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Iron–magnesium alloying at high pressures and temperatures

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Abstract

At ambient pressure the solubility of magnesium in iron is very limited (of the order of 0.025 at.% in the liquid state), and vice versa. In a series of experiments using the piston–cylinder and multi-anvil apparatus at pressures up to 20 GPa and temperatures up to 2000 °C, we found an increase in the solid solubility of magnesium in iron up to 4 at.% Mg. The solution of magnesium in the bcc-structured Fe-based alloy increases the lattice parameter by approximately 2.4% with respect to that of pure iron.

1. Introduction

Magnesium is among the lightest of all the metals, and is also the sixth most abundant element on Earth [1]. It is ductile and the most machinable of all the metals [1]. Magnesium has a protective film, to protect against corrosion; however, chlorides, sulfates, and other chemicals can easily corrode it. Mg is principally used to make alloys with aluminium, lead, zinc, and other *nonferrous* metals [1]. The low density of magnesium ($\sim 1.74 \text{ g cm}^{-3}$), coupled with its favourable casting properties, makes it the material of choice for lightweight components [2]. Magnesium alloys are used in wrought form, including extruded bars, sections, and tubes, as well as forged material and rolled sheet. Several wrought alloys are based on the Mg–Al–Zn system and are used in a range of engineering applications. Magnesium-based alloy castings and wrought products make up about 20% of free-market magnesium shipments [1]. The brittleness of steels increases significantly if magnesium is present; hence care is normally taken to remove even trace amounts of Mg from commercially used iron alloys [3]. Iron or steel containers are conventionally used for melting magnesium and its alloys because iron has extremely low solubility in magnesium [4].

The complete Mg–Fe phase diagram has not yet been determined [4, 5]. The maximum solid solubility of Fe in Mg is 0.00041 at.% Fe, and according to [4], the Fe concentration at the eutectic point is estimated to be less than 0.008 at.%. Below 1000 °C the solubility of Mg in Fe is below the detection limit, while the maximum solid solubility of Mg in δ -Fe is approximately 0.25 at.% Mg at the monotectic temperature [5]. There is clear evidence

that magnesium and iron do not mix in the liquid state at ambient pressure [5]. At the same time, two close chemical analogues of iron, namely nickel and cobalt, do form intermetallic compounds with magnesium, and at high temperatures, they form solid solutions. Although the reason for such a dramatic difference in the behaviour of iron compared to cobalt and nickel is not clear, it raises the possibility that alloying of iron and magnesium may be more favourable under different conditions.

The potential alloying of iron and magnesium at high pressures and temperatures could be important for Earth sciences, based on the high abundance of both elements and the fact that the molten Fe-dominated core is surrounded by the Mg-containing mantle (in the form of complex oxides, where Mg-containing oxides are a primary component). The goal of our work was to investigate the effect of pressure on the solubility of magnesium in iron.

2. Experimental details

As starting materials we used chemically pure powders of Fe (99.999%) and Mg (99.999%) supplied by Alfa Inc.

Experiments at pressures below 4 GPa were conducted using an end-loaded piston–cylinder type apparatus [6]. The sample material was loaded into 6 mm diameter, 13 mm long MgO capsules (sample area 3 mm diameter, 6 mm long) which were placed into 1/2 inch talc–Pyrex sample assemblies. These sample assemblies contained an internal, tapered, graphite resistance furnace to ensure minimal temperature gradients along the length of the capsule. The temperature gradients are estimated to be less than 25 °C for the experimental conditions used [7]. Pressure was calibrated against the quartz–coesite and kyanite–sillimanite transitions, as well as the melting point of diopside, and pressures are considered accurate to within less than $\pm 5\%$ of the stated value. Temperatures were measured with a Pt–Pt_{10%}Rh thermocouple. No correction for the effects of pressure on the thermocouple EMF was applied. Experiments involved pressurization to within 90% of the desired run pressure, and then heating at 200 °C min⁻¹ to the final run temperature before the full pressurization. Run pressures and temperatures were continually monitored and maintained for the duration of the runs. Experiments were quenched isobarically by turning off power to the heating circuit, and quench rates are estimated to be of the order of 200 °C s⁻¹.

At 20 GPa experiments were performed using a 5000-tonne multi-anvil press [8]. We used mixtures of pure Fe and Mg powders in various proportions as starting materials (table 1), and the samples were contained in a MgO capsule. The sample assembly consisted of a MgO (+5 wt% Cr₂O₃) octahedron (18 mm edge length) containing a LaCrO₃ heater. The octahedron was compressed using 54 mm tungsten carbide anvils with a truncation edge length of 11 mm and pyrophyllite gaskets. Temperature was monitored with a W₃Re/W₂₅Re thermocouple located axially with respect to the heater and with the junction close to the MgO capsule. The *P–T* uncertainties are estimated to be ± 1 GPa and ± 50 K, respectively. In each experiment the sample was first compressed to the desired pressure, and then the temperature was raised at ~ 100 K min⁻¹ to the desired run temperature. The heating duration was 20 min. The samples were either quenched by switching off power to the furnace, or gradually cooled at a rate of ~ 10 K min⁻¹, and then slowly decompressed. Upon completion of each experiment the capsule was carefully removed and the treated material was mechanically cleaned. Samples from the 5000-tonne press came out as compact solid cylinders approximately 1.8 mm in diameter and 3 mm in length.

The homogeneity, chemical composition, and texture of the samples were analysed using a LEO-1530 scanning electron microscope, and a Cameca Camebax electron microprobe with a beam of 1–2 μm operating at an accelerating voltage of 20 kV and a beam current of 18 mA.

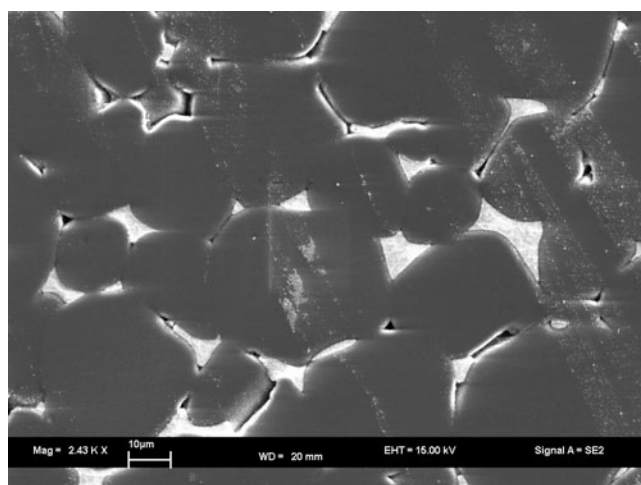


Figure 1. A SEM secondary electron image of the polished quenched product of the experiment on Fe–Mg (50:50 at.%) mixture treated for 15 min in a piston–cylinder apparatus at 1 GPa and 1700 °C ('Expt 2'). White particles are Fe–0.3 at.% Mg alloy, and dark grey particles are magnesium.

Table 1. Summary of experimental details.

Expt	Chemical composition of initial mixture	Apparatus	P, T conditions	Duration of heating (min)	Phases observed	Analytical methods
1	50% Fe, 50% Mg	Piston–cylinder	1 GPa, 1000 °C	20	α -Fe, Mg, MgO	SEM, micro-probe, XRDA
2	50% Fe, 50% Mg	Piston–cylinder	1 GPa, 1700 °C	15	α -Fe-max. 0.3 at.% Mg, MgO, Mg	SEM, micro-probe, XRDA
3	50% Fe, 50% Mg	Piston–cylinder	3.5 GPa, 1700 °C	10	α -Fe-2.2(5) at.% Mg, MgO, Mg	SEM, micro-probe, XRDA, Mössbauer
4	96% Fe, 4% Mg	Piston–cylinder	3.5 GPa, 1700 °C	23	α -Fe-1.8(2) at.% Mg, MgO	SEM, micro-probe, XRDA
5 ^a	50% Fe, 50% Mg	Multi-anvil	20 GPa, 2000 °C	20	α -Fe-4.5(5) at.% Mg, MgO, Mg, new Mg-rich phase	SEM, micro-probe, XRDA, Mössbauer
6	92% Fe, 8% Mg	Multi-anvil	20 GPa, 2000 °C	20	α -Fe-4.1(1)at.% Mg, MgO	SEM, micro-probe, XRDA

^a This represents two experiments performed at the same conditions except for the rate of cooling: the first run was with quenching, while the second run was with gradual cooling at the rate $\sim 10 \text{ K min}^{-1}$. The cooling rate did not influence the results.

X-ray powder diffraction data were obtained using a STOE STADI P diffractometer (Co $K\alpha$ radiation, 40 kV, 30 mA). Mössbauer spectra were recorded at room temperature (293 K) in transmission mode on a constant acceleration Mössbauer spectrometer using a nominal 370 MBq ^{57}Co high specific activity source in a 12 μm Rh matrix (point source). The velocity scale was calibrated relative to 25 μm α -Fe foil using the positions certified for

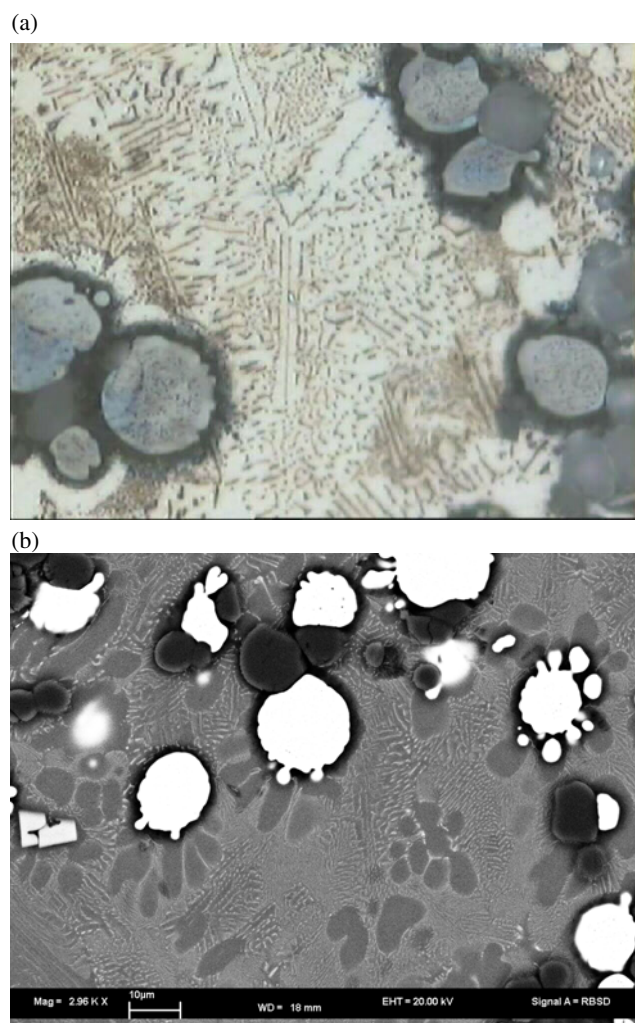


Figure 2. An optical micrograph (a) and a SEM backscattered electron image (b) of the polished quenched product of the experiment on Fe–Mg (50:50 at.%) mixture treated for 10 min in a piston–cylinder apparatus at 3.5 GPa and 1700 °C (‘Expt 3’). White spherical particles are Fe–2.2(5) at.% Mg, dark grey spherical particles are MgO, and the grey matrix is magnesium.

(This figure is in colour only in the electronic version)

National Bureau of Standards standard reference material No 1541; linewidths of 0.36 mm s^{-1} for the outer lines of α -Fe were obtained at room temperature. Mössbauer spectra were fitted to Lorentzian lineshapes using the commercially available fitting program NORMOS written by R A Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

3. Results

We conducted a series of experiments at pressures up to 20 GPa and temperatures up to 2000 °C using piston–cylinder and multi-anvil type apparatus to investigate the possible alloying of magnesium and iron at high pressures and temperatures (table 1).

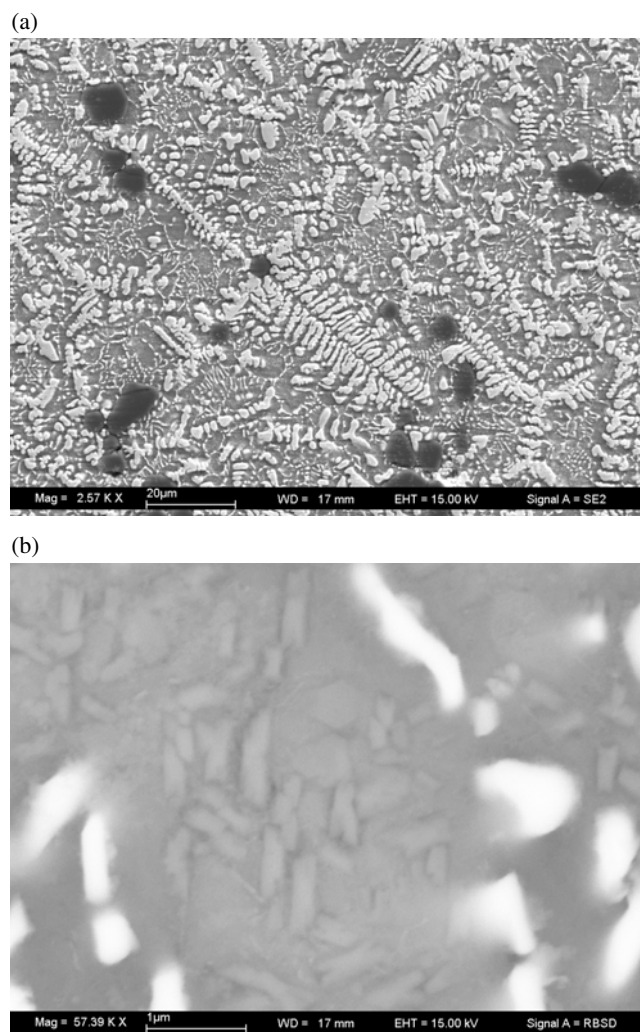


Figure 3. A SEM secondary electron image (a) and an enlarged SEM backscattered electron image (b) of the sample formed from Fe:Mg (50:50 at.%) mixture after treatment in the multi-anvil apparatus for 20 min at 20 GPa and 2000 °C ('Expt 5'). Light-coloured dendrites are Fe–4.5(5) at.% Mg alloy, dark grey spherical particles are MgO, and the light grey matrix with crystals (see the enlarged image) is a Mg-rich alloy/compound.

At 1 GPa and 1000 °C there was no detectable evidence of alloying between iron and magnesium ('Expt 1'). Similar to the results obtained at ambient pressure [5], after heating the Fe–Mg mixture (50:50 at.%) at 1 GPa and 1700 °C ('Expt 2'), the run products contained pure magnesium and iron with up to 0.3 at.% Mg (figure 1). X-ray powder diffraction data showed the presence of α -Fe, hexagonal magnesium, and periclase MgO, which implies that the oxygen fugacity in our experiment was controlled by the Mg/MgO buffer.

Figure 2 shows optical micrograph and SEM images of the polished quenched product of the experiment on the Fe–Mg (50:50 at.%) mixture reacted for 10 min in a piston–cylinder apparatus at 3.5 GPa and 1700 °C ('Expt 3'). There are clear textural differences between the

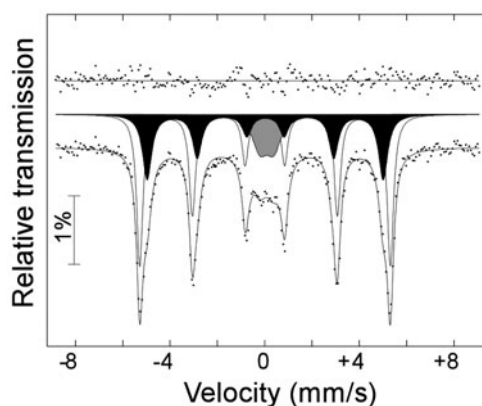


Figure 4. The room temperature Mössbauer spectrum of the material recovered after treatment at 20 GPa and 2000 °C ('Expt 5'). Subspectra are assigned to a non-magnetic Mg-rich alloy/compound (grey doublet) and alloy (black sextet). The unshaded sextet shows hyperfine parameters close to those for pure iron, and may correspond to iron atoms in the Fe-4.5(5) at.% Mg alloy with no Mg next-nearest neighbours.

samples recovered from experiments at 1 GPa (figure 1) and at 3.5 GPa (figure 2). Both MgO and iron-rich particles appear as spherical droplets in the material treated at 3.5 GPa. While there is no detectable amount of iron in magnesium, iron-rich droplets contain 1.7–2.7 at.% of Mg. The lattice parameter of this α -Fe-based alloy is 2.8686(5) Å, while the lattice parameter of pure α -Fe is 2.8665 Å [9].

Annealing the Fe–Mg (50:50 at.%) mixture for 20 min in the multi-anvil apparatus at 20 GPa and 2000 °C ('Expt 5') resulted in the formation of a distinct texture in the quenched material (figure 3). An iron-rich phase with 4–5 at.% Mg forms dendrites, while the matrix consists of a mixture of MgO plus a Mg-rich alloy or compound. Chemical analysis of the mixture is difficult due to submicron grain sizes. X-ray powder diffraction data show the presence of non-reacted Mg and MgO in the sample, consistent with the Mg/MgO buffer controlling oxygen fugacity. The lattice parameter of the bcc-structured Fe–Mg alloy is 2.8733(4) Å, which is significantly higher ($\sim 2.4\%$) than the lattice parameter of pure α -Fe. The Mössbauer spectrum of the sample can be fitted to two magnetic sextets plus a quadrupole doublet (figure 4). The doublet ($CS = 0.09(2) \text{ mm s}^{-1}$; $QS = 0.58(5) \text{ mm s}^{-1}$) is assigned to the non-magnetic Mg-rich alloy or compound, and while one magnetic sextet shows hyperfine parameters close to those for pure α -Fe ($CS = 0.10(1) \text{ mm s}^{-1}$; $B = 32.8(5) \text{ T}$), the other shows a magnetic hyperfine field that is distinctly different ($CS = 0.09(1) \text{ mm s}^{-1}$; $B = 30.9(9) \text{ T}$). The two magnetic sextets could correspond to a single-phase Fe-rich alloy containing 4–5 at.% Mg, where the local magnetic environment of iron atoms differs depending on the number of Mg next-nearest neighbours.

Experiments on the 50:50 at.% Fe–Mg mixture indicate that a significant amount of Mg (2–5 at.%) can dissolve in iron at pressures higher than 3.5 GPa. To verify these observations, we conducted additional runs at 3.5 GPa and 1700 °C on a 96:4 at.% Fe:Mg mixture using a piston–cylinder apparatus ('Expt 4'), and at 20 GPa and 2000 °C on a 92:8 at.% Fe:Mg mixture using a multi-anvil press ('Expt 6'). As recorded by SEM images of the samples recovered after the experiments (figure 5), uniform alloys are found that contain 1.8(2) at.% Mg (at 3.5 GPa) and 4.1(1) at.% Mg (at 20 GPa). X-ray powder diffraction of the alloys (figure 6)

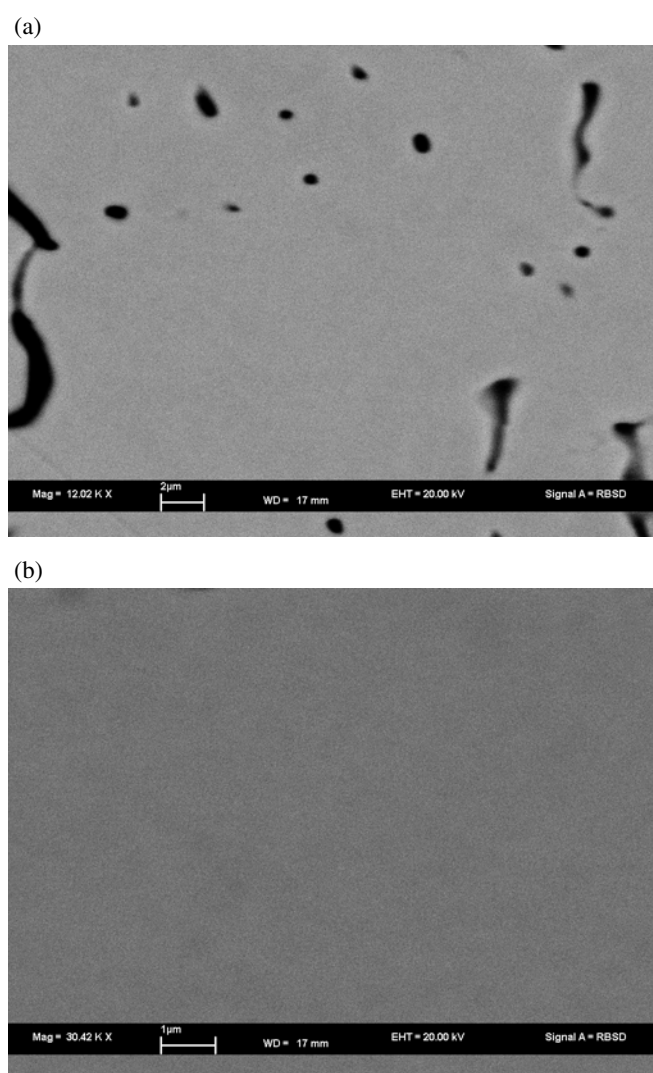


Figure 5. SEM backscattered electron images of the materials obtained by treatment of Fe:Mg (96:4 at.%) mixture in a piston–cylinder apparatus at 3.5 GPa and 1700 °C (‘Expt 4’) (a) and 92:8 at.% Fe:Mg mixture in a multi-anvil press at 20 GPa and 2000 °C (‘Expt 6’) (b).

confirmed their phase homogeneity. As mentioned above, incorporation of magnesium results in lattice expansion of the bcc-structured alloy (up to approximately 2.4% for a concentration of 4 at.% Mg).

4. Conclusions

It is usually assumed that the geometric factor, namely the large difference in atomic size of iron and magnesium, is responsible for the immiscibility of these two metals (at ambient conditions the molar volume of α -Fe is 7.09 cm³ compared to that for Mg of 14.00 cm³). We have demonstrated, however, that at high temperatures and relatively moderate pressures

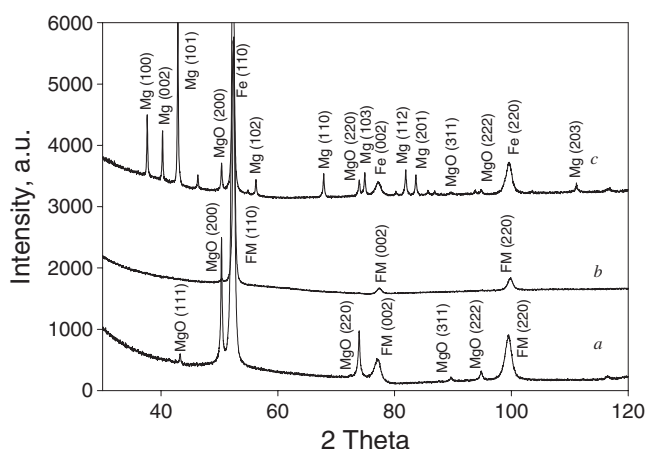


Figure 6. X-ray diffraction patterns of the samples prepared from a mixture of iron and magnesium powders in the atomic ratios 96:4 (*a*) and 92:8 (*b*) ('Expt 4' and 'Expt 6'). In both cases magnesium was partly oxidized and formed periclase (MgO). 'FM' marks reflections from the Fe–Mg alloy. The diffractogram for the sample synthesized from Fe–Mg (50:50 at.%) mixture treated for 15 min in a piston–cylinder apparatus at 1 GPa and 1700 °C ('Expt 2') (*c*) shows the presence of α -Fe, hexagonal magnesium, and periclase MgO.

(20 GPa), it is possible to synthesize a homogeneous iron–magnesium alloy with up to 4 at.% Mg.

Acknowledgments

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References

- [1] Aune T K, Haug A T, Hustoft O-M, Kittelsen B, Mezoff J G, Olsen A L, Oymo D and Westengen H 1998 *Magnesium Alloys* ed F Habashi (New York: Wiley–VCH) pp 151–64
- [2] Busk R S 1986 *Magnesium Products Designs* (New York: Dekker)
- [3] Properties and selection: non-ferrous alloys and pure metals *Metals Handbook* 1979 vol 2 (Metals Park, OH: American Society for Metals)
- [4] Haitani T, Tamura Y, Motegi T, Kono N and Tamehiro H 2003 Solubility of iron in pure magnesium and cast structure of Mg–Fe alloys *Mater. Sci. Forum* **419–422** 697–702
- [5] Nayeb-Hashemi A A, Clark J B and Swartzendruber L J 1985 Iron–magnesium *Bull. Alloy Phase Diagr.* **6** 1076–8
- [6] Bromiley G D and Keppler H 2003 An experimental investigation of hydroxyl solubility in jadeite and Na-rich clinopyroxenes *Contrib. Mineral. Petrol.* at press
- [7] Bromiley G, unpublished results
- [8] Dubrovinsky L, Dubrovinskaia N, Langenhorst F, Dobson D, Rubie D, Geßmann C, Abrikosov I and Johansson B 2003 Iron–silica interaction at extreme conditions and the nature of the electrically conducting layer at the base of earth's mantle *Nature* **422** 58–61
- [9] Kohlhaas R, Duenner P and Schmitz-Pranghe N 1965 Ueber die Temperaturabhaengigkeit der Gitterparameter von Eisen, Kobalt und Nickel im Bereich hoher Temperaturen *Trans. Metall. Soc. Am.* **233** 1519–25