <sup>65</sup>Zn, onto one sample at the same time. The initial thickness of the samples was around 1.5-2.0 mm and the initial ac-

tivities of the sources were 2.62 μCi (<sup>57</sup>Co), 4.77 μCi (<sup>54</sup>Mn), 3.97 μCi (<sup>65</sup>Zn). We estimated the necessary initial activity of each isotope by considering the sample thickness and a presumed value of the diffusion coefficient. After applying the diffusion source, we performed a diffusion anneal under pre-determined experimental conditions. We chose 1100°C as diffusion temperature and performed the experiments at three different oxygen partial pressures (P<sub>O<sub>2</sub></sub>=0.21, 1.4 · 10<sup>-2</sup>, 2.2 · 10<sup>-4</sup> bar). The diffusion time was fixed to obtain a diffusion length around 500 μm and the heating and cooling rates were set as high as possible in order to prohibit any disturbance of the diffusion profile during temperature change.

After the diffusion anneal, we attached the sample to a glass plate which can be installed directly to the sample holder of the grinding machine. We normally kept the thickness of one ground section around 10 μm through the whole sectioning procedure. For sample grinding we used SiC grinding paper (Carbimet, Buehler Co., 600 grit). After each sectioning step, we cleaned out the sample with methyl alcohol and collected all the remaining powder on the sample surface with plastic tape. We used all products including grinding paper, plastic tape and so on for detection by the tracer sectioning method and used the remaining bulk sample for the residual activity method. The contribution of each isotope to the measured activity can be separated by measuring the γ-spectrum with the γ-ray detector and the multichannel analyser. We analysed two characteristic peaks (122.06, 136.48 keV) for <sup>57</sup>Co, one peak (834.83 keV) for <sup>54</sup>Mn and one peak (1115.52 keV) for <sup>65</sup>Zn, respectively.

Counting was performed till the net number of counts would be at least 100000 in order to reduce the counting error below 0.3%. The duration for each detection was different with respect to the sectioning technique and the position of the section in the sample. As expected due to the high counting rate, the necessary time for the residual activity method was shorter than for the tracer sectioning method. After compiling all the results from each sectioning step, we could get the penetration profile of each tracer.

### IV. Experimental Results and Discussion

Typical examples of diffusion profiles from the tracer sectioning method and the residual activity method are given in Figs. 2 and 3. To extract the diffusion coefficients from the penetration profiles normal mathematical fitting procedures were used: In the case of the tracer sectioning method we could use the infinite thin film solution of diffusion (Eq.1)

$$c(x, t) = \frac{M^*}{\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right) \quad (1)$$

where D\* is the tracer diffusion coefficient, x the pene-

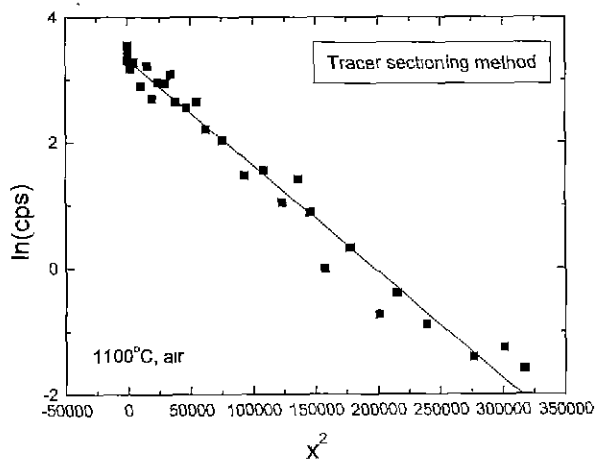


Fig. 2.  $^{57}\text{Co}$  tracer diffusion profile from the tracer sectioning method.

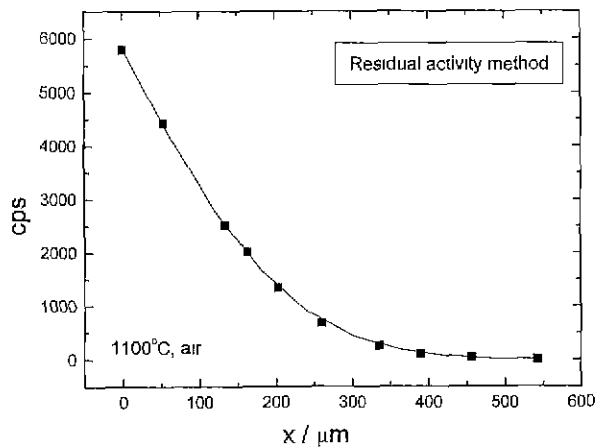


Fig. 3.  $^{57}\text{Co}$  tracer diffusion profile from the residual activity method.

tration distance,  $M^*$  the initial tracer amount per area and  $t$  the time of the diffusion anneal. As one can see in Eq.1, the infinite thin film solution for the tracer sectioning method has a normal Gaussian functional form without any correction factor, i.e. a plot  $\ln(c)$  vs.  $x^2$  yields a straight line (see Fig.2) the slope of which gives the diffusion coefficient  $D^*$ .

However, the residual activity profile which normally has an error functional form (integral of the Gaussian from the sectioning method) must be corrected by two

correction factors, a geometrical correction factor ( $\beta$ ) and the self absorption coefficient ( $\alpha$ ), both of which should be determined before the main diffusion experiment. As a result the residual activity can be written as<sup>(2)</sup> ( $K$  is a constant)

$$A_R(x) = K \exp(\alpha x) \left\{ 1 - \operatorname{erf} \left[ (\beta + \alpha) \sqrt{D^* t} + \frac{x}{2\sqrt{D^* t}} \right] \right\} \quad (2)$$

Now, the tracer diffusion coefficient must be calculated by a non-linear least square fit of Eq.(2) to the experimental data (see Fig.3).

The results for the diffusion coefficients, the self diffusion coefficient of  $^{57}\text{Co}$  and the impurity diffusion coefficients of  $^{51}\text{Mn}$  and  $^{65}\text{Zn}$  from both the residual activity method and the tracer sectioning method are summarized in Tables 1-3. The results for  $D_{\text{Co}}$  and  $D_{\text{Mn}}$  were obtained directly from the diffusion profiles without any correction for the background activity. But, in the case of Zn due to its high volatility, subtraction of the background activity was needed in the residual activity method. The dependence of each diffusion coefficient on the oxygen partial pressure is shown in Figs. 4-6. We plotted the results from both the residual activity method and the tracer sectioning method in the same figure. The results from the two independent methods agree well within experimental error, demonstrating the reliability of our experimental methods. Such a good coincidence of the results from both methods is very important because the concurrent trial of both methods at the same time is quite unusual in tracer diffusion studies.

According to the results, the diffusion coefficients of the aliovalent impurity cation Mn are similar in magnitude with the host cation Co. But the homovalent impurity cation Zn has slightly larger diffusion coefficients than the host cation Co. The diffusion coefficients of Co and Mn show a similar oxygen partial pressure dependence with a slope 1/4 (as this is well known for  $\text{Co}^{2+}$ ). This means that the impurity Mn moves also by a normal vacancy mechanism. On the other hand, the diffusion coefficient of Zn shows a slightly weaker dependence on  $\log P_{\text{O}_2}$ , but still with a positive slope. This might be an indication for an additional diffusion mechanism. However, more data are necessary to confirm this result and to obtain a detailed picture about

Table 1.  $D_{\text{Co}}^*$  ( $\text{cm}^2\text{sec}^{-1}$ ) in CoO at 1100°C

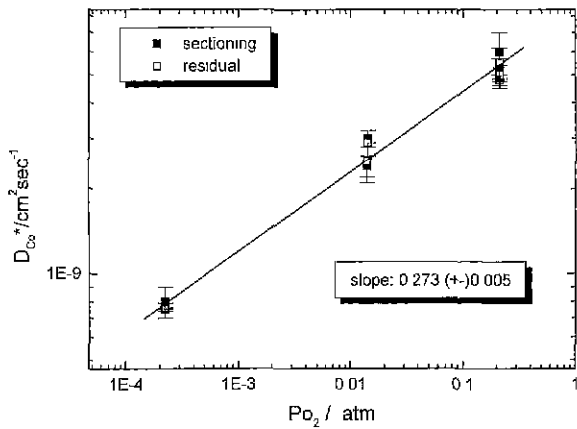
| $P_{\text{O}_2}/\text{atm}$ | Sectioning<br>(122.06 keV)      | Residual activity<br>(122.06 keV) | Sectioning<br>(136.48 keV)     | Residual activity<br>(136.48 keV) |
|-----------------------------|---------------------------------|-----------------------------------|--------------------------------|-----------------------------------|
| 0.21                        | $(4.9 \pm 0.4) \times 10^{-11}$ | $(4.80 \pm 0.06) \times 10^{-9}$  |                                |                                   |
| 0.21                        | $(5.1 \pm 0.6) \times 10^{-9}$  | $(5.0 \pm 0.4) \times 10^{-9}$    | $(6 \pm 1) \times 10^{-9}$     | $(5.5 \pm 0.7) \times 10^{-9}$    |
| $1.4 \times 10^{-2}$        | $(3.0 \pm 0.2) \times 10^{-9}$  | $(2.9 \pm 0.3) \times 10^{-9}$    | $(2.4 \pm 0.2) \times 10^{-9}$ | $(2.5 \pm 0.4) \times 10^{-9}$    |
| $2.2 \times 10^{-4}$        | $(8 \pm 1) \times 10^{-10}$     | $(7.7 \pm 0.2) \times 10^{-10}$   | $(8 \pm 1) \times 10^{-10}$    | $(7.5 \pm 0.1) \times 10^{-10}$   |

**Table 2.**  $D_{Mn}^*$  ( $cm^2sec^{-1}$ ) in CoO at 1100°C (\* $D_{Mn}^*$  in ref. 10:  $4 \times 10^{-9} cm^2sec^{-1}$ )

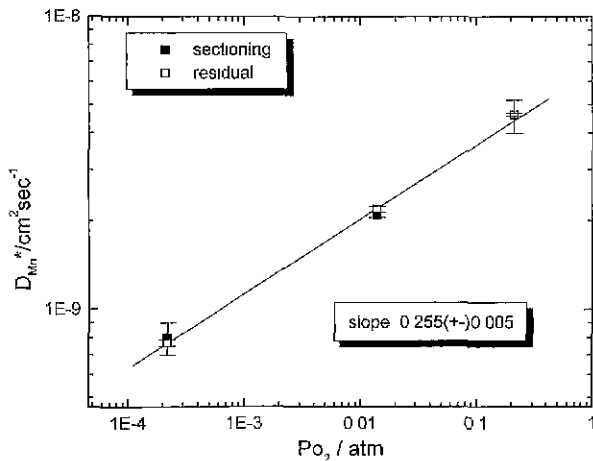
| Po <sub>2</sub> /atm | Sectioning (834.83 keV)          | Residual activity (834.83 keV)     |
|----------------------|----------------------------------|------------------------------------|
| 0.21                 | $(4.6 \pm 0.6) \times 10^{-9}$ * | $(4.63 \pm 0.05) \times 10^{-9}$ * |
| $1.4 \times 10^{-2}$ | $(2.1 \pm 0.4) \times 10^{-9}$   | $(2.2 \pm 0.5) \times 10^{-9}$     |
| $2.2 \times 10^{-4}$ | $(8 \pm 1) \times 10^{-10}$      | $(7.7 \pm 0.2) \times 10^{-10}$    |

**Table 3.**  $D_{Zn}^*$  ( $cm^2sec^{-1}$ ) in CoO at 1100°C

| Po <sub>2</sub> /atm | Sectioning (1115.52 keV)       | Residual activity (1115.52 keV)  |
|----------------------|--------------------------------|----------------------------------|
| 0.21                 | $(1.3 \pm 0.2) \times 10^{-8}$ | $(1.48 \pm 0.03) \times 10^{-8}$ |
| $1.4 \times 10^{-2}$ | $(9 \pm 1) \times 10^{-9}$     | $(1.00 \pm 0.04) \times 10^{-8}$ |
| $2.2 \times 10^{-4}$ | $(3.3 \pm 0.6) \times 10^{-9}$ | $(4.0 \pm 0.2) \times 10^{-9}$   |



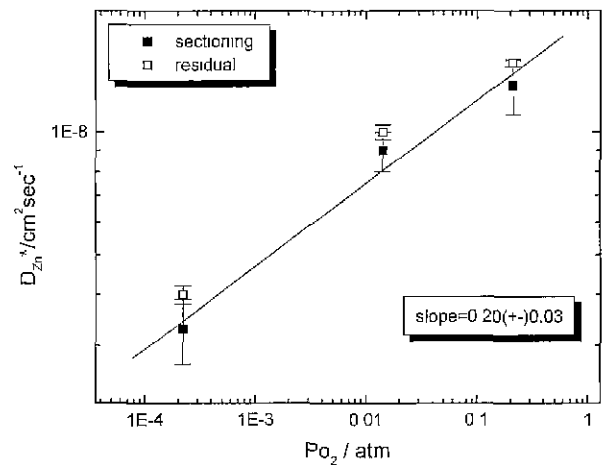
**Fig. 4.** Tracer diffusion coefficient of <sup>67</sup>Co in CoO as a function of oxygen partial pressure at T=1100°C.



**Fig. 5.** Tracer diffusion coefficient of <sup>54</sup>Mn in CoO as a function of oxygen partial pressure at T=1100°C.

the diffusion mechanism for Zn in CoO.

If we compare our results for  $D_{Co}^*$  with reported data<sup>b)</sup> we find good agreement. In the case of Mn, only one



**Fig. 6.** Tracer diffusion coefficient of <sup>65</sup>Zn in CoO as a function of oxygen partial pressure at T=1100°C.

value in air was reported in the literature<sup>10)</sup> which also agrees well with our data while for Zn there are no reference data existing.

### V. Conclusion

We have performed tracer diffusion experiments for self- (<sup>67</sup>Co) and impurity (<sup>61</sup>Mn, <sup>65</sup>Zn) diffusion in CoO at 1100°C and three different oxygen partial pressures. We have applied the residual activity method and the tracer sectioning method simultaneously to the analysis of our diffusion experiments. Concurrent application of both methods has not often been used in such diffusion studies. According to the analysis, the diffusion coefficients obtained from both methods are identical within experimental error, demonstrating the reliability of our experimental methods. The diffusion coefficients of the aliovalent impurity cation Mn are similar in magnitude with the host cation Co. But the homovalent impurity cation Zn has slightly larger diffusion coefficients than the host cation Co. All the cations show oxygen partial pressure dependences with a positive slope indicating a vacancy mechanism.

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