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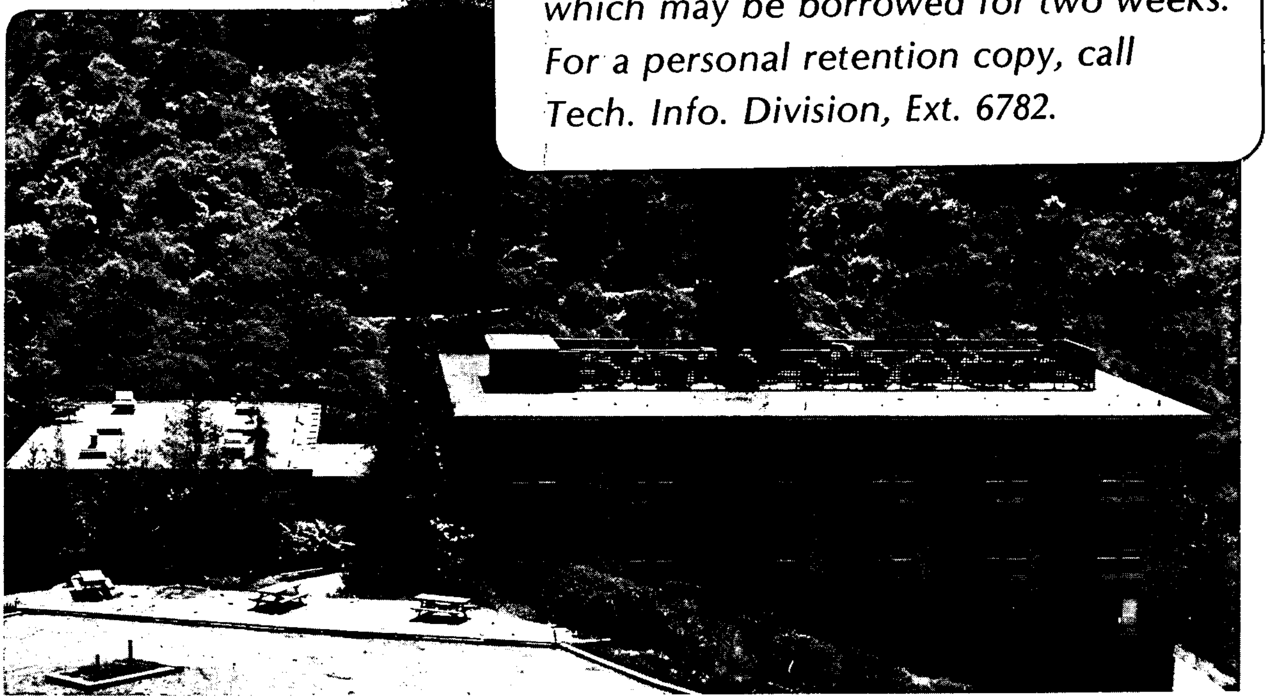

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ABSTRACT

Tracer diffusion coefficients of Fe, D^*_{Fe}, in single crystal of rutile and of 0-2.0% Fe doped rutile were measured. The oxygen pressure dependence of D^*_{Fe} in pure rutile showed complicated behavior. The values of D^*_{Fe} may consist of contributions from Fe^{2+} ions diffusing by an interstitial mechanism and from Fe^{3+} ions diffusing by an interstitialcy mechanism in cooperation with tetravalent titanium interstitial ions, $Ti_i^{\bullet\bullet\bullet\bullet}$. The value of D^*_{Fe} in Fe doped rutile attains a saturation value when the Fe content reaches about 0.1%; D^*_{Fe} decreases drastically when the Fe content exceeds about 0.35%. Complex impedance measurements of electrical conductivity confirm the existence of ionic conduction for Fe doped rutile containing less than 0.35% of Fe. The measured ionic conductivity is much lower than expected from the values of D^*_{Fe} suggesting that only a small fraction of the iron ions are highly mobile. Above 0.35% Fe, the observed drastic decrease in D^*_{Fe} may result from the formation of a shear structure in highly doped rutile.

INTRODUCTION

Ionic conductivity σ_i may be described by the relation

$$\sigma_i = n_i \bullet q_i \bullet m_i \tag{1}$$

where n_i, q_i, and m_i are the concentration, electrical charge, and mobility of the mobile ions, respectively. The mobility m_i and diffusion coefficient D_i of the mobile ions are related by the Nernst-Einstein equation,

$$\frac{D_i}{m_i} = \frac{kT}{q_i} \tag{2}$$

where k is Boltzmann constant and T is the absolute temperature. Numerous studies have been conducted on the development of new ionic conductive materials. Fast ionic conductors generally have special crystal structures which permit large values of n_i or/and m_i.

Rutile has "channels" of low electron density parallel to the c-axis. Since there are no channels perpendicular to the c-axis, preferential diffusion parallel to the c-axis is expected. Sasaki and Peterson [1] have measured tracer diffusion of several cation impurities in rutile single crystal. The results indicated very fast diffusion of divalent ions parallel to the c-axis by an interstitial mechanism. Triand tetravalent ions diffuse more slowly with reduced anisotropy in D*, the tracer diffusion coefficient; the oxygen pressure dependence of D* suggests diffusion occurs by an interstitialcy mechanism with the aid of $Ti_i^{\bullet\bullet\bullet\bullet}$. Although Fe diffusion shows strong anisotropy, the oxygen pressure dependence of D^{*}_{Fe} is similar to that observed for trivalent ions. Apparently, iron ions exist in both the 2+ and 3+ states in rutile.

Figure 1 shows the Arrhenius plots for tracer diffusion of several impurities in rutile together with typical results for fast ionic conductors. It is quite obvious that mono- and divalent ions diffuse fast enough in rutile to be comparable with fast ionic conductors.

The solubility limit of Fe in rutile is thought to be about 1% [8]. If the Fe ions dissolve in both interstitial and substitutional sites, the following reaction will occur;

$$Fe_2O_3 \rightleftharpoons 2\ Fe_i^{\cdot\cdot} + 4\ e' + \frac{3}{2}\ O_2(g) \tag{3}$$

$$2\ Fe_2O_3 \rightleftharpoons 4\ Fe'_{Ti} + 6\ O_O^x + Ti_i^{\cdot\cdot\cdot\cdot} \quad . \tag{4}$$

Point defect equilibria in rutile may be represented by the reactions,

$$Ti_{Ti}^x + 2\ O_O^x = Ti_i^{\cdot\cdot\cdot\cdot} + 4\ e' + O_2(g) \tag{5}$$

$$O_O^x = V_O^{\cdot\cdot} + 2\ e' + \frac{1}{2}\ O_2(g) \quad . \tag{6}$$

Several ESR measurements [9,10] support the preferential occupation of Fe at substitutional site. When Eq. 4 is the dominant reaction, the doping of Fe decreases the concentration of electron (see Eq. 5), and eventually reaches the intrinsic electron-hole equilibrium. Doping of rutile with Fe increases the concentration of mobile Fe and decreases the concentration of electron, thus enhancing ionic conductivity while decreasing electronic conductivity.

In the present work, we report the tracer diffusion behavior of Fe in rutile and Fe doped rutile. We also report on the relationship between conductivity and D^{*}_{Fe} in Fe doped rutile.

EXPERIMENTAL PROCEDURE

Materials

Pure rutile single crystal. The single crystal rutile used in this work was purchased from Commercial Crystal Company. Spectroscopic chemical analysis indicated 160 ppm of Al as the major impurity. Rectangular samples were cut from the single crystal boule. The c-axis of each sample was determined from Laue X-ray patterns to within ±1°. The samples were polished and preannealed at the same temperature and oxygen partial pressure that were latter used for the diffusion anneal.

Fe doped rutile. In order to make Fe doped rutile, a thin Fe foil, which had been cut to shape and weighed in advance, was sandwiched between two rutile crystals. The samples, with their c-axis perpendicular to the Fe foil, were carefully bound with Pt wire and annealed at 1400°C and 2×10^{-3} atm of oxygen partial pressure for several days in order to obtain a uniform Fe distribution. A small part of each sample was removed for spectroscopic chemical analysis.

Diffusion Measurements

The values of D^{*}_{Fe} were obtained using the radioactive tracer sectioning method. The experimental procedures are described in detail elsewhere [1]. The indiffused ^{59}Fe is expected to have a Gaussian distribution in the sample given by the expression

$$C = \frac{S}{(\pi D t)^{1/2}} \exp\left(-\frac{x^2}{4 D t}\right) \tag{7}$$

where S is the radioactivity per unit area deposited at $t = 0$ and $x = 0$, and t is the diffusion time. The diffusion coefficient is calculated from the slope of a plot of log C vs. x^2. Figure 2 shows typical penetration plots for the diffusion of ^{59}Fe parallel to the c-axis. Since all plots are straight lines deep inside the sample, the values of D^{*}_{Fe} calculated from these plots represent bulk diffusion.

Electrical Conductivity Measurements

The complex impedance method was used to measure the electrical conductivity of several samples after diffusion measurement. Platinum paste and Pt plates were used for electrodes. The complex impedance was measured over the frequency range from 5 MHz to 1 Hz using a sinewave-generator and gain phase meter. In the frequency range from 1 Hz to 0.01 Hz, Lissajous ellipses were recorded on an X-Y recorder to deduce the complex impedance.

RESULTS AND DISCUSSION

Fe Diffusion in Nominally Pure Rutile

Figure 3 shows the oxygen pressure dependence of D^{*}_{Fe} in rutile together with the oxygen pressure dependence of $[Ti_i^{\cdot\cdot\cdot\cdot}]$ calculated from thermogravimetric data obtained by Marucco et al. [11]. The major point defects in rutile are $Ti_i^{\cdot\cdot\cdot\cdot}$ and $V_O^{\cdot\cdot}$; the concentrations of these defects are a function of temperature and oxygen partial pressure. Generally speaking, $Ti_i^{\cdot\cdot\cdot\cdot}$ is the dominant defect at high temprature, and $V_O^{\cdot\cdot}$ is the dominant defect at low temperature and low oxygen partial pressure. Using the reactions represented by Eqs. 5 and 6 the oxygen pressure dependences of these defect concentrations are given by the relation:

(i) for

$$[Ti_i^{\cdot\cdot\cdot\cdot}] \gg [V_O^{\cdot\cdot}]$$

$$[Ti_i^{\cdot\cdot\cdot\cdot}] \propto p_{O_2}^{-1/5}$$

$$[V_O^{\cdot\cdot}] \propto p_{O_2}^{-1/10} \qquad (8)$$

(ii) for

$$[V_O^{\cdot\cdot}] \gg [Ti_i^{\cdot\cdot\cdot\cdot}]$$

$$[Ti_i^{\cdot\cdot\cdot\cdot}] \propto p_{O_2}^{-1/3}$$

$$[V_O^{\cdot\cdot}] \propto p_{O_2}^{-1/6} \qquad (9)$$

The single crystal of rutile used in the present experiments contains 160 ppm Al. Aluminum proved to have significant effects on the defect equilibria; 160 ppm of Al in rutile is sufficient to produce an extrinsic region at temperatures as high as 1300°C. The Al content may produce both $\mathrm{Ti}_i^{\cdot\cdot\cdot\cdot}$ and $V_0^{\cdot\cdot}$ in the following way [12]:

$$2\ \mathrm{Al_2O_3} \rightleftharpoons 4\ \mathrm{Al}'_{\mathrm{Ti}} + 6\ \mathrm{O}_0^{x} + \mathrm{Ti}_i^{\cdot\cdot\cdot\cdot} \tag{10}$$

$$\mathrm{Al_2O_3} \rightleftharpoons 2\ \mathrm{Al}'_{\mathrm{Ti}} + 3\ \mathrm{O}_0^{x} + V_0^{\cdot\cdot} \tag{11}$$

The oxygen pressure dependence of $^{46}\mathrm{Sc}$ diffusion in rutile showed that $D^{\star}_{\mathrm{Sc}}$ is proportional to $p_{\mathrm{O}_2}^{-1/5}$ in the intrinsic region [1]. The values of $D^{\star}_{\mathrm{Sc}}$ are consistent with the oxygen pressure dependence of $[\mathrm{Ti}_i^{\cdot\cdot\cdot\cdot}]$ calculated from previous thermogravimetric data [11]. We concluded that Sc preferentially occupies substitutional sites and migrates via substitutional and interstitial sites with the aid of $\mathrm{Ti}_i^{\cdot\cdot\cdot\cdot}$ by the interstitialcy mechanism. This simple behavior may be due to the stability of Sc ions in the trivalent charge state. In contrast with Sc, the oxygen pressure dependence of $D^{\star}_{\mathrm{Fe}}$ shows somewhat more complicated behavior, probably due to the possible variation of the $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$ ratio in reducing atmospheres.

If the ratio of Fe^{2+} to all Fe ions is represented by f, the apparent diffusion coefficient is given by

$$D_{\mathrm{app}} = f\ D_{\mathrm{II}} + (1-f)\ D_{\mathrm{III}} \tag{12}$$

where D_{II} and D_{III} are the diffusion coefficients of Fe^{2+} and Fe^{3+} ions, respectively. The equilibrium of these ions may be given by

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-} \qquad (13)$$

with

$$k = \frac{[Fe^{3+}]\,[e]}{[Fe^{2+}]} \qquad (14)$$

Therefore, Eq. 12 may be rewritten in the form

$$D_{app} = \frac{1}{1 + k/[e]}\, D_{II} + \frac{k/[e]}{1 + k/[e]}\, D_{III} \qquad (15)$$

If $[Fe^{2+}] \gg [Fe^{3+}]$,

$$D_{app} \cong D_{II} \qquad (16)$$

If $[Fe^{3+}] \gg [Fe^{2+}]$,

$$D_{app} \cong D_{III} \qquad (17)$$

The oxygen pressure dependence of D_{III} must be consistent with that of $[Ti_i^{\cdot\cdot\cdot\cdot}]$ shown in Fig. 3. However, the experimental results suggest that both D_{II} and D_{III} are important. Accordingly, Fe ions exist as Fe^{2+} and Fe^{3+} ions over a broad oxygen pressure region. Since divalent ions prefer to occupy interstitial sites and migrate by the interstitial mechanism along the open channels parallel to the c-axis [1], Fe^{2+} ions and Fe^{3+} ions occupy the interstitial and substitutional sites respectively. One ESR measurement [10] indicates that more than 70% of all Fe ions occupy substitutional sites. In order to separate the two terms in Eq. 15, it is necessary to obtain the ratio of Fe^{2+}/Fe^{3+} in rutile as a function of oxygen pressure, which is unknown at this time. An unusual behavior in the oxygen pressure dependence of D^{*}_{Fe} is observed in Fig. 3 at about $10^{-1} - 10^{-2}$ atm of oxygen. Although no conclusive explanation is apparent for this sudden change in D^{*}_{Fe}, this oxygen pressure coincides with the oxygen pressure where the type of electronic conductivity changes from n-type to p-type. When the defect equilibrium constant is much larger than the intrinsic electronic equilibrium constant, there is a drastic change of the concentration of electronic species (electrons and holes). Since the ratio of Fe^{2+} to Fe^{3+} is a function of the concentration of electrons (see Eq. 14), the ratio of Fe^{2+} to Fe^{3+} may decrease drastically at the oxygen pressure where n-type conduction changes to p-type conduction.

Fe Diffusion in Fe Doped Rutile

Figure 4 shows D^{*}_{Fe} as a function of the Fe content in rutile at 800°C. All the diffusion coefficients were measured in 2×10^{-3} atm of oxygen partial pressure to avoid the complicated behavior of D^{*}_{Fe} at about $10^{-1} - 10^{-2}$ atm of oxygen pressure. It is quite obvious from the figure that up to 0.35% Fe content D^{*}_{Fe} is constant. Although D^{*}_{Fe} will decrease as the Fe content decreases (dashed line in Fig. 4). This speculation is partially supported by the low values of D^{*}_{Fe} in pure rutile (this sample also contains 30 ppm of Fe). The saturation of D^{*}_{Fe} with increasing Fe content can be explained by the saturation of substitutional sites by Fe^{3+} ions and subsequent occupation of interstitial sites by Fe^{2+} ions. If Fe^{2+} ions become dominant, D^{*}_{Fe} should be relatively independent of the Fe content shown in Eq. 16.

When the Fe content exceeds 0.35% the diffusion coefficient decreases rapidly. A similar behavior was observed when self-diffusion of Ti was measured at very low oxygen pressure where rutile is no longer stable, and the shear structure becomes important [13]. This behavior was explained by the obstruction of ion movement by the shear planes. As reported in electron microscopic studies of the Fe-Ti-O system [14,15], the rutile field of Fe doped rutile may be quite small.

Conductivity Measurement of Fe Doped Rutile

The electrical conductivity of a 0.34% Fe doped rutile sample was determined as a function of oxygen pressure at 800°C using the complex impedance technique. The ionic conductivity σ_i and the conductivity due to electrons σ_e are shown as a function of oxygen pressure in Fig. 5. Values of σ_i(cal.) calculated from D^*_{Fe} and the [Fe] using Eqs. 1 and 2 are also shown. Experimental results for 0.2% Fe doped rutile sample obtained by Rudolph [16] are shown for comparison.

The reason for the large difference between σ_i and σ_i(cal.) is not clear. One possible explanation can be developed involving the interplay of free point defects, Wadsley defect, and shear structure. The appearance of Wadsley defect or shear structure may decrease the effective concentration of mobile Fe ions in rutile and result in the decrease of ionic conductivity. However, such explanations require additional supporting evidence.

For further discussion it is necessary to obtain information about the charge state of Fe ions and the occupational sites. Electrochemical measurements are useful for determining the ionic conductivity and transference number.

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FIGURE CAPTIONS

Fig. 1. Arrhenius plots for impurity diffusion in rutile and diffusion in several solid ionic conductors.

Fig. 2. Penetration plots for the diffusion of ^{59}Fe in Fe doped rutile.

Fig. 3. Oxygen pressure dependence of ^{59}Fe diffusion and $[\mathrm{Ti}_i^{\cdot\cdot\cdot\cdot}]$ in 160 ppm Al doped rutile.

Fig. 4. [Fe] doping dependence of ^{59}Fe diffusion coefficient parallel to the c-axis in rutile.

Fig. 5. Oxygen pressure dependence of electrical conductivity in Fe doped rutile at 800°C. The electronic and ionic components of the conductivity (σ_e and σ_i), σ_i(cal.) determined from tracer diffusion measurements, and similar measurement of Rudolph [16] are also shown.

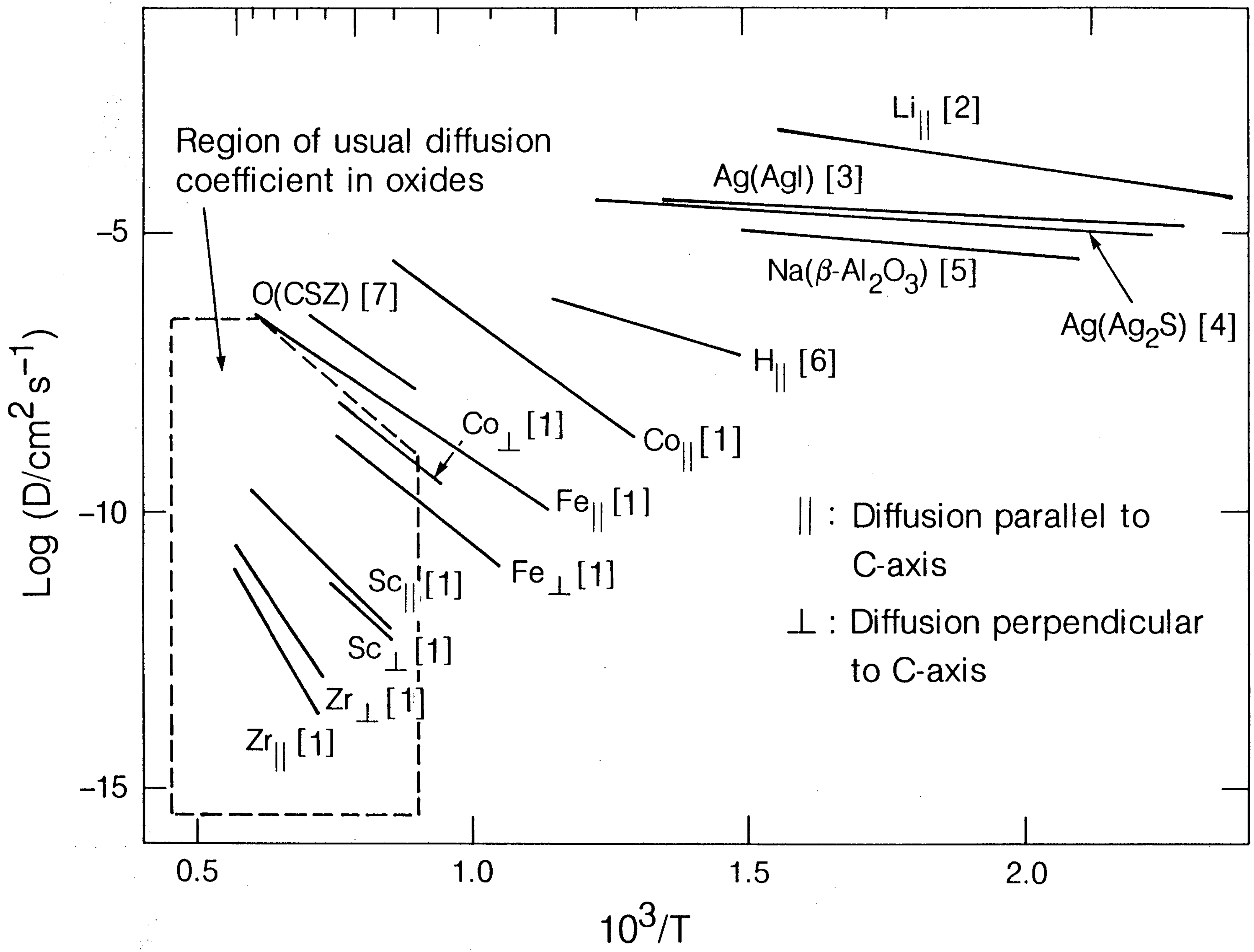

Figure 1

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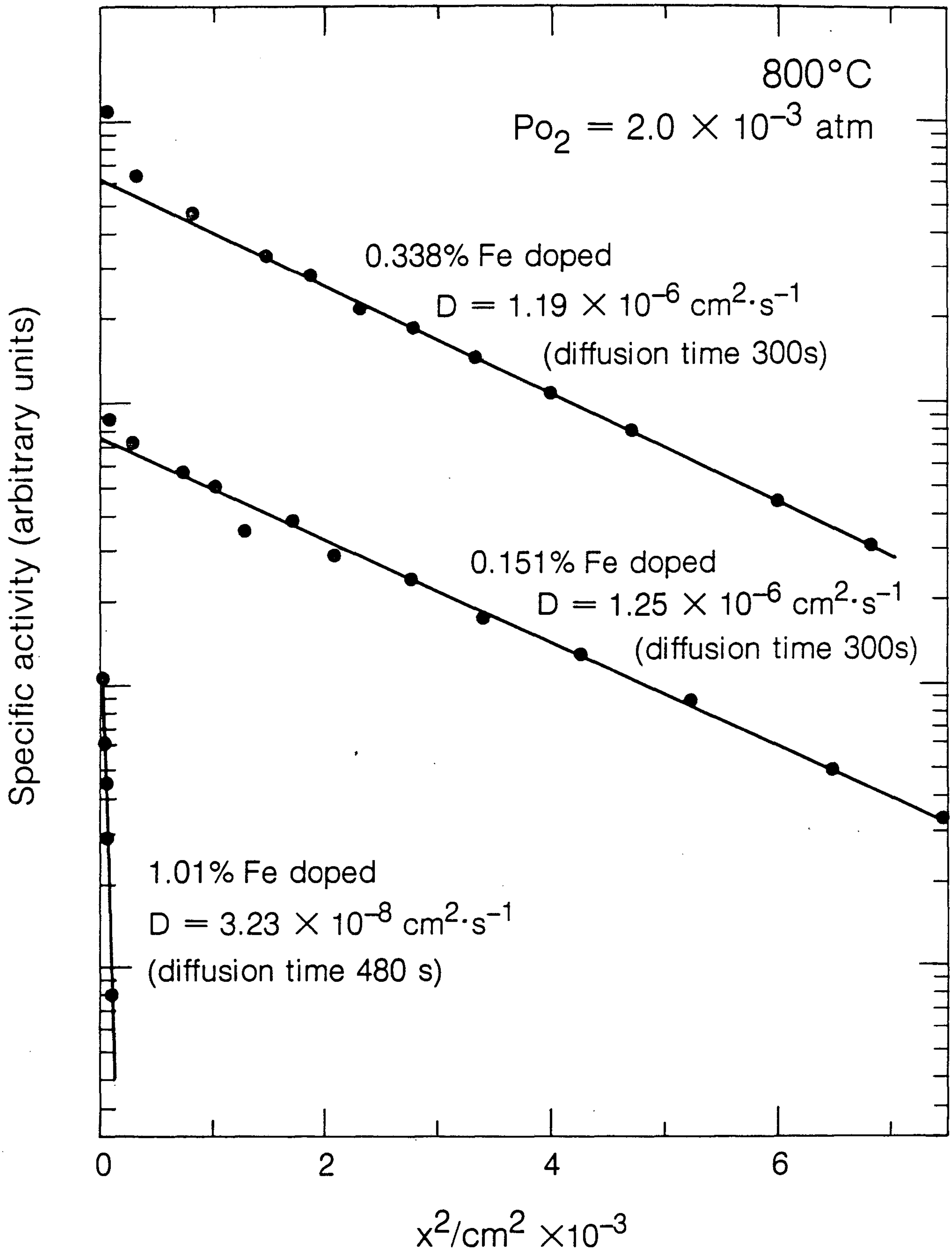

Figure 2

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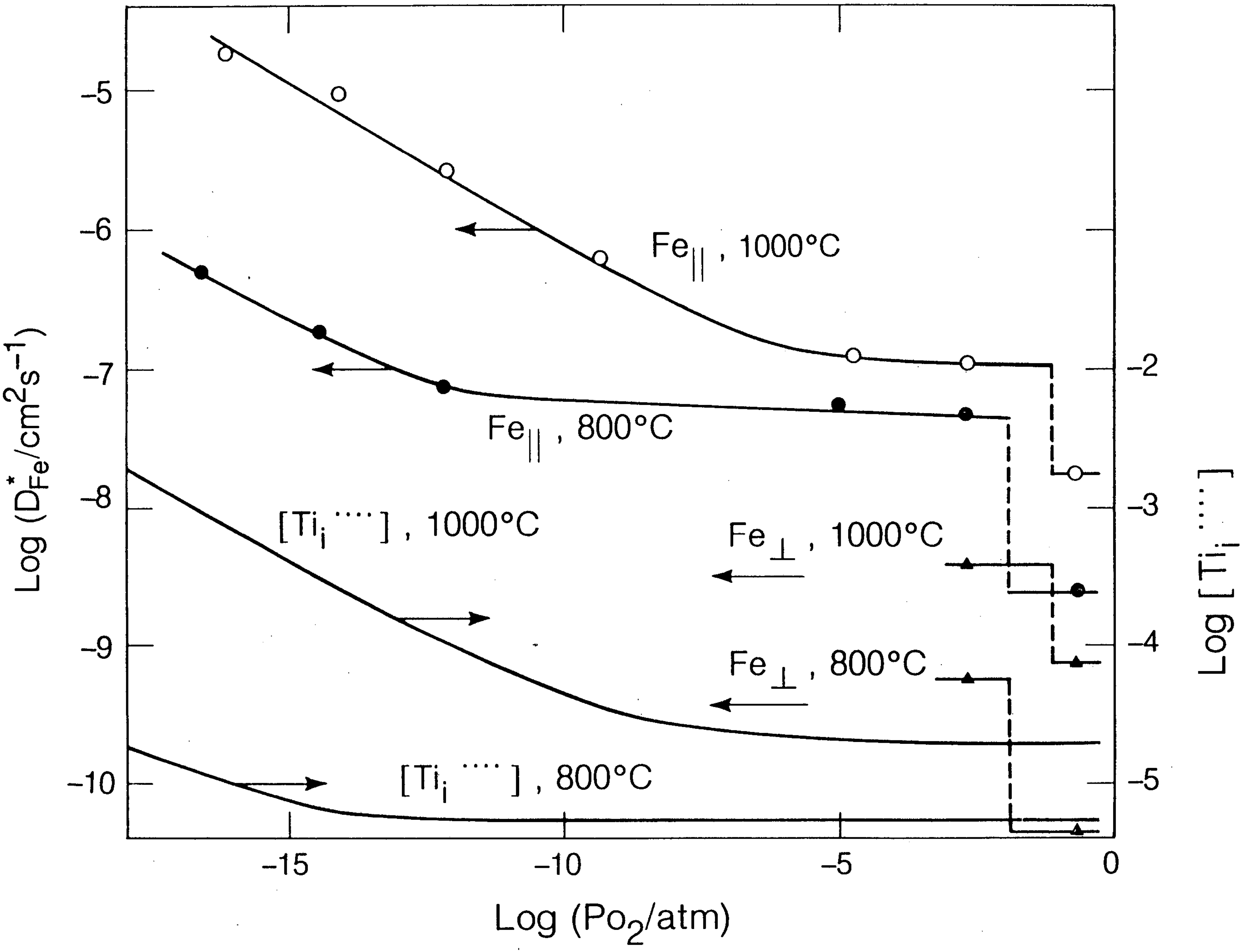

Figure 3

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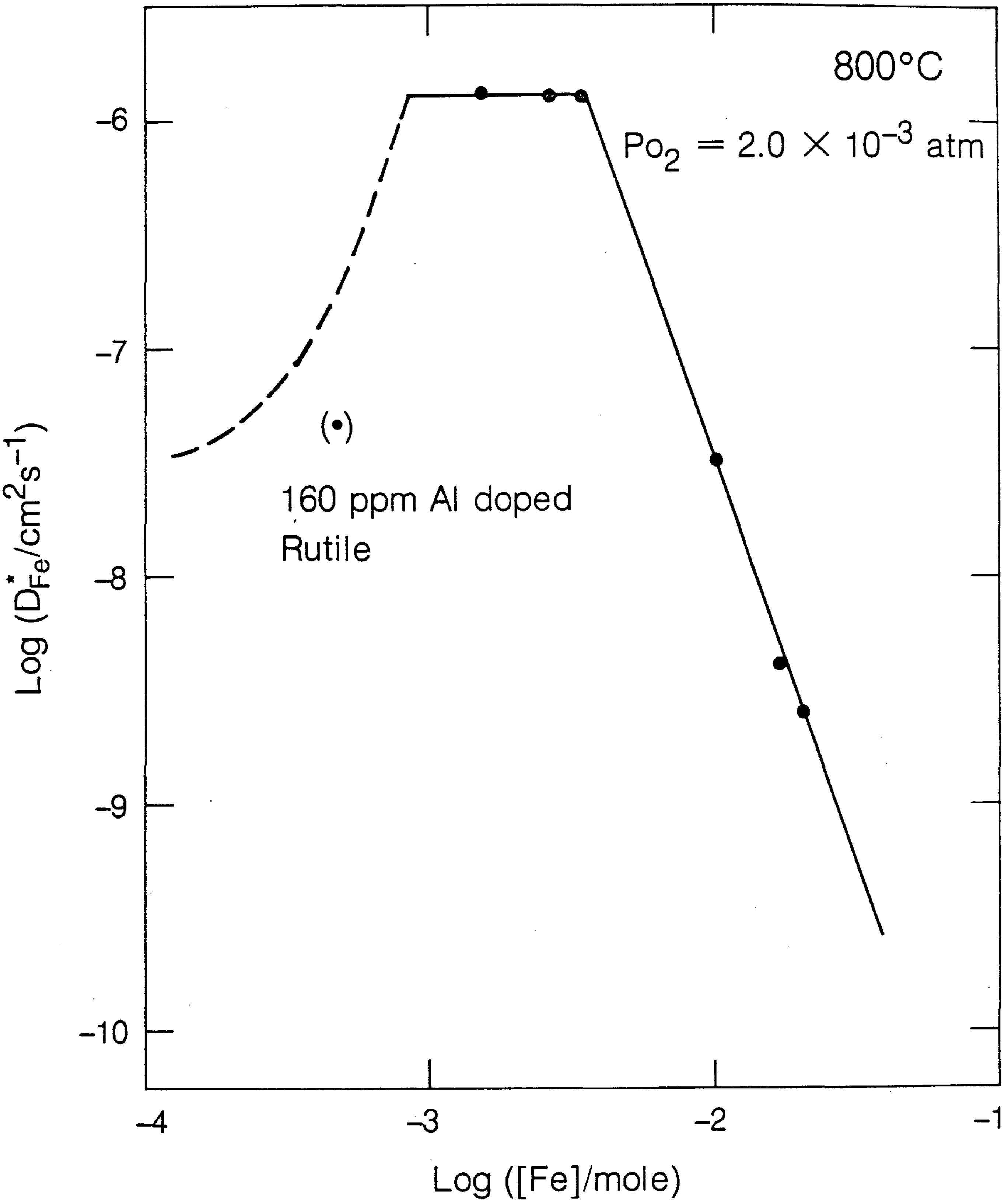

Figure 4

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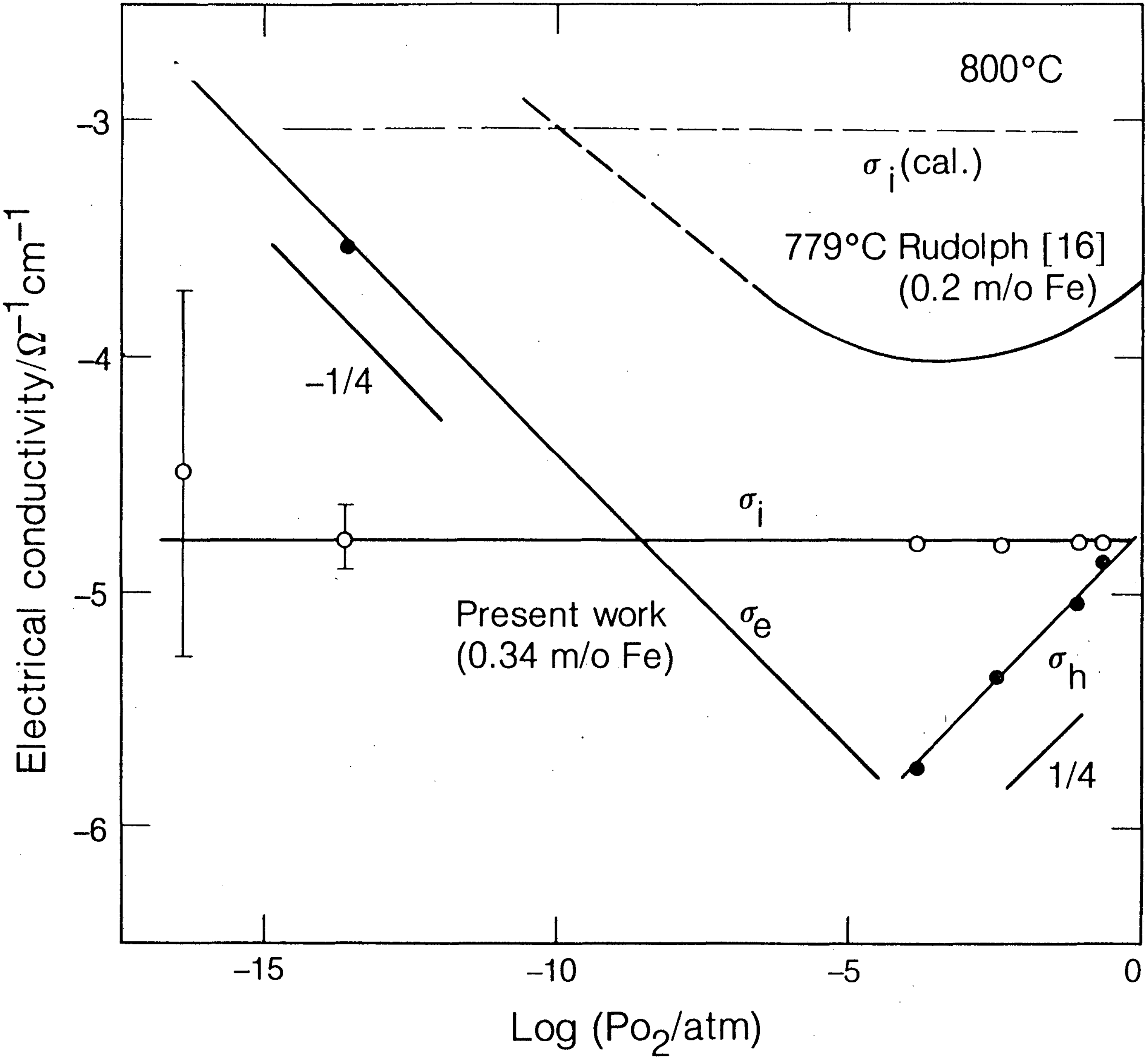

Figure 5

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