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Isotope Effect for Cation Self-Diffusion in Single Crystals of NiO†

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The isotope effect for cation self-diffusion was determined by simultaneous diffusion of ^{57}Ni and ^{66}Ni tracers in NiO crystals. The strength of the isotope effect $f\Delta K$ is 0.613 ± 0.021, independent of temperature in the range from 1201 to 1678 °C. This result is consistent with cation self-diffusion by a vacancy mechanism only, and $\Delta K = 0.784 \pm 0.027$.

I. INTRODUCTION

In a previous study on the temperature and oxygen-pressure dependence of the transport properties of nickel oxide,[1] we found evidence that self-diffusion occurs predominantly via a vacancy mechanism. One of the objectives of the present investigation was to help establish the mechanism by measuring the isotope effect for cation self-diffusion in this oxide as a function of temperature. This was to be done cooperatively with an isotope-effect study on cation self-diffusion in CoO.[2] By investigating isotope effects in self-diffusion and impurity diffusion in these materials, not only can possible differences in mechanism be detected, but information concerning atomic jump frequencies and their temperature dependence can be obtained.[3] In addition, studies of self-diffusion in dilute solid solutions of these oxides are planned to provide a

test for theories[4] on the effect of solute upon solvent self-diffusion.

It has been well established, both theoretically and by experimental studies on metals, alkali halides, and recently on CoO, that isotope-effect experiments can provide a direct and unequivocal evaluation of the diffusion mechanism. This is so by virtue of the relationship between the experimentally measured isotope effect E_β and the correlation coefficient f,[3]

$$E_\beta = \left(1 - \frac{D_\beta}{D_\alpha}\right) \Big/ \left[1 - \left(\frac{(n-1)m + m_\alpha}{(n-1)m + m_\beta}\right)^{1/2}\right]$$

$$= f\Delta K. \tag{1}$$

In Eq. (1), f depends solely upon the diffusion mechanism and geometrical structure of the diffusion medium. The D's are diffusion coefficients for isotopes of mass m_α and m_β. The number of atoms

involved in a jump process is n, and m is the average mass of the nontracer atoms. The quantity $1 - \Delta K$ is the fraction of the kinetic energy of the diffusing particle which is given to the lattice, and therefore ΔK depends upon the nature of the material as well as upon the mechanism. However, inasmuch as the magnitude of ΔK must lie between zero and unity, a measure of E_β provides a lower limit for the value of f. In many cases, this condition suffices to determine the diffusion mechanism. If this can be done, then the same measurements provide an unambiguous value for ΔK.

Our previous studies[1] found that while vacancies dominated the diffusion process in NiO, some contribution might be made by interstitials, and that this contribution, if it occurred, would vary with temperature. Therefore, it is particularly important in the present experiments to determine the effect that temperature has upon the isotope effect.

II. EXPERIMENTAL

The experimental quantity to be measured is the "relative diffusion coefficient" $1 - D_\beta/D_\alpha$. It can be readily shown[5] that for the boundary conditions appropriate to diffusion from an instantaneous source into a semi-infinite medium, and for any penetration distance x,

$$\ln(C_\beta/C_\alpha)_x = \text{const} + (1 - D_\beta/D_\alpha)\ln(C_\beta)_x , \qquad (2)$$

where C_α, C_β are isotopic concentrations or specific activities. Thus a plot of $\ln(C_\beta/C_\alpha)$ vs $\ln C_\beta$ suffices to give the relative diffusion coefficient. In our case the isotope pair used was ^{57}Ni and ^{66}Ni; the former was designated as the β isotope, and the latter as the α isotope. The specific activity ratios C_{57}/C_{66} were determined by γ-ray spectrometry, using a Ge(Li) detector in conjunction with a 2048-channel analyzer.[6] Because of the geometry errors inherent in this apparatus, the absolute activities C_{57} and C_{66} were calculated from these activity ratios and the total activities $C_{57} + C_{66}$, as determined with a NaI(Tl) scintillation counter. Details of the method are given below.

A. Materials

All of the isotope-effect experiments were performed on high-purity single crystals, about 99.999% pure (see Ref. 1 for spectrographic analysis), at 1 atm in oxygen.

The ^{57}Ni was prepared by 20-MeV α-particle bombardment of ^{54}Fe in the Argonne National Laboratory (ANL) cyclotron. The ^{66}Ni was produced by neutron bombardment of ^{64}Ni at a flux of 2.45 $\times 10^{15}$ n/cm^2 sec in the Oak Ridge high-flux isotope reactor.[7] Both isotopes were purified at ANL by ion-exchange methods; analysis of the final products by both γ-ray spectrometry and half-life determination showed that the concentrations of
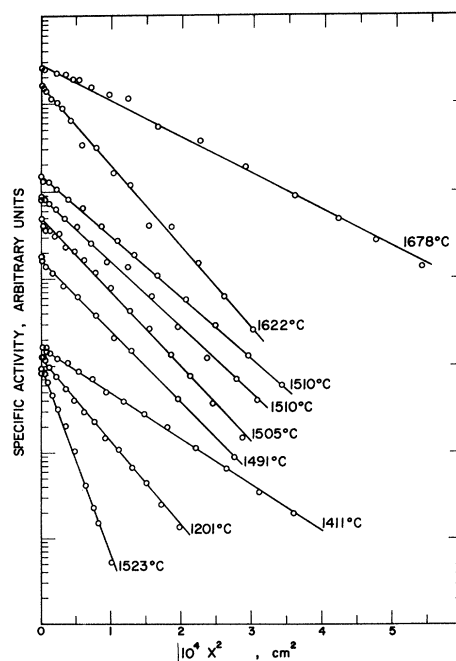

FIG. 1. Log_{10} specific activity ^{57}Ni vs square of the penetration distance for the diffusion of ^{57}Ni in NiO at 1 atm of oxygen.

long-lived impurities (mostly ^{56}Ni in ^{57}Ni and ^{110}Ag in ^{66}Ni) were less than 0.2% for both isotopes. The ^{57}Ni was essentially carrier free. The ^{66}Ni specific activity was usually 30×10^6 counts/min/mg (NaI counter). Half-lives determined by the Ge(Li) spectrometer were 54.50 h for ^{66}Ni and 35.38 h for ^{57}Ni. (Literature values[8] are 54.8 h and 35.7 h, respectively.)

B. Procedures

The diffusion-anneal and preanneal techniques were the same as previously described.[1] The temperatures were usually controlled to $\pm 1\,°C$. For the runs made above 1600 °C, the maximum temperature error was $\pm 5\%$.

The isotope-effect experiments were carried out by depositing a solution of ^{57}Ni and ^{66}Ni as NiSO$_4$, along with a trace of H$_2$SO$_4$, on one face of a single crystal of NiO (dimensions $1 \times 1 \times 0.3$ cm) that had been preannealed previously. The specific activity was always great enough to keep the layer thickness to less than $0.1Dt$ so that boundary conditions for diffusion of an instantaneous plane source into a semi-infinite medium were always satisfied.[9] Decomposition to NiO was accomplished after evaporation of the liquid by heating at 850 °C for 5–10 min. Diffusion anneals were carried out for times long enough to provide a penetration of 100–200 μm. Sectioning was accomplished with a precision polishing machine, and the total activity and activity

ratio of each section were measured by the counting methods described below. These data were used with Eq. (2) to calculate the relative diffusion coefficient.

C. Counting Methods

A dual-detector Ge(Li) spectrometer was used to determine the ratio of ^{57}Ni to ^{66}Ni activity using the 1.039-MeV photopeak of the Cu daughter of ^{66}Ni and the 1.397-MeV peak from ^{57}Ni.[10] Resolution of these isotopes by half-life separation methods[11] proved impractical because of the small difference in half-lives. The high precision required for the measurement of these ratios could not be attained by NaI(Tl) spectrometry because of the presence of incompletely resolved radiation peaks from impurities. Attempts to use the pair ^{57}Ni-^{63}Ni also failed because sufficiently precise counting methods for ^{63}Ni were not available.

Because of inherent geometry errors, the absolute specific activity C_{57}, called for in Eq. (2), had to be calculated from the ratios C_{57}/C_{66} measured by the Ge(Li) spectrometer and the total activity $A_{57}+A_{66}=A_T$ obtained by gross counting using a NaI(Tl) detector. Appropriate corrections were made for background and for isotope decay during counting.[12] The ratios and absolute activities of each section were corrected to a single zero time unique for each diffusion run.

Limitations on both the upper and lower counting limits of the section activities dictated by the Ge(Li) spectrometer made it impractical to accumulate more than about 200 000–500 000 gross counts for the two photopeaks, collected over counting periods ranging from about 1 h to 1.5 days. In spite of this limitation the measured activity ratios had an overall precision of from 0.4% to 0.7%.

D. Calculations

Specific-activity ratios for each section C_{57}/C_{66} $=\rho$, corrected for decay both during counting time

TABLE I. Relative diffusion coefficient and strength of the isotope effect for ^{57}Ni and ^{66}Ni diffusion in NiO at 1 atm of oxygen.

Temperature (°C)	Relative diffusion coeff. $D_{57}/D_{66}-1$	Isotope effect[a] E_{57}
1201	0.0451 ± 0.0020	0.593 ± 0.026
1411	0.0452 ± 0.0018	0.595 ± 0.024
1491	0.0466 ± 0.0014	0.614 ± 0.019
1505	0.0469 ± 0.0018	0.617 ± 0.023
1510	0.0476 ± 0.0018	0.627 ± 0.023
1510	0.0513 ± 0.0012	0.675 ± 0.016
1523	0.0453 ± 0.0011	0.596 ± 0.015
1622	0.0455 ± 0.0015	0.599 ± 0.020
1678	0.0454 ± 0.0014	0.597 ± 0.018
Mean value	0.0465 ± 0.0016	0.613 ± 0.021

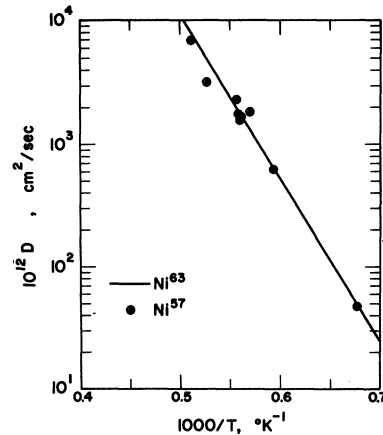[a]Calculated from Eq. (1) with $n=1$.

FIG. 2. Arrhenius plot for cation self-diffusion in NiO. Points were obtained from this research. Line is least-squares fit of data for diffusion of ^{63}Ni from Ref. 1. Oxygen pressure was 1 atm for all data.

and from the selected "zero time," were calculated from the equation

$$\rho = \frac{(\lambda_{57}/\lambda_{66})(A_{57}/A_{66})e^{(\lambda_{57}-\lambda_{66})t}(1-e^{-\lambda_{66}\tau})}{1-e^{-\lambda_{57}\tau}}, \quad (3)$$

where the λ's are decay constants obtained with the Ge(Li) detector, t is the time elapsed between the zero time and the start of counting the section, τ is the elapsed counting time, and the A's are the net photopeak areas corrected for background.

The specific activities of the individual isotopes C_{57} and C_{66} were calculated from these ratios and the total gross activity (corrected for counter dead-time and background) A_T as measured by the NaI(Tl) counter.

This calculation was complicated by the facts that A_T contains a small contribution from incompletely resolved long-lived impurities and that Ge(Li) counting was done at a different time than NaI(Tl) counting. Although they were present to an extent of less than 0.2%, the impurities caused the apparent decay constants measured by gross counting with the NaI(Tl) detector to be slightly smaller than those measured with the more selective Ge(Li) detector. This was so in spite of the use of a sophisticated isotope-separation computer program on the NaI(Tl) counting data. The values obtained by gross counting were (in units of days^{-1}) $\lambda'_{57}=0.4642$ and $\lambda'_{66}=0.3013$, while the Ge(Li) method gave $\lambda_{57}=0.4702$ and $\lambda_{66}=0.3052$. To minimize the effect of these impurities, C_{57} and C_{66} were calculated by a method in which decay corrections for ρ were made using λ_{57} and λ_{66}, while decay corrections for C_{57} and C_{66} utilized λ'_{57} and λ'_{66}. The details of this method should be apparent from the following equations for C_{57} and C_{66}:
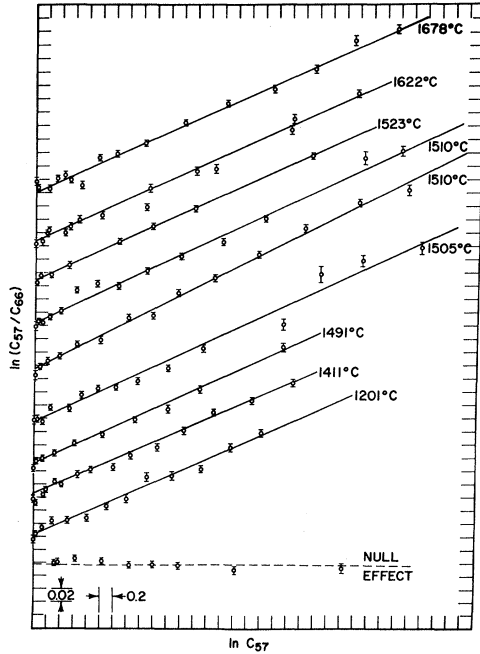
FIG. 3. $\ln(C_{57}/C_{66})$ vs $\ln(C_{57})$ for cation self-diffusion in NiO at 1 atm of oxygen. $\ln(C_{57}/C_{66})$ increases from the bottom to the top and $\ln(C_{57})$ increases from right to left.

$$C_{66} = \frac{(A_T/W)e^{\lambda'_{66}t_1}}{1 + \rho e^{(\alpha_{66} - \lambda_{57})t_1}} , \qquad (4)$$

$$C_{57} = C_{66}e^{(\Delta\lambda_{66} - \Delta\lambda_{57})t_1} , \qquad (5)$$

where t_1 is the time elapsed from counting with the Ge(Li) detector to the time counted with the NaI(Tl) counter, W is the sample weight, $\Delta\lambda_{66} = \lambda_{66} - \lambda'_{66}$, and $\Delta\lambda_{57} = \lambda_{57} - \lambda'_{57}$. Because of the small magnitude of $\Delta\lambda_{66}$ and $\Delta\lambda_{57}$, the estimated maximum error in $f\Delta K$ due to this impurity effect is judged to be less than $\frac{1}{2}\%$ and is probably much less than that.

In order to make sure that the boundary conditions were satisfied, penetration plots of $\ln C_{57}$ vs x^2 were made for each run. If the boundary conditions appropriate to Eq. (2) hold, then such plots should be linear following the equation

$$\ln C_{57} = \ln C_{57}^0 - x^2/4D_{57}t , \qquad (6)$$

where x is the penetration distance, C_{57}^0 is the specific activity at $x = 0$, D_{57} is the diffusion coefficient for ^{57}Ni, and t is the diffusion time. The penetration distance was calculated from the crystal weight and thickness before sectioning, and its weight after each thin section was removed.[1] The penetration plot served the additional purpose of providing an accurate value for D_{57} for each run.

III. RESULTS AND DISCUSSION

Penetration plots for all of the runs made in this

investigation are presented in Fig. 1. Their linearity demonstrates the absence of such experimental errors as loss of tracer by evaporation, lack of proper diffusion geometry, or appreciable amounts of "short-circuit" diffusion via subgrain boundaries or dislocations. The diffusion coefficients calculated from these lines agree well with those previously obtained with ^{63}Ni (see Fig. 2).

The isotope-effect measurements were made at eight temperatures, ranging from 1201 to 1678 °C. The plots of $\ln\rho$ vs $\ln C_{57}$, shown in Fig. 3, are linear and are parallel within the experimental error of 4%. The points labeled "null effect" show that the measured isotope ratios are unaffected by counting rate. Some of these null points were obtained by counting and analyzing, as described above, aliquots of the ^{57}Ni-^{66}Ni mixture before diffusion into NiO; others are the result of counting a single section many times as its activity decayed. The error bars on each point were calculated by standard methods[12] from the gross-peak heights and backgrounds of the ^{66}Ni 1.039-MeV and ^{57}Ni 1.397-MeV peaks. The relative diffusion coefficient $D_{57}/D_{66} - 1$, obtained from a least-squares fit of the data of Fig. 3 to Eq. (2) and E_{57}, calculated from Eq. (1), are listed in Table I. It is seen that the relative diffusion coefficients are independent of temperature within experimental error from 1201 to 1678 °C. The average value of the isotope effect, calculated from Eq. (1) with $n = 1$, is close to the value for cobalt self-diffusion in CoO (0.582) reported by Chen et al.[2] We would conclude from this that both the diffusion mechanism and the effective kinetic energy of the migrating atom are nearly identical in both compounds.

Table II shows values of ΔK [calculated from Eq. (1) and known values for f] needed to make various postulated diffusion mechanisms consistent with the average value of $D_{57}/D_{66} - 1$. As with CoO, the oxygen diffusion coefficient in NiO is much lower than the nickel diffusion coefficient,[13] and so f for vacancy-pair diffusion can be taken to be almost zero. Since $0 \leq \Delta K \leq 1$, the only allowed diffusion mechanisms for cation self-diffusion in NiO are

TABLE II. Experimental values of ΔK for the various possible diffusion mechanisms.

Mechanism	ΔK
Interstitial	0.613
Vacancy	0.784
Vacancy pair	$\gg 1.0$
Interstitialcy:	
collinear	1.91
noncollinear	1.31
Direct exchange	1.26
4-ring exchange	2.47

the interstitial and vacancy mechanisms. We have evidence from two sources that strongly suggests that the vacancy mechanism is the one that applies to NiO. First, in general it is found that whenever an interstitial mechanism is applicable, ΔK is close to unity.[14] Second, Volpe and Reddy[1] showed that interstitial diffusion could account for only a fraction of the total diffusion in NiO; in addition, that fraction would vary (at 1 atm in O_2) from about 5% at high temperatures to about 20% at low temperatures. Inasmuch as the relative diffusion coefficient observed in this research was found to be independent of temperature, we conclude that interstitial diffusion cannot be important for NiO under our experimental conditions. The lack of temperature dependence of the relative diffusion coefficient also argues against the simultaneous occurrence of any other mechanism such as the interstitialcy, along with the vacancy mechanism.

The fact that ΔK is nearly the same for cation diffusion in both CoO and NiO, although both the activation energies and pressure dependencies differ, is notable. Evidently, the most important factor influencing kinetic-energy transfer to the lattice is the nature of the anion nearest neighbors.

ACKNOWLEDGMENTS

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Magneto-Optic Study of the Jahn-Teller Effect in the Excited Level of the F^+ Centers in CaO

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The magnetic circular dichroism was measured in both the zero-phonon line and the broad band of the F^+ centers in CaO. The spin-orbit coupling constant in the relaxed excited state was found to be -0.58 cm^{-1}. Comparison with the same constant measured in the broad band gives for the Ham reduction factor a value $K(T_1) = 0.02$. Analysis by the method of moments of the circular dichroism in the broad band allowed the determination of the coupling coefficients of the centers to cubic and noncubic modes of vibration. The values found for these coefficients explain quite well the observed shape of the band.

I. INTRODUCTION

It has been pointed out in a review article by Ham[1] that in the presence of Jahn-Teller coupling the ground vibronic level keeps the same degeneracy and symmetry as the orbital electronic level it originates from. The matrix elements of electronic operators taken inside the ground vibronic level