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ABSTRACT

Diffusion kinetics and mechanisms were studied in the MgO phase of

the Fe-MgO (vacuum), NiO-MgO (vacuum and air), and Fe_2O_3-MgO (air)

systems. In the Fe-MgO system Fe entered the MgO lattice by a redox

reaction; the diffusivity and activation energy were found to be concen-

tration dependent. In the NiO-MgO system in air the diffusivity was

found to be concentration dependent and the activation energy, concen-

tration independent; in vacuum both the diffusivity and activation

energy were concentration independent. In the Fe_2O_3-MgO system the

diffusivity and activation energy were concentration independent; because

of the 3 phase 2 moving boundary nature of the diffusion problem, the Appel modification of the Boltzmann-Matano solution was used.

Impurities in the MgO were responsible for sufficient chemically created vacancies to place the diffusion results in the extrinsic region. Formation of trivalent ions, and consequently chemically created vacancies, in the Fe-MgO and NiO-MgO (air) systems resulted in the concentration dependence of the diffusivity of primarily Fe^{+2} ions. Concentration dependence of activation energy in the Fe-MgO system is associated with development of structural changes by some of the Fe^{+3} ions moving into tetrahedral sites. In the Fe_2O_3-MgO system it is presumed that the Fe^{+3} ions remain on octahedral sites at diffusion temperatures and that the observed precipitates form on cooling. Identification of Fe^{+2} and Fe^{+3} ions and their position in the lattice were determined by electron paramagnetic resonance and optical spectroscopy.

I. INTRODUCTION

Because diffusion plays such a significant role in all high-temperature solid-state reactions involving condensed phases, a knowledge of the diffusivities and of the diffusion mechanisms in inorganic oxides is of great practical and theoretical value. This paper reports on such studies relative to Fe and Ni ions in MgO single crystals.

Many reviews have been written on the subject of diffusion in condensed phases.[1-5] The vacancy mechanism is the most widely accepted for diffusion in ionic solids. At temperatures above absolute zero, the lattice of an ionic crystal contains some thermally-created vacancies. Vacancies, however, may also be created chemically. In a divalent matrix such as MgO, two trivalent ions (e.g., Fe^{+3}) introduced into the lattice would require the formation of one cation vacancy for electroneutrality to be retained.

The self-diffusion coefficient of Mg^{+2} in MgO was measured by Lindner and Parfitt[6] using Mg^{28} as a tracer. Their results show that at 1400-1600°C $\underline{D}$ = 0.249 exp (-79.0 kcal/RT). It should be noted that this high value suggests that their material was sufficiently pure to be in the intrinsic diffusivity region.

NiO, which also has the NaCl structure, has a lattice parameter (4.177Å) similar to MgO (4.213Å). It is, however, non-stoichiometric in air containing some Ni^{+3}. Self-diffusion coefficients of Ni^{+2} in NiO have been determined by several investigators.[7-10] In the temperature range from 1000-1470°C Choi[8] found $\underline{D}$ = 1.82 x 10^{-3} exp (-45.6 kcal/RT).

Wüstite, Fe_xO, is also a non-stoichiometric compound with the NaCl structure. The self diffusion of Fe^{+2} in Fe_xO has been studied by Himmel[11] who found $\underline{D} = 0.118 \exp (-29.7 \text{ kcal/RT})$ for a composition of $Fe_{0.907}O$ at 700-1000°C. Roth[12] showed by neutron scattering techniques that the defects consisted of both atom vacancies and some Fe^{+3} ions in tetrahedral sites. Koch and Cohen,[13] using X-ray diffraction techniques with a single crystal of $Fe_{0.902}O$, identified the presence of periodically spaced clusters of vacancies, each cluster of neighboring octahedral cation sites grouped about occupied tetrahedral cation sites.

Himmel[11] also found that the self-diffusion of Fe in magnetite of composition $Fe_{2.993}O_4$ (inverse spinel structure) followed the relationship $\underline{D} = 5.2 \exp (-55.0 \text{ kcal/RT})$ in the temperature range 750-1000°C.

Hematite, αFe_2O_3, has the corundum structure with the HCP oxygen ions slightly distorted. The Fe^{+3} ions occupy 2/3 of the octahedral sites. In the temperature range 950-1050°C Izvekov[14] found that the diffusion of Fe in Fe_2O_3 in air followed the relationship $\underline{D} = 1.3 \times 10^6 \exp (-100,200/RT)$.

Under reducing conditions MgO and Fe_xO have been reported to form a continuous series of solid solutions at high temperature. It has been found that Mg^{+2} in wüstite does not act purely as a diluent but lowers the ratio of Fe^{+3}/Fe^{+2}. Several investigations have been made on the diffusion of Fe in MgO under various oxygen partial pressures.[14-21] Wuensch and Vasilos[20] found that the variation in diffusion coefficient with temperature in air was represented by $\underline{D} = 8.83 \times 10^{-5} \exp (-41.6 \text{ kcal/RT})$. Rigby and Cutler[18] found that the mutual diffusion coefficient in the Fe_xO-MgO system was concentration dependent, but that

the activation energy was constant at 47.5 kcal/mole. In our study the activation energy as well was found to be concentration dependent.

The reaction between Fe_2O_3 and MgO has been studied by several investigators.[22-26] Carter,[23] using pores as "inert" markers, stated that solid state reactions forming both $MgAl_2O_4$ and $MgFe_2O_4$ occurred by counterdiffusion of the Mg^{+2} and the trivalent cations through a relatively rigid oxygen lattice. He found that the ratio of ferrite formed on the MgO side of the initial interface to that formed on the Fe_2O_3 side was 1:2.7 which was considered to be consistent with the diffusion of Fe^{+3}. The $Fe^{+3}-Mg^{+2}$ interdiffusion model predicts a ratio of 1:3. Fresh and Dooling[26] stated that at 1000-1300°C the rate controlling step in the reaction process was the diffusion of the oxide components through the ferrite product layer. Schaeffer and Brindley[27,28] and Ficalora[29] found that "fingers" and isolated "islands" of $MgFe_2O_4$ developed in the crystals of (Fe, Mg)O upon oxidation.

Speidel's[30] 1300°C isothermal section of the $MgO-FeO-Fe_2O_3$ system shows that under atmospheric conditions $MgFe_2O_4$ in the presence of excess Fe_2O_3 will form solid solutions containing some Fe_3O_4 as well as Fe_2O_3. It also shows the presence of some Fe^{+3} in MgO containing iron even at low pressures.

A complete series of solid solutions occurs between NiO and MgO. Hahn and Muan[31] have reported it to be ideal within experimental error for oxygen partial pressures between 10^{-5} and 10^{-10} atm. Wuensch and Vasilos[20] found that Ni^{+2} diffusion in MgO followed the relation $\underline{D} = 1.80 \times 10^{-5} \exp(-48.3 \text{ kcal}/RT)$. Choi[32] found that the interdiffusivity and activation energy were concentration dependent. Our

study showed that only the pre-exponential term was concentration dependent in air and that neither was concentration dependent in vacuum.

II. EXPERIMENTAL PROCEDURE

Preparation of Diffusion Couples

Reagent grade NiO powder,[*] dried at 150°C for 24 hours, was used for all of the MgO-polycrystalline NiO diffusion runs. Single crystals of MgO were purchased from the Norton Company.[**] Diffusion couples were prepared by packing a cleaved single crystal of MgO in NiO powder in a 1/2" steel die and pressing at room temperature to approximately 5000 psi. The compacts were placed in alumina crucibles and transferred to a quench type furnace ($MoSi_2$ elements) which was used for all of the air atmosphere diffusion runs. Anneals were made in the temperature range 1200-1400°C for 25-200 hours.

Duffusion runs were also carried out in a high vacuum furnace. The same practice for sample preparation was used except that the alumina crucibles were loosely covered and wrapped in Ta foil in order to keep the oxygen partial pressure as low as possible. The system was flushed with He gas 3 times, and after each flush was pumped down to 10^{-6} torr. The diffusion runs were made at 10^{-6} torr. Temperatures ranged from 1200-1400°C for times from 25-150 hours.

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[*] Chemical analysis (Baker Analyzed Reagent Grade – Lot 7498): N 0.005%, Cl 0.005, SO_4 0.010, Pb 0.010, Cu 0.005, Co 0.02, Fe 0.005, Zn 0.10, and alkalies and earths as SO_4 0.01.

[**] Spectroscopic analysis: Fe 0.01%, Mn 0.0015, Al 0.005, Cu 0.0015, Ca 0.01, and Cr 0.001.

A single crystal MgO vs single crystal NiO diffusion run was also made. Single crystals of NiO were purchased from Marabeni-Iida Co., Japan,* and cleaved into samples approximately 0.5 x 0.5 x 0.5 cm. Cleaved (100) faces of both NiO and MgO single crystals were placed in contact in a die with MgO powder surrounding the two crystals, and pressed. The crystals were offset from one another in order to establish an identification of the initial interface between them. The MgO powder surrounding the two crystals allowed measurement of the single crystal vs polycrystal diffusion zone as well as the interdiffusion between the two single crystals. The diffusion specimens were removed from the furnaces, cut with a diamond saw, mounted in resin, and polished.

The Fe-MgO diffusion couples were prepared by burying a cleaved single crystal of MgO in iron powder in a recrystallized alumina crucible which was previously heated with iron powder in vacuum to 1500°C. The set-up was covered, wrapped in tantalum foil and heated in vacuum, as described before, for the diffusion runs. Runs were made at 1150, 1250, and 1350°C for given lengths of time.

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* Spectroscopic analysis: Mg 0.01%, Al <0.003, Si <0.005, Ca 0.007, Ti <0.003, Cr <0.002, Mn <0.002, Fe 0.008, Co <0.01, Cu <0.0008, Sr <0.003, Sn <0.005, Ba <0.001, and W <0.2.

Reagent grade ferric oxide[*] was used for all polycrystalline Fe_2O_3-MgO diffusion runs in air. Cleaved samples of MgO were packed in the powder (after drying at 150°C for 24 hours) and pressed in a 3/4" die at approximately 5000 psi. A single crystal Fe_2O_3[**] vs single crystal MgO imbedded in powdered Fe_2O_3 diffusion run was also made at a temperature of 1330°C for 163 hours.

Diffusion specimens were normally air-cooled or cooled with the furnace rather than quenched into water in order to prevent shattering of the MgO single crystals. Several specimens, however, were quenched into cold water from 1350 and 1500°C for the purpose of obtaining specimens for EPR and optical absorption studies. All of the diffusion specimens required polishing, and in some cases carbon coating, for subsequent examinations. Polishing was accomplished by lapping with successively finer abrasives, from 600 grit SiC through 0.1μ Al_2O_3. The polished samples were coated with carbon by vapor deposition to render their surfaces electrically conductive.

Experimental Analysis

An Applied Research Laboratories electron microprobe analyzer was used to determine the diffusion profiles. The $K\alpha$ X-ray emission line was monitored for all the cations in the system. The specimen current was $0.03\mu a$. Each spectrometer output was fed to a pulse height analyzer and then to a scaler. The data output from the electron microprobe was

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[*] Chemical analysis (Baker Analyzed Reagent - Lot 2611): Insoluble in HCl 0104%, PO_4 0.02, SO_4 0.003, Cu 0.03, Mn 0.003, and Zn 0.003.

[**] Specimen from Rio Marina, Island of Elba, Italy.

automatically typed for each reading. It was then punched on computer cards. These were fed to a CDC 6600 computer in order to apply the various correction factors necessary to convert counts to concentrations.

Specimens were prepared for the EPR studies in the same manner as for the diffusion studies. Portions of the Fe_2O_3-MgO specimens were either cleaved off or ground down in order to obtain varying concentrations of iron ions. Samples were also obtained from the diffusion zone of specimens analyzed by the microprobe in both the Fe-MgO and Fe_2O_3-MgO systems. MgO single crystals were also examined. The EPR data was obtained using a microwave spectrometer equipped with a 9 GHz klystron, a reflection cavity, and a crystal detection unit. The spectrometer was calibrated by observing the sample signals along with two standards: (a) A standard of $5 \times 10^{+14}$ spins of Cr^{+3} in MgO (g = 1.987), and (b) Diphenyl-picryl hydrazyl (D.P.P.H.) with a g value of 2.0037.

Optical absorption patterns were obtained on a number of the diffusion specimens from a wavelength of 250 mμ to 10μ. Two spectrometers were used: A Beckman IR-4 for the region 1-10μ, and a Cary 14 in the 250 mμ-1 region. Patterns were taken using the double beam mode thereby balancing out any peaks which may be due to gases, such as H_2O, CO_2, etc., in the paths.

Mathematical Analysis

The concentration vs distance profiles for the Fe-MgO and NiO-MgO diffusion couples were analyzed by the Boltzmann-Matano[1,4,33] approach to determine the diffusivity variation with concentration. Graphical

solution of

$$\int_0^{C_o} x dC = 0 \tag{1}$$

defined the plane at which $x = 0$ which is referred to as the Matano interface and corresponds to the original interface. With this value, $D_{c=c'}$ was calculated using a computerized graphical integration and differentiation of $c(x)$ using Eq. (2). The derivation of this equation is reported in the literature.[1]

$$D_{c=c'} = - \frac{1}{2t} \left(\frac{dx}{dc}\right)_{c=c'} \int_0^{c'} x dC \tag{2}$$

In the Fe_2O_3-MgO system, because of the appearance of the magnesio-ferrite phase, the solution of the diffusion equation becomes a three phase-two moving boundary problem with discontinuities in the diffusion profiles as illustrated schematically in Fig. 1b for the isothermal cut shown in Fig. 1a. The Boltzmann-Matano approach is not applicable. Appel[34] has provided a mathematical solution which surmounts this difficulty. The resulting counterpart of Eq. (1) to determine the $x=0$ plane, which can be referred to as the Matano-Appel interface, becomes

$$\int_0^{C_{I,II}} x dc + \int_{C_{II,I}}^{C_{II,III}} x dc - (C_{II,I} - C_{I,II}) \chi = 0 \tag{3}$$

where χ is the distance the boundary has moved and $C_{II,III}$ represents

Fe_2O_3 containing no MgO. For values of $C < C_{I,II}$ the diffusivities are

therefore obtained by straightforward integration of Eq. (2). For

values of $C > C_{II,I}$, however, the diffusivities are obtained by inte-

gration of the following equation

$$D_{c=c'} = -\frac{1}{2t} \left(\frac{dx}{dc}\right)_{c=c'} \left[\int_0^{C_{I,II}} xdc + \int_{C_{II,I}}^{c'} xdc - (C_{II,I} - C_{I,II})\chi\right] \quad (4)$$

This approach was applied to one of the diffusion profiles. The other

profiles were analyzed by a solution developed by Dorn and Blank[35]

which is an extension of Crank's solution[1] for a two phase moving

boundary case. In this solution the assumptions were made that the

diffusivity is not a function of concentration and that the boundary

did not move, i.e., the original interface is located at the boundary

$\bar{X}_{I,II}$. These assumptions are reasonable in this particular case because

the growth of the new phase was not excessive; calculations by the two

independent methods gave results which differed by less than a factor

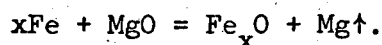of two for the same specimen. The solution is then

$$\frac{C_I}{C_{I,II}} = \left[1-\text{erf}\left(\frac{x}{2\sqrt{D_I t}}\right)\right] \quad (5)$$

from which D_I (Fe in MgO) was calculated. This value is therefore for

some average composition within the diffusion zone.

III. RESULTS

Fe-MgO System

In a vacuum and in the temperature range 1100-1350°C Fe entered MgO and Mg was removed by the reaction:

$$xFe + MgO = Fe_xO + Mg\uparrow.$$

A typical diffusion profile of Fe is shown in Fig. 2; no precipitates were observed. The relationship between ln D and a/o Fe at 1150, 1250, and 1350°C, shown in Fig. 3, is linear from about 1 to 2 a/o Fe to the Fe concentration at the interface, which was constant for all times at a given temperature; the diffusivity thus shows an exponential increase with Fe concentration. Because of the source of Fe there was no moving boundary on diffusion, and the actual and Matano interfaces are thus identical. The plot of ln D vs 1/T for several concentrations of Fe is shown in Fig. 4. It can be seen from the listed values that both D_o and ΔH^* increase with an increase of total Fe. The indicated trend in ΔH^* was opposite to that expected. Since ΔH^* is 30 kcal/mole in Fe_xO and 79 kcal/mole in MgO, the ΔH^* would be expected to decrease with Fe concentration rather than increase. This behavior suggested the occurrence of structural changes in the lattice. Investigations were then made of the NiO-MgO and Fe_2O_3-MgO systems.

NiO-MgO Systems

Figure 5 shows a typical diffusion profile of Ni in the NiO-MgO system obtained using single crystals in air at 1370°C for 335 hours. The Matano interface, at 290μ, which corresponds to the initial interface and represents the equal area point, lies on the high Ni side of the 25 a/o concentration point and thus indicates that a net mass flow of excess

Mg^{+2}, and an equivalent amount of $O^=$ ions, has occurred in this system. The result is a moving boundary. In the MgO single crystal-NiO powder couples the powders were sufficiently densified to obtain the entire diffusion profiles. The Matano interface in all cases was determined graphically, and the diffusivities were determined by the Boltzmann-Matano solution. The relationship between ln D and a/o Ni is shown and listed in Fig. 6. The D_o term varies by a factor of about 3-4 from 2-25 a/o Ni at a given temperature in contrast to a factor of about 100 for the same concentration range in the Fe-MgO system. Figure 7 shows the ln D vs 1/T plot and lists the values for D_o and ΔH^*. It can be seen that ΔH^* is not a function of composition, in contrast to the Fe-MgO system.

Diffusion studies of NiO-MgO in vacuum indicated that within experimental error the interdiffusivity at a given temperature was concentration independent. The measured diffusivities were 2.05×10^{-12} cm^2/sec at 1211°C, 5.5×10^{-12} at 1310°C, and 1.09×10^{-11} at 1400°C. The activation energy plot for these values is shown as line A in Fig. 7.

Fe_2O_3-MgO System

Figure 8 shows a typical computer-drawn diffusion profile of Fe in the Fe_2O_3-MgO couple heated in air at 1460°C for 42 hrs. The irregularities in the profile in MgO starting at approximately 1 a/o Fe represent ferrite precipitates formed on cooling. These increased in size as the Fe content increased. Since the limit of detection in the electron microprobe under the conditions used for analysis is estimated to be about 1μ, the smallest detectable precipitates at about 1 a/o Fe

are probably of this order of size. At about 890μ the concentration increases discontinuously to the atomic fraction of Fe in the ferrite; the value of about 0.32 instead of the 0.29 expected on the basis of $MgFe_2O_4$ indicates the presence of some Fe^{+2}. None of the profiles in this system indicated an excess of Mg beyond the stoichiometric amount in $MgFe_2O_4$. The peak in the profile at about 1000μ represents a Fe_2O_3 precipitate in the ferrite phase. Optical examination of diffusion specimens showed that the precipitates within the diffusion zone in MgO were coherent, and those in the ferrite zone, incoherent.

Diffusivities were calculated for an average composition within the diffusion zone for a number of temperatures ranging from 1020 to 1460°C according to Eq. (5). The relationship $\underline{D}$ = 8.83 3xp (-74.6 kcal/RT) was then determined from the Arrhenius plot shown in Fig. 9. This analysis did not provide a determination of any concentration dependence if it existed.

Figure 10 shows a complete Fe profile in a couple heated at 1300°C for 43 hours. The curve represents a smooth average plot with the precipitates not shown. The Matano-Appel interface calculated according to Eq. (3) is shown at 543μ.[*] The diffusivity in MgO and ferrite was calculated by use of Eqs. (2) and (4). This analysis indicated that the diffusivity in the MgO phase was 1.24×10^{-9} cm²/sec and was concentration independent; in the ferrite phase, the diffusivity was concentration dependent with an average value of 5.58×10^{-8} cm²/sec. The diffusivity obtained in the MgO phase using the Dorn-Blank solution with the assumption

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* Calculation performed by M. Appel in this laboratory.

of a concentration independent diffusivity was 6.5×10^{-10} cm^2/sec which compares favorably with the more accurate treatment. It would thus be expected that the ΔH^* would likewise be concentration independent in the MgO phase and concentration dependent in the ferrite phase.

A single crystal MgO(001) vs single crystal Fe$_2$O$_3$(0001) diffusion profile made at 1330°C for 162.5 hrs showed similar features. In this case X-ray diffraction analysis using the Laue' back reflection technique showed that the reaction zone of ferrite was a single crystal with its (100) face coincident with the (100) face of the MgO.

In some of the diffusion profiles Fe$_2$O$_3$ precipitates within the ferrite zone were observed to be in direct contact with the MgO single crystal zone. Since no Mg was noted in the Fe$_2$O$_3$ precipitates, they must not have been present during annealing and thus must have formed on cooling. A large solubility of Fe$_2$O$_3$ in MgFe$_2$O$_4$ at the annealing temperatures is therefore indicated. The diffusion profiles between the ferrite reaction layer and the Fe$_2$O$_3$ were also essentially discontinuous, being less than the effective beam diameter (3μ) which indicates essentially no solubility of MgO or MgFe$_2$O$_4$ in Fe$_2$O$_3$.

Electron Paramagnetic Resonance Studies

Figure 11 shows the EPR pattern at -160°C of the Norton single crystal MgO as received with an addition of DPPH (diphenyl-picryl hydrazyl) as a standard (g = 2.0037). The sextet of peaks is due to octahedrally coordinated Mn^{+2} (spectroscopic analysis shows 0.0015% Mn). Each peak is the central line of a group of 5 lines representing the 1/2 → -1/2 transition, and all should be of equal intensity. The g-value, at the center of the sextet, is reported as being at approximately

$g = 2.0014.$[36] The figure shows that the 4th $1/2 \to -1/2$ Mn^{+2} transition is significantly more intense than the other 5 with a $g = 1.98$. The pattern also shows a peak located at $g = 1.993$.

A standard sample of polycrystalline MgO with $5 \times 10^{+14}$ spins of Cr^{+3} ($g = 1.98$) showed a Cr^{+3} peak directly in line with the 4th Mn^{+2} peak. The anomalous intensity of this peak was thus considered to be due to the chromium impurity in the original MgO material (spectroscopic analysis shows 0.001% Cr_2O_3). Further studies showed that the peak located at $g = 1.993$ was due to Fe^{+3} in octahedral coordination. The introduction of small quantities of Fe^{+3} into these MgO crystals by diffusion in air caused the intensity of this peak to increase and the g value to shift to higher values. Lack of magnetism in specimens with less than 0.2 a/o Fe also indicated that the Fe^{+3} ions were on octahedral sites. Heating at 10^{-6} torr and 1200°C for 48 hrs caused the Fe^{+3} to disappear; the peak, however, was still present after heating at 1400°C for 1 hr and 35 min suggesting that the reduction was kinetic in nature and dependent on diffusion.

Specimens from the diffusion zone of a Fe_2O_3-MgO couple containing 0.20 a/o total iron (chemical analysis) showed similar behavior to the single crystals on heating in air and at low pressures, but with the g value for Fe^{+3} in the former case being at $g = 2.003$. Figure 12 shows the spectrum obtained from a section of crystal containing the entire iron profile inside the MgO. The important features are the relatively sharp transition at $g = 2.56$ and the very broad absorption starting at approximately 1000 gauss. The figure also shows the spectrum after reduction at 1300°C for 10 hours (10^{-6} torr). The transition at $g = 2.56$

has disappeared but the broad absorption band still persists but has shifted to the g = 2.44 region. Both specimens were ferrimagnetic, indicating that some of the tetrahedral sites in the crystal were occupied by Fe^{+3} ions and that these were not as easily reduced as Fe^{+3} in octahedral sites. The Curie point value was approximately 330-400°C which corresponded to ferrite. The Curie point for iron metal is 770°C.

From the overall EPR results the following assignments were made. The peak at g = 2.0037 which broadens and shifts to g = 2.56 is assigned to Fe^{+3} coordinated in a distorted octahedral site which shifts in g value because with increasing Fe concentrations it comes closer to the vicinity of ferrimagnetic centers. The field as seen by such an Fe^{+3} will be considerably different from that seen by an Fe^{+3} in a strictly paramagnetic environment. The ferrimagnetic centers tend to concentrate the external magnetic field, and the Fe^{+3} ions would therefore see a higher local field than that measured by the gauss meter. The broad peaks in Fig. 12 are thus assigned to the ferrimagnetic resonance peak of relatively large particles of ferrite.

EPR spectra were obtained on sections from the diffusion zone in the Fe-MgO system annealed at 1200°C in vacuum. These showed the presence of a small amount of octahedral Fe^{+3} and a broad ferrimagnetic resonance peak. The latter indicated that some of the Fe^{+3} ions were occupying tetrahedral sites.

Optical Studies

Optical absorption studies were also made in attempting to determine the species present in the diffusion zones. Figure 13 shows the absorption pattern obtained for MgO in the wavelength region of 0.300 to 2.4μ.

The spectrum was extended to 10μ but no significant features were found above 2.4μ. The figure also shows the spectra obtained for a specimen from the diffusion zone of a Fe-MgO couple run in vacuum which contained mostly Fe^{+2} and the same sample after heating in air for 48 hours at $1200°C$. The appearance of a large broad peak can be seen centered about the $0.9-1.0\mu$ region which deteriorated into a broad absorption zone; similarly, there is a significant increase in absorption below about 0.7μ which is significantly increased on oxidation. The peak centered about the $0.9-1\mu$ region is attributed to Fe^{+2} in octahedral coordination and the absorption occurring below the 0.7μ region is assigned to Fe^{+3} octahedrally coordinated. The general increase in absorption is probably due to the appearance of ferrimagnetic precipitates indicated in the EPR studies.

Figure 14 shows four optical spectra obtained with specimens from the Fe_2O_3-MgO diffusion couples. The lowest curve is for a specimen with 0.2 a/o Fe annealed at $1200°C$ in air. A small peak can be seen at about the 1.0μ region and the optical absorption below about 0.7μ is high. The spectrum labeled "reduced" is for the same specimen after heating at $1200°C$ for 48 hours at 10^{-6} torr. The peak has broadened with a general increase in absorption, and the absorption below 0.6μ has significantly decreased. EPR studies showed that no octahedral Fe^{+3} ions are present. The dashed spectrum marked "reoxidized" is again for the same specimen after reheating in air at $1200°C$ for 24 hours. The pattern marked "quenched" is for a specimen from a Fe_2O_3-MgO couple quenched from $1350°C$. The optical spectra show a considerable concentration of octahedral Fe^{+2} ions. The iron oxide material in contact with the MgO

crystal in the latter sample was found to be Fe_2O_3 and not Fe_3O_4. These observations support the fact that the nature of the Fe at temperature was different than that indicated at room temperature after slow cooling.

IV. DISCUSSION

Effect of Impurities on Diffusion Kinetics

It is known from diffusion studies on materials with the NaCl-type structure that as the vacancy concentration increases over the equilibrium concentration of thermally-created vacancies the activation energy changes from that in the intrinsic region ($\Delta H_m^* + 1/2\ \Delta H_f^*$) to that in the extrinsic or impurity controlled region (ΔH_m^*). Introduction of Fe^{+3} as impurity ions substitutionally on lattice sites in pure MgO results in chemically-created vacancies since one empty site forms for every two Fe^{+3} ions. It would then be expected that the activation energy for primarily Fe^{+2} diffusion would start at a value of about 79 kcal/mole and reach a minimum, equivalent to ΔH_m^*, as the concentration of chemically-created vacancies with additions of Fe^{+3} or other trivalent ions approaches and exceeds that of the thermally-created vacancies. The diffusivity, D_o, would be dependent upon the concentration of vacancies.

If, however, the trivalent ions, or Fe^{+3}, should assume interstitial or tetrahedrally-coordinated sites, the resulting effect would be a structural change since these are not normal lattice sites. The local structure would tend to that for the inverse spinel. The activation energy for diffusion of predominantly Fe^{+2} in such cases would be expected to be higher than that for the extrinsic region in MgO with

substitutions on octahedral sites.

The MgO single crystals that were available at the time of this work contained a total of 0.016 w/o of elements that could be present in a trivalent state. The lower limit of trivalent impurities, as set by Al, was 0.005 w/o. The corresponding calculated concentration of chemically-created vacancies was four orders of magnitude greater than the equilibrium concentration of thermally-created vacancies in pure MgO at 1200°C. The diffusion results on these crystals then must be in the extrinsic diffusivity region, and the activation energy values should be those for the heat of motion.

Fe-MgO System

Both ΔH^* and D_o in this system are concentration dependent. The ΔH^* values increase from about 29 kcal at 5 a/o Fe to 43 kcal at 20 a/o Fe. Literature reports indicate the appearance of some Fe^{+3} in this system and analytical studies of diffusion specimens with varying iron content suggest the appearance of some of these ions on tetrahedral or non-lattice sites in the MgO. These must form by reaction when some amount of Fe^{+2} enters the lattice. Examination of an MgO structural model indicates that the presence of a Fe^{+3} ion on a tetrahedral site would require the four adjoining, or nearest neighbor, octahedral sites to be empty in order to avoid extremely high cation-cation repulsive energies. The resulting defect can also be considered as an embryonic element of the inverse spinel structure, and thus as a potential nucleus for the formation of a $(Mg,Fe)Fe_2O_4$ precipitate on cooling. Let us now consider the effect of such an embryonic element on diffusion.

If all of the Fe^{+3} ions formed remained on octahedral sites, a vacancy would exist in the vicinity of each two Fe^{+3} ions. The bond strength between one Mg^{+2} and its coordinating O^{-2} would be only slightly increased due to the presence of the vacancy over that in pure MgO. Under these conditions the energy of motion of a vacancy in the system would not be expected to change significantly with increase of Fe^{+2} since the energy of motion of a Mg^{+2} ion would not be significantly altered. The diffusivity of Fe^{+2}, however, should increase due to the increasing number of vacancies. If a Fe^{+3} ion moves into a tetrahedral site (for an extended period of time as compared to its jump frequency), the resulting coordinated octahedral vacancies would have a pronounced effect on the bond strength of the nearby octahedrally coordinated Mg^{+2} ions. The Mg^{+2} coordinated with any of the four O^{-2} associated with the tetrahedral site could have their bond strength greatly increased. It could then be expected that the energy for motion of the Mg^{+2} ions would be increased. Since the number of tetrahedral Fe^{+3} ions increases with total Fe, this situation could then account for the increase in activation energy with increase in the Fe concentration. The diffusivity would also increase, as before, due to the increasing D_o term. Furthermore, the Fe^{+3} ions on tetrahedral sites would be expected to have considerably slower rates of diffusion than the Fe^{+2} ions; this fact plus their formation within the lattice would then account for the shape of the Fe diffusion profile.

NiO-MgO System

The diffusivity in this system is concentration dependent in an air atmosphere but essentially concentration independent in vacuum, and

the ΔH_m^* is essentially the same and concentration independent in both cases. These results indicate that the concentration of Ni^{+3} ions is small or non-existent in vacuum but of sufficient amount to result in a concentration dependence of the diffusivity by a factor of 5 in an air atmosphere. Since the ΔH_m^* is not concentration dependent, it is expected that all of the cations (Mg^{+2}, Ni^{+2}, Ni^{+3}) are substitutional and remain on octahedral sites. Hence, there is no structural change. Support is gained on the basis that no known compound exists in the NiO-MgO system.

An explanation for the higher ΔH_m^* of 42.8 kcal/mole in comparison with a value of about 29 for diffusion in the Fe-MgO system can be suggested on the basis of the octahedral preference energies for different cations in the spinel structure whose oxygen packing is similar to the MgO structure. The energy for motion of an ion should be related in some way to its relative stability or preference for octahedral and tetrahedral sites since an ion diffusing from one octahedral site to another must pass through a tetrahedral position. If the octahedral preference energy for an ion is high, the energy necessary to move it through a tetrahedral site should also be high. In this case the octahedral preference energy[37] for Ni^{+2} is considerably higher than that for Fe^{+2}.

Fe_2O_3-MgO System

The presence of concentration independent D_o and ΔH_m^* terms based on the diffusion profile in the MgO phase suggests the absence of a structural change with diffusion of Fe^{+3} into the MgO. It can then be

postulated that at the test temperature Fe^{+3} ions stay on octahedral

sites and that the diffusion mechanism is some complex cooperative

interdiffusion between the Mg^{+2} ions and two Fe^{+3} ions and a vacancy.

This complex mechanism accounts for the higher ΔH_m^* and also means that

the accompanying vacancies are not available for subsequent trivalent

diffusing species, hence the concentration independence of the dif-

fusivity. It can be further postulated that the small number of Fe^{+2}

ions that are formed, or enter the MgO phase from the ferrite, stay on

octahedral sites without affecting the Fe^{+3} on octahedral sites. In

the Fe-MgO system at low pressures, in contrast, the dominance of Fe^{+2}

ions leads to the formation of a small amount of Fe^{+3} ions which occur

primarily on tetrahedral sites leading to the development of structure.

On cooling the Fe_2O_3-MgO couples, precipitates of ferrite develop within

the diffusion zone by rearrangement of the cations with some of the

Fe^{+3} ions moving into tetrahedral sites, with possibly the existing

Fe^{+2} ions playing a key role.

Weight losses have been observed on heating Fe_2O_3 and MgO in air

to form ferrite.[22,38] These would be expected to be primarily due to

Fe^{+2} formation in the ferrite phase on the basis of the reported phase

relations.[30] Since there is essentially no solubility of MgO in Fe_2O_3,

interdiffusion of Mg^{+2} into Fe_2O_3 results in the formation of ferrite

which requires some of the Fe^{+3} ions to move into tetrahedral sites

with the adjoining octahedral sites vacant. Nearby octahedrally-

coordinated Fe^{+3} ions then do not have a sufficient number of vacancy

sites for local charge balance thus creating a driving force for re-

duction of Fe^{+3} to Fe^{+2} with the removal of oxygen atoms from the

surface. Reduction of tetrahedrally-coordinated Fe^{+3} is not as easy, as verified experimentally, since Fe^{+2} ions have a high octahedral preference energy. The concentration dependence of Fe diffusivity in the ferrite phase can thus be explained on the basis of a changing structure with change in composition.

V. SUMMARY AND CONCLUSIONS

The MgO single crystals used had a sufficient number of vacancies due to trivalent impurities to place the diffusion results in the extrinsic region. The activation energies determined in this study thus are those for motion, ΔH_m^*.

The results indicate that the diffusion characteristics are sensitive to the nature of the sites occupied by the incoming cations and that certain generalizations exist:

(a) If substitutional, octahedral or lattice sites are occupied, no structural changes occur and ΔH^* remains constant; and if the number of vacancies remains constant, then D_o also remains constant.

(b) If with the diffusing species a small amount of a species of a higher valence occurs but stays on lattice sites, then with increasing cation vacancies D_o increases and ΔH^* remains constant.

(c) If some of the small number of higher valence cations occupy interstitial, tetrahedral, or non-lattice sites, structural changes occur and ΔH^* changes (increases in this case); these structural changes also affect the number of cation vacancies and D_o likewise increases.

(d) If the principal diffusing species is of higher valence than the host lattice cation, the resulting vacancies are not available for subsequent cations because they must in some complex way move along

with the diffusion species in order to maintain electrovalence balance, e.g., two trivalent cations and a vacancy interdiffusing with three divalent cations. The three systems studied provide examples of all these possibilities.

The use of the electron microprobe provides an atomic concentration profile; it does not distinguish between different valences of an element. The valences of the cations and their distributions must be determined or inferred on the basis of chemical and physical information available for the system. In any case, however, a profile would be expected to be continuous at the test temperature; the precipitates existing in any profile thus must have formed on cooling by localized rearrangements and short distance movements because of the short times involved.

The NiO-MgO system had a concentration independent D_o term in vacuum and a concentration dependent D_o in air; the ΔH^* was essentially the same for both conditions. The principal diffusing species was Ni^{2+}; in air sufficient amounts of Ni^{+3} were formed which stayed on octahedral sites.

The Fe-MgO system in vacuum had Fe ions enter the MgO lattice by reaction and showed increasing D_o and ΔH^* values with an increasing concentration of Fe in MgO. The principal diffusing species was Fe^{+2}. In this environment Fe^{+3} was formed by reaction and its content was dependent on the amount of Fe^{+2}. Under these conditions at least some of the Fe^{+3} appeared to occupy interstitial or tetrahedral sites which corresponded to a structural change.

The Fe_2O_3-MgO system in air had an intermediate ferrite compound formed by reaction which had varying solid solutions of Fe_2O_3 and Fe_3O_4 depending on position relative to the reacting oxides; an excess of (Mg, Fe)O was not observed in any of the couples. Analysis of the Fe diffusion profile in the MgO phase indicated a concentration independent diffusivity and consequently also a constant ΔH^* term. The principal diffusing species was Fe^{+3} which apparently stayed on octahedral sites at the test temperature. Analysis of the Fe profile in the ferrite phase showed a concentration dependent diffusivity; presumably ΔH^* would also be concentration dependent. The principal diffusing species was Fe^{+3} probably on octahedral sites; structural complications, however, occur because some portion of the Fe^{+3} ions must be on tetrahedral sites in the ferrite phase and because some Fe^{+2} ions form by reaction which would stay on octahedral sites and contribute to the diffusivity.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. MgO-Fe$_2$O$_3$ Phase Diagram and Schematic Diffusion Profile for Three Phase Diffusion Problem.

Fig. 2. Typical Diffusion Profile in the Fe-MgO System in Vacuum.

Fig. 3. Diffusivity vs Iron Concentration at 1150, 1250 and 1350°C in the Fe-MgO System in Vacuum.

Fig. 4. Diffusivity vs Reciprocal Temperature for Several Iron Concentrations in the Fe-MgO System in Vacuum.

Fig. 5. Diffusion Profile in the NiO-MgO System in Air at 1370°C for 335 Hours.

Fig. 6. Diffusivity vs Nickel Concentration at Several Temperatures in the NiO-MgO System in Air.

Fig. 7. Diffusivity vs Reciprocal Temperature for Several Nickel Concentrations in the NiO-MgO System in Air.

Fig. 8. Diffusion Profile in the Fe$_2$O$_3$-MgO System in Air at 1460°C for 42 Hours.

Fig. 9. Diffusivity vs Reciprocal Temperature for the Fe$_2$O$_3$-MgO System in Air.

Fig. 10. Diffusion Profile in the Fe$_2$O$_3$-MgO System in Air at 1300°C for 43 Hours.

Fig. 11. EPR Spectrum at -160°C of MgO Single Crystal with DPPH.

Fig. 12. EPR Spectra at -150°C of Section of MgO Single Crystal Containing Entire Iron Diffusion Profile from an Fe$_2$O$_3$-MgO Couple, and of Same Specimen after Reduction.

Fig. 13. Optical Spectra of MgO Single Crystal and Specimen from Fe-MgO Couple as Run in Vacuum and after Heating in Air.

Fig. 14. Optical Spectra of Specimens from Fe_2O_3-MgO Couples.
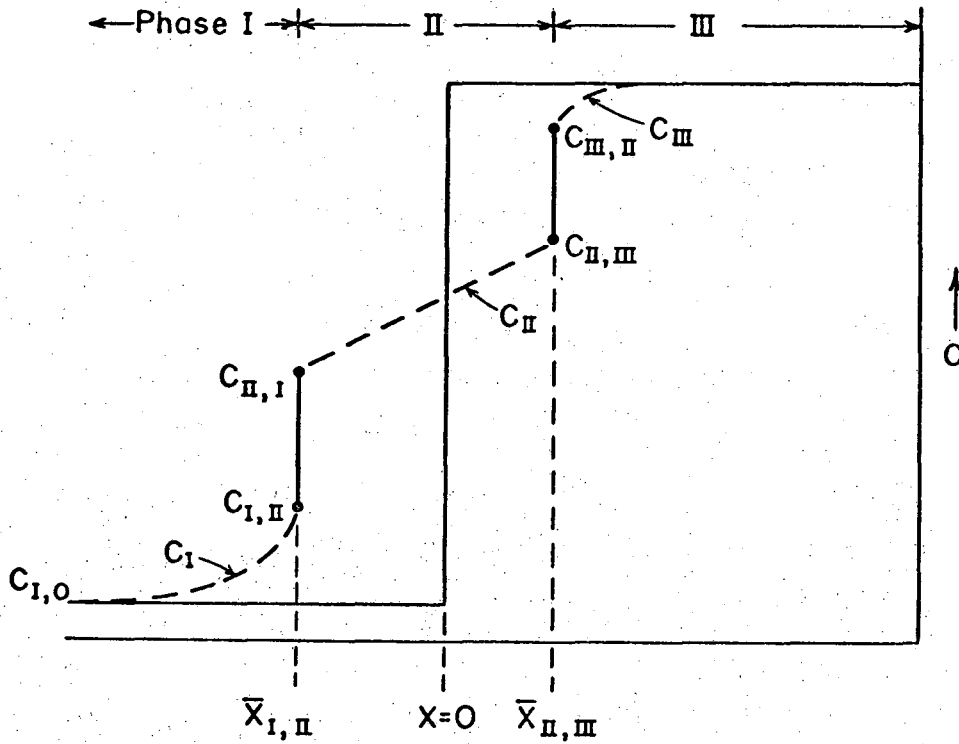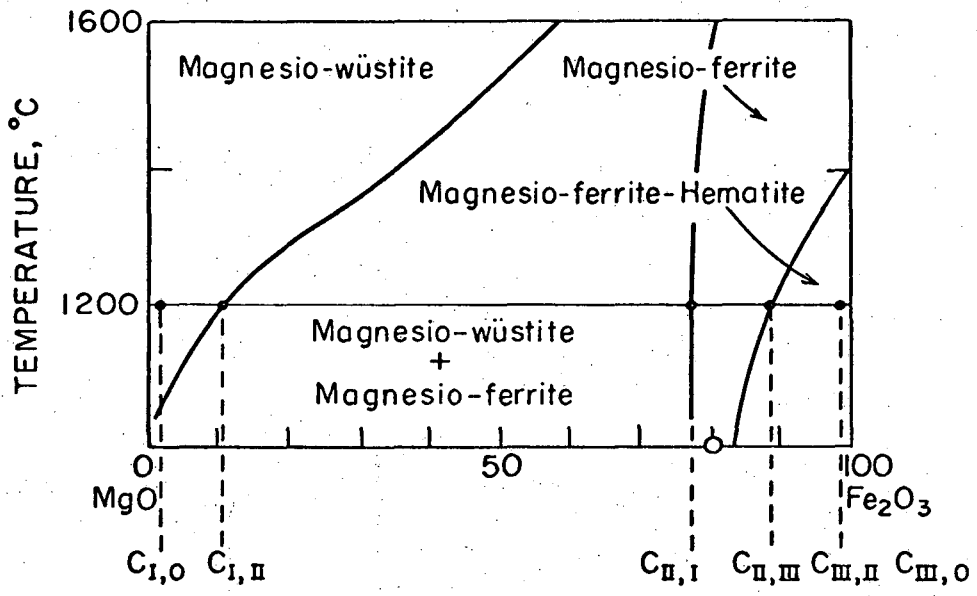
XBL 685-750

Fig. 1
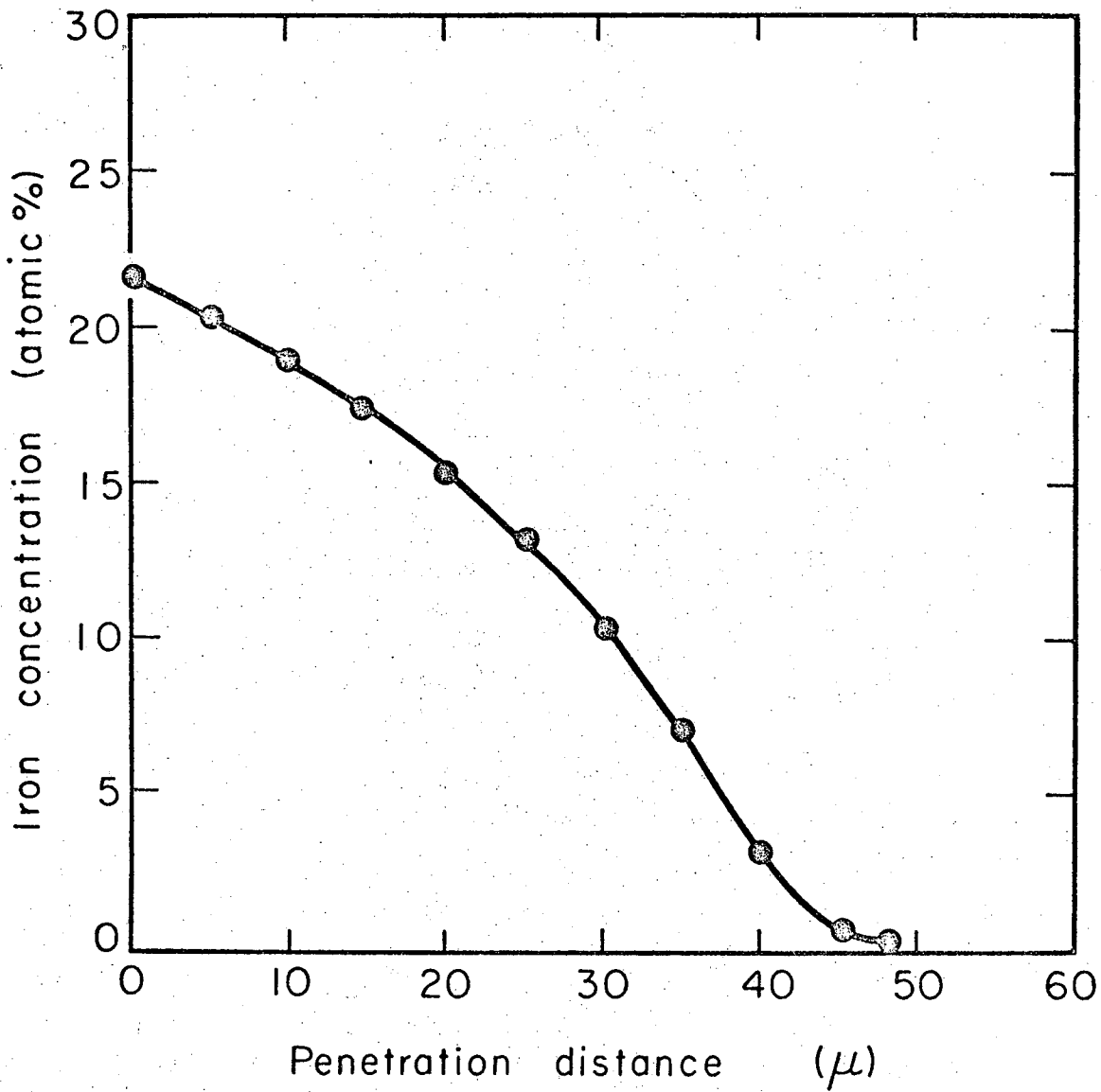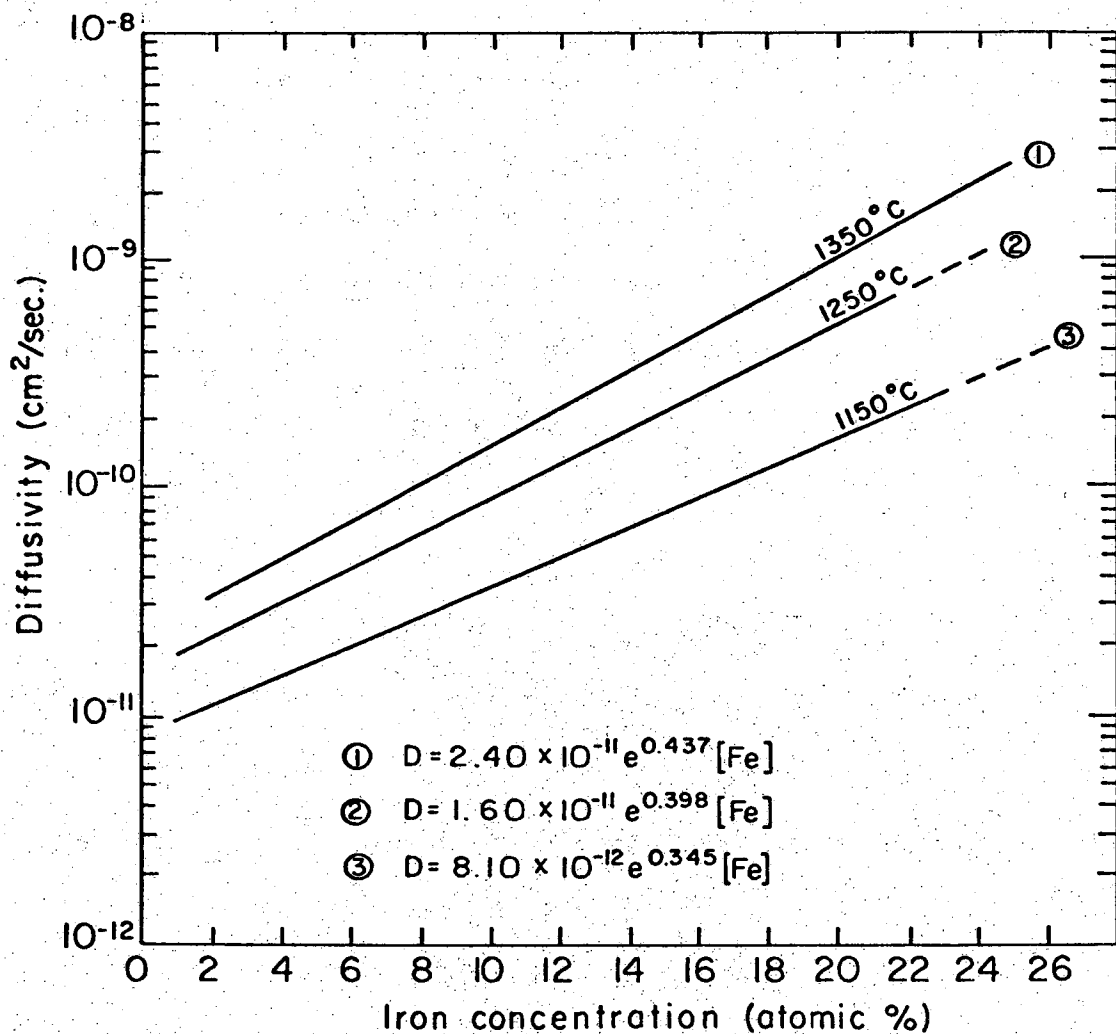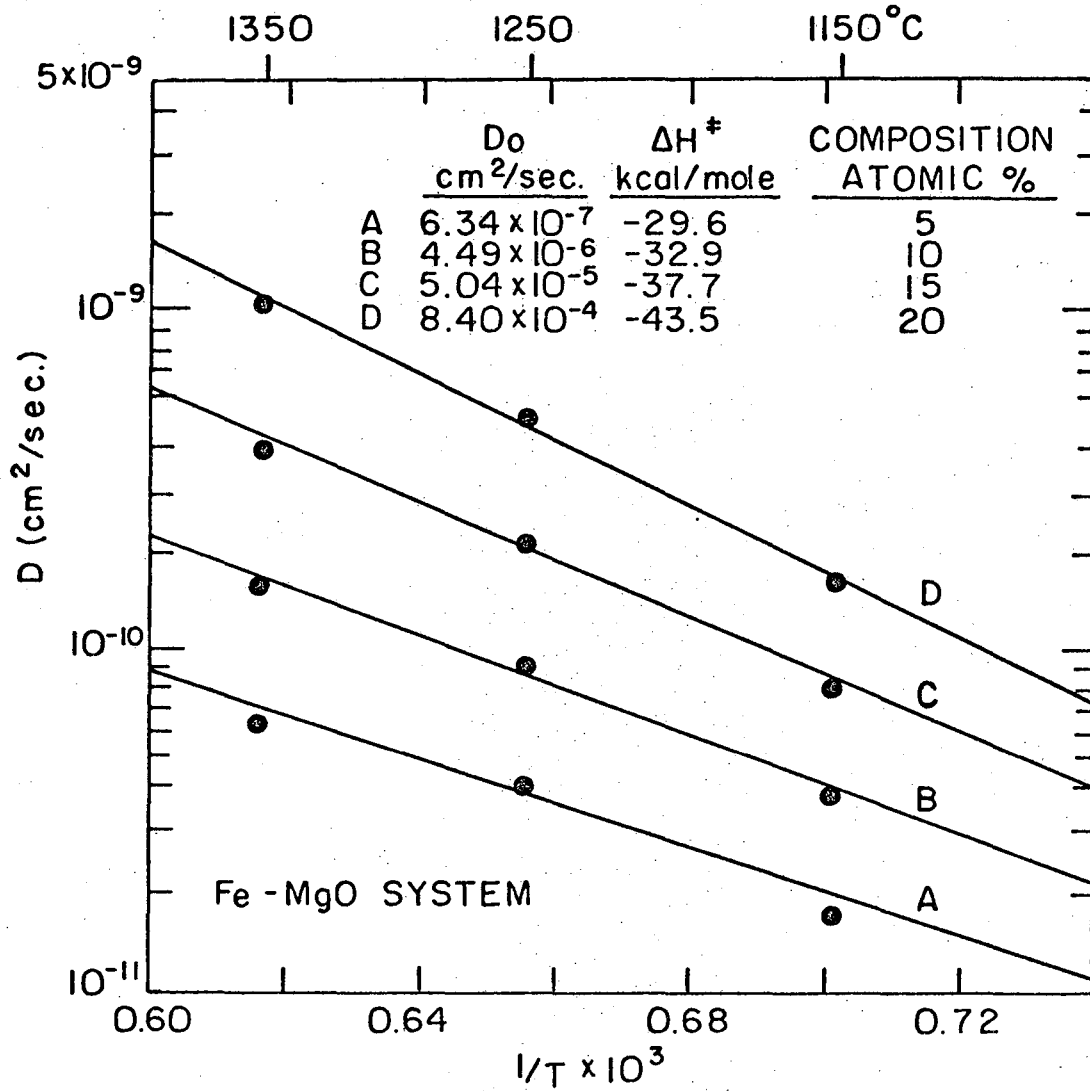
Fig. 2

MU-32845

Fig. 3

Fig. 4

XBL 674-1024
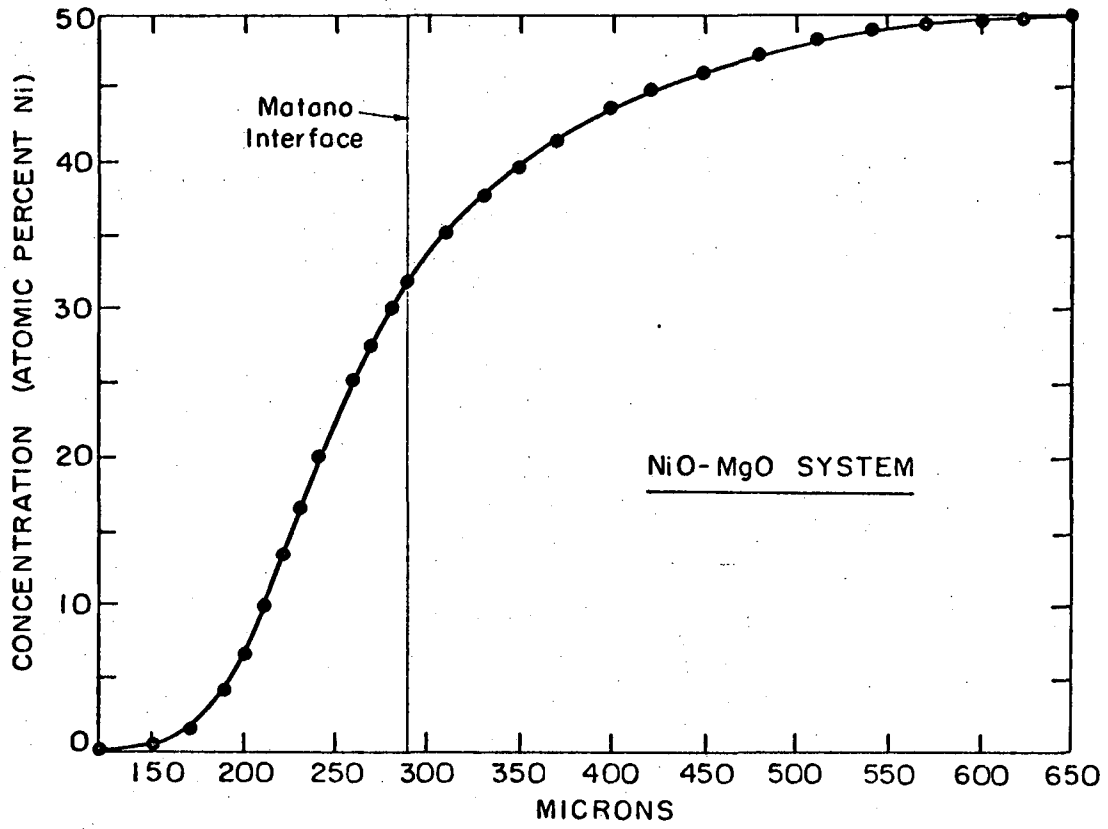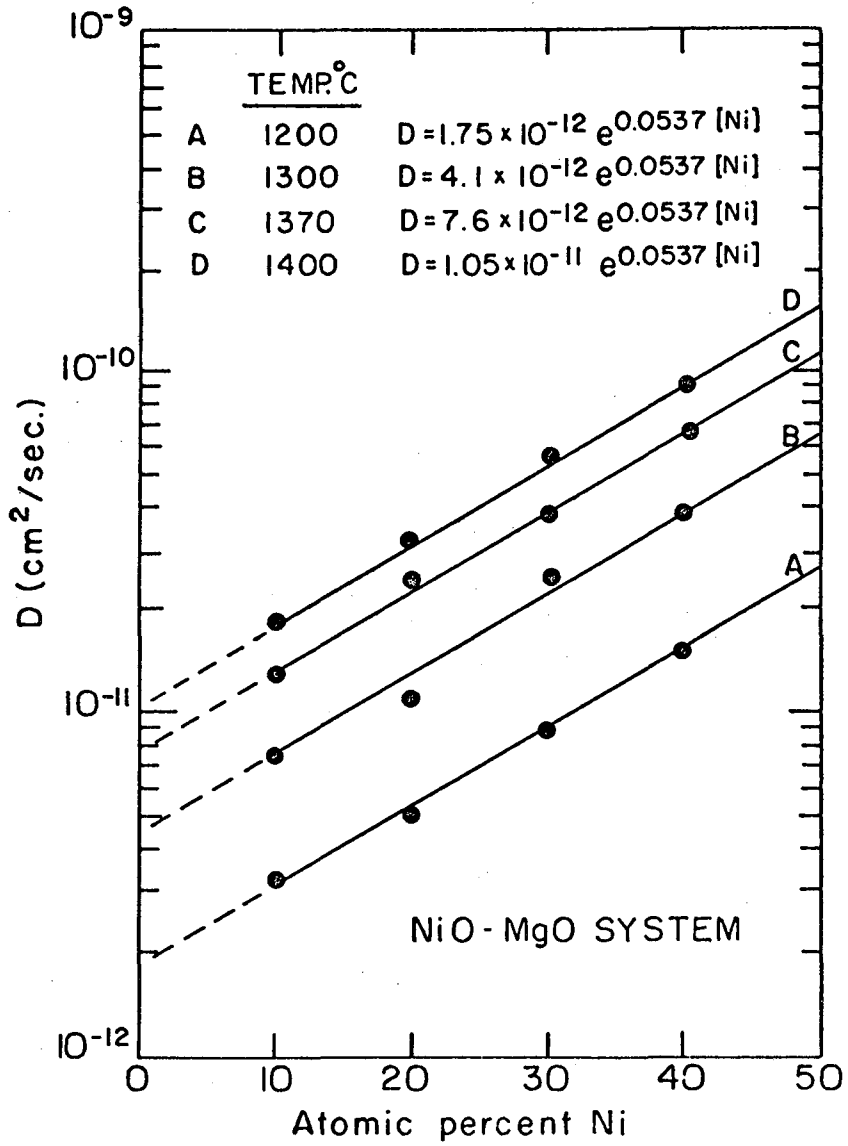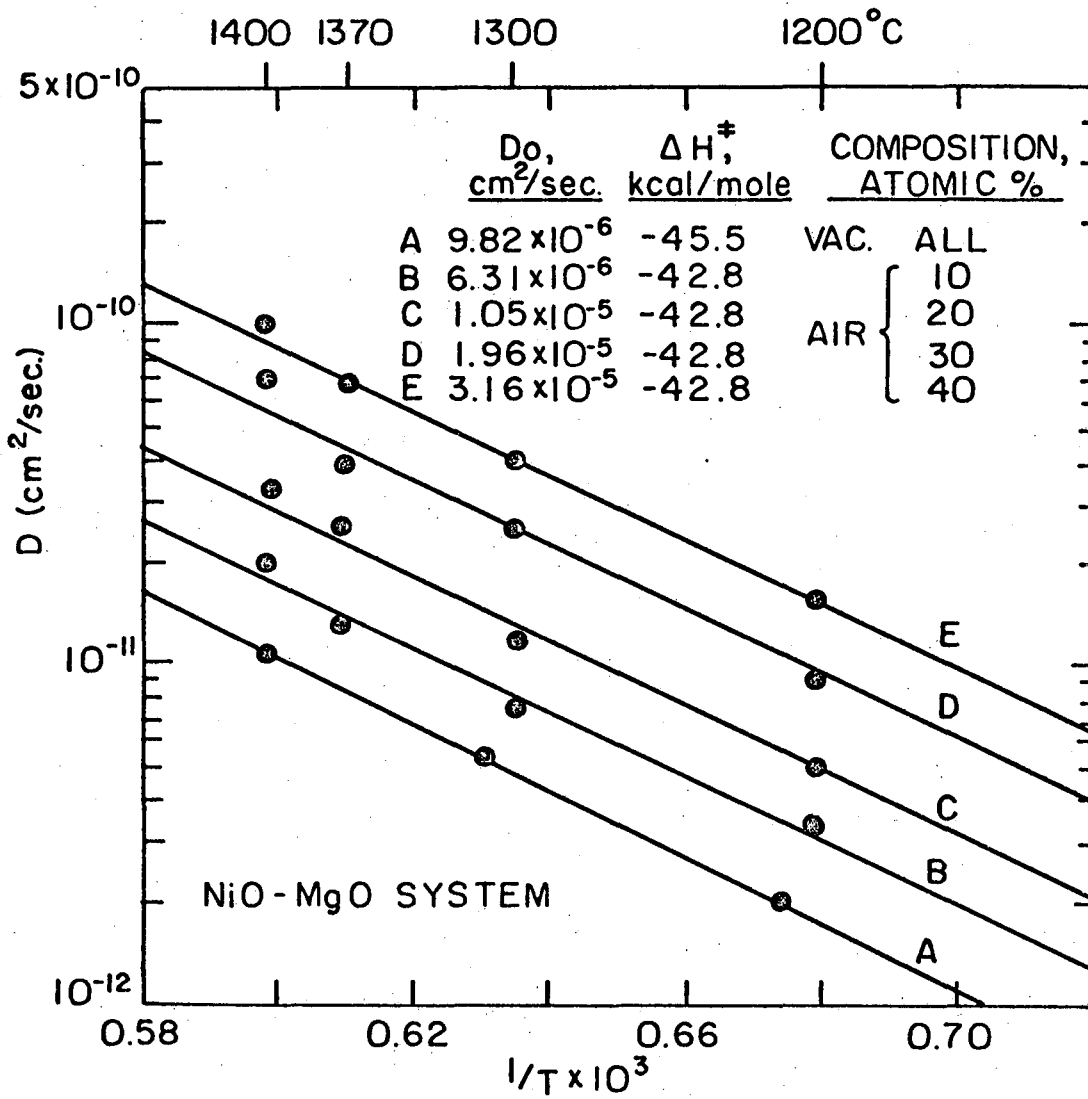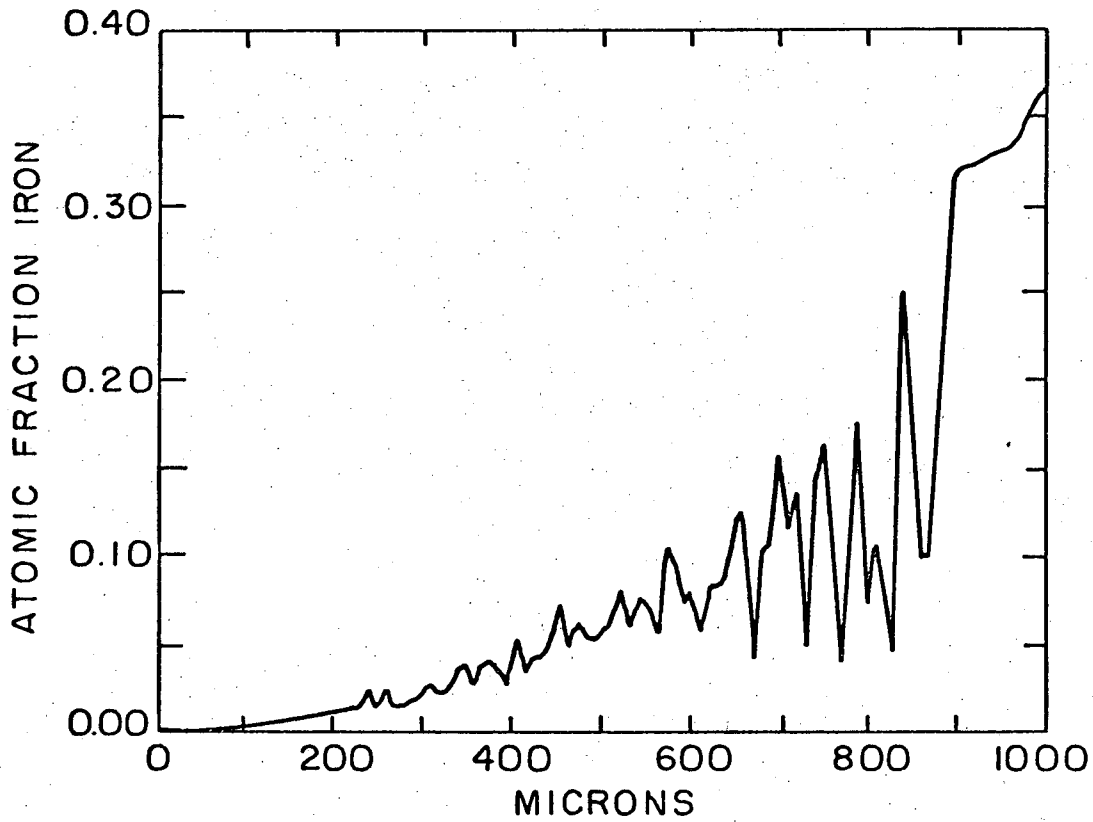
Fig. 5

Fig. 6

Fig. 7

Fig. 8

XBL 674-1028

$Fe_2O_3 - MgO$ SYSTEM

$D = 8.83 \exp(-74.6 \, k \, cal/RT)$

Fig. 9

Fig. 10

Fig. 11

XBL 685-751

g = 2.56

g=2.44
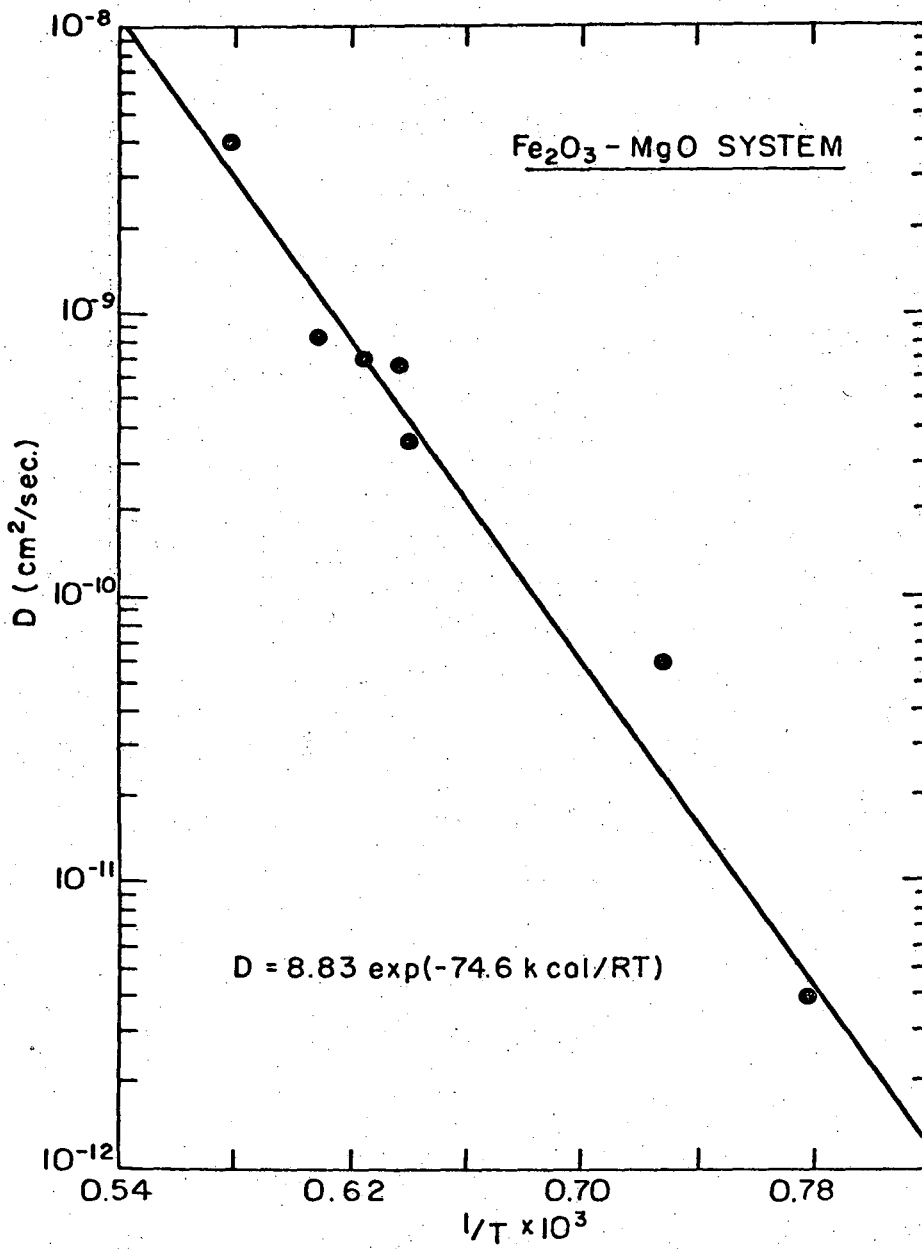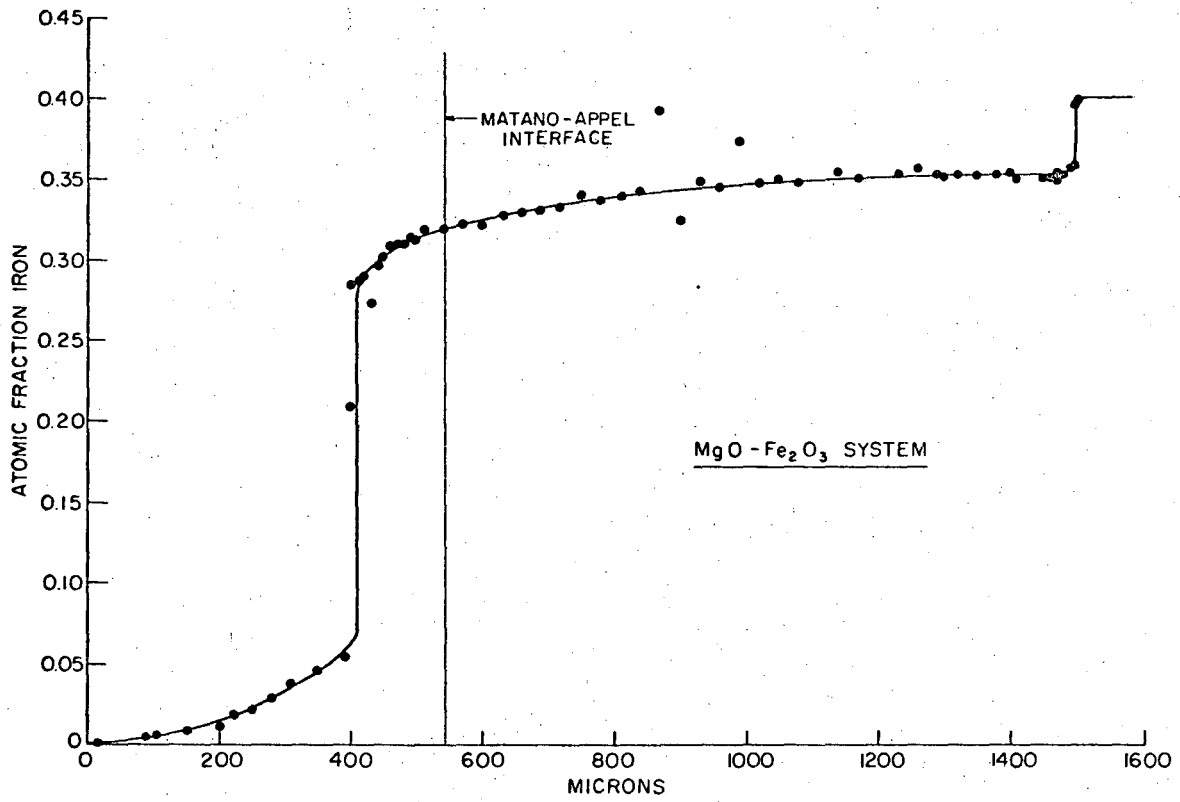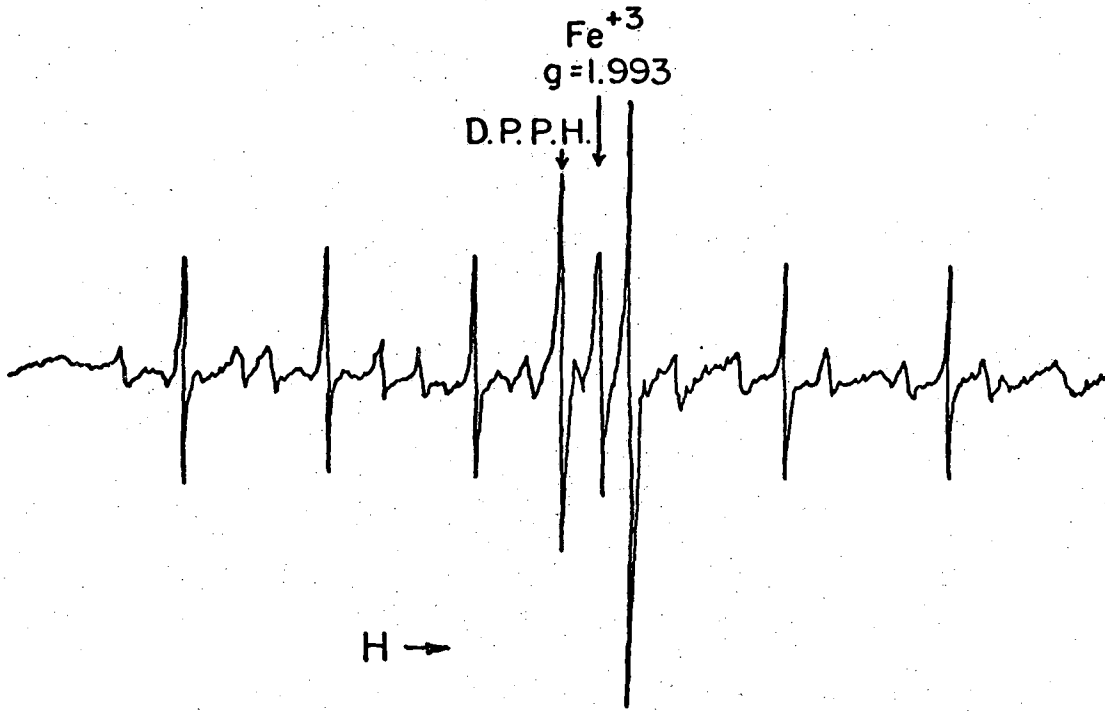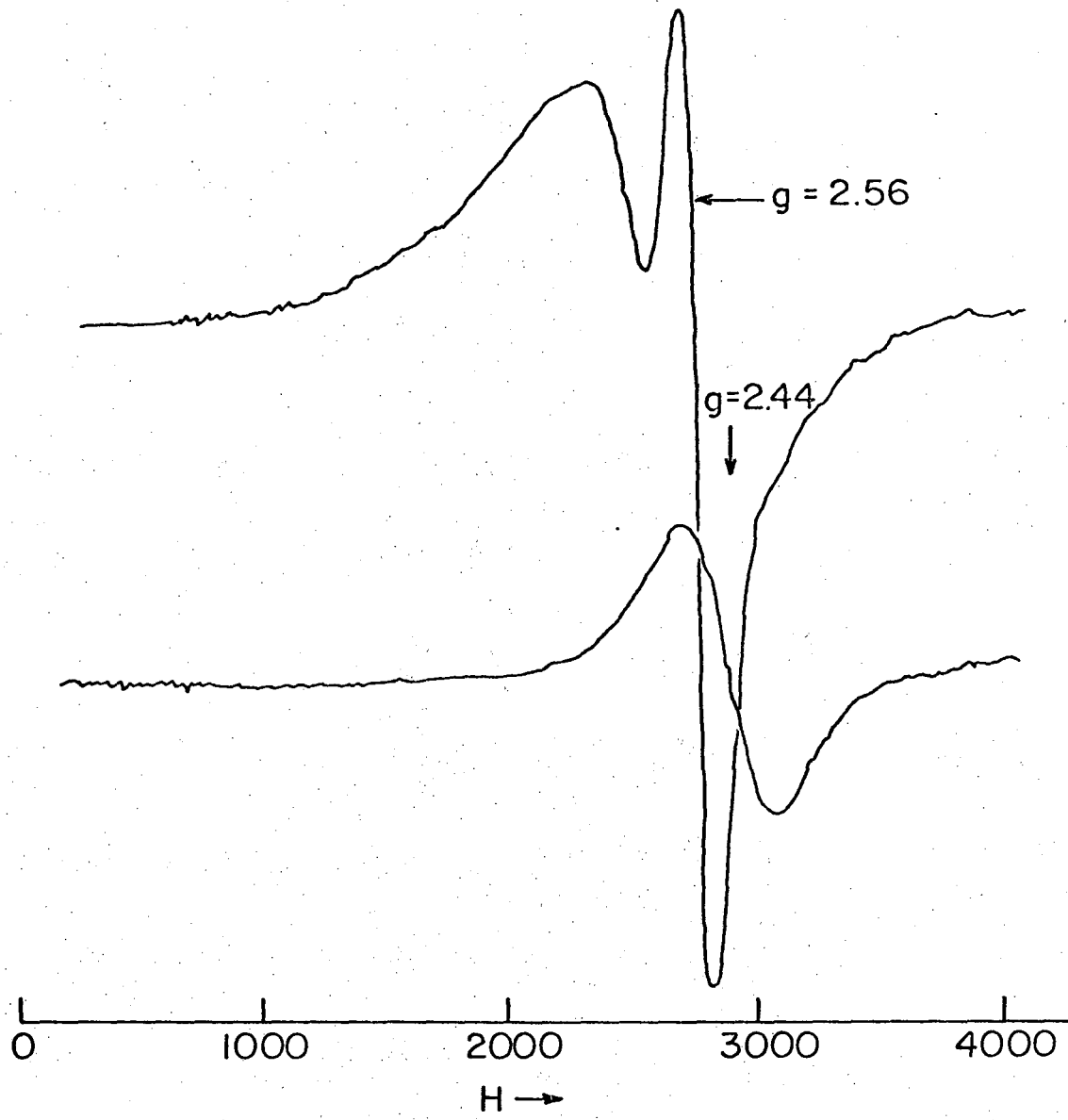
XBL 685-752

Fig. 12

XBL 674-1033

Fig. 13

Fig. 14