

liquids and glasses

Are there clusters in Fe-Ni-S molten alloys?

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We have performed a neutron diffraction study on molten alloys of Fe-Ni and Fe-Ni-S systems searching for evidence of clustering in these liquids, which are supposed to be constituents of the Earth's outer core. The presence of clusters could explain the observed anomaly in sound propagation. Although we have found large structural differences on adding sulphur to Fe-Ni alloys, we have not found any evidence of clustering, and the question about the origin of the anomaly in the sound velocity remains open.

The present understanding

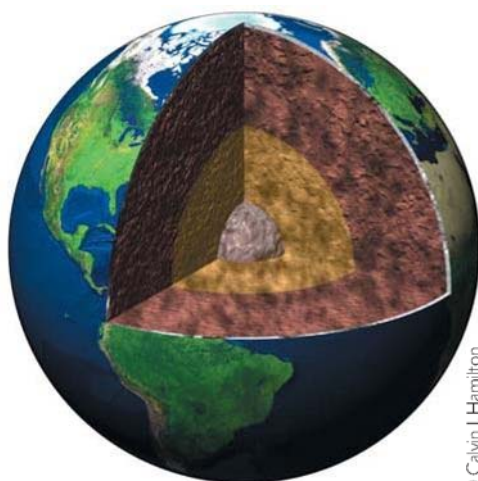
of the nature of the inner core of planets identifies light alloying elements as necessary ingredients to explain a wealth of seismic data. The outer liquid core of the Earth is less dense than bulk iron [1]; several light elements (e.g., O, S, Si and C) have been suggested as possible alloying elements, which upon dissolving in liquid Fe in the outer core can account for its lower density. Special attention was paid to the characterisation of thermal and mechanical properties of mixtures such as Fe-Ni sulphide alloys, since their accurate knowledge is required as input for thermo-mechanical models of the planetary cores.

This kind of result is relevant also to studies of solar system formation and comparative planetology. The Earth, Io, Ganymede and Mars seem to be the only bodies in the solar system for which a metallic core has been directly detected either by means of seismic waves or by measurements of the gravitational field. Given their relative locations in the solar system, this remarkable similarity must be accounted for in theories of the solar system's origin and evolution.

A highly anomalous behaviour has been recently reported [2] on the ultrasonic sound velocity and attenuation in the mixture 85%Fe-5%Ni-10%S for temperatures above the melting point up to 2000 K under its saturated vapour pressure. In fact, and contrary to data for the pure liquid-metal components [3], the acoustic velocity for such a sample increases with temperature, whereas in molten Fe, Ni and S it decreases. The existence of some form of microscopic aggregation is postulated as a

plausible explanation for the observed acoustic anomaly [2]. In fact, some electronic properties of the pure liquid components are shown to be deeply affected by the presence of elements such as Si or S [4], something that is expected to lead to substantial changes of structure. If such "molecular" units exist in the liquid as a consequence of some sort of S-induced rearrangements, then the break-up of these units with increasing temperature could explain the increase in sound velocity as well as the anomalous behaviour of its attenuation.

We have performed on D4 (the liquid and amorphous diffractometer at the ILL) a neutron diffraction study of the liquid mixtures referred to above within the temperature range 1700 - 2000 K aiming to



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Figure 1: Artistic view of the Earth's interior.

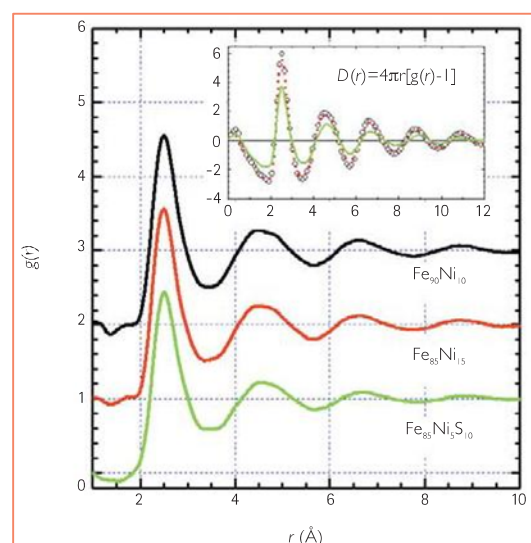


Figure 2: Pair correlation functions and density functions (inset) for the three samples.

detect significant differences of structure at scales of a few tens of Å's. The obtained pair distribution functions show the presence of significant oscillations that reveal rather long-ranged density correlations extending up to distances as long as 15 Å (figure 2). The most remarkable feature here is the closeness of the phases of all three weighted pair distribution functions for distances smaller than 6 Å, as well as the notable differences exhibited by the $\text{Fe}_{85}\text{Ni}_5\text{S}_{10}$ samples with respect to the two binary alloys above such a cut-off value.

The radial distribution functions, the integral of which measures the number of particles within a volume element defined by a sphere of a given radius, show significant differences between all three samples. In fact, a rough estimate of the differences in microscopic densities is provided by integrals of such functions using as upper limits their local minima that are located at about 3.3 Å and 5.6 Å. The particle numbers obtained are 13.7, 12.6 and 12.2 corresponding to the first peak of $\text{Fe}_{90}\text{Ni}_{10}$, $\text{Fe}_{85}\text{Ni}_{15}$ and $\text{Fe}_{85}\text{Ni}_5\text{S}_{10}$, respectively.

To understand in greater detail the observed trends in terms of particle configurations, we have carried out a set of Reverse Monte Carlo simulations [5]. For such a purpose we have constructed simulation cells containing 20000 atoms with proportions corresponding to the three compositions. Several starting configurations were chosen. First we chose a random configuration of all the atomic species with the only imposed constraint being that the distance between all atoms can-

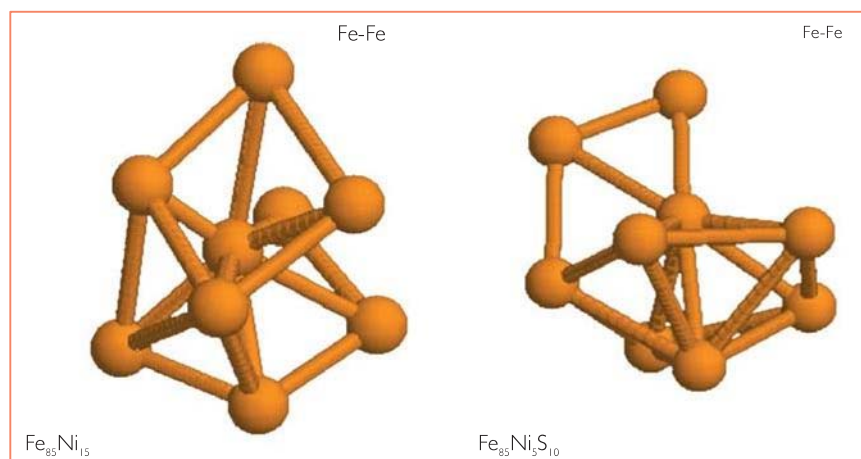


Figure 3: Two snapshots of the Fe environment as obtained from Reverse Monte Carlo simulations.

not be less than 1.8 Å. A second set of simulations was carried out for the Fe-Ni-S sample where the initial configuration consisted of all sulphur atoms arranged in S–S pairs and S–S–S triplets. In all cases the initial configurations were later modified following a Monte Carlo strategy [5] so that the calculated structure functions fitted the experimental neutron diffraction patterns. This algorithm adequately reproduces the experimental observations in terms of particle configurations which give plausible atomic structures compatible with the observed structure factors.

No significant S–S correlations were found in $\text{Fe}_{85}\text{Ni}_5\text{S}_{10}$ after extensive searches over many particle configurations and initial conditions. Our present data, and the subsequent analysis on the basis of Reverse Monte Carlo results, are consistent with a fully randomised distribution of S atoms over the whole metallic Fe-Ni matrix. Moreover, no clear signature of a well defined S–S bond is seen, either as a molecular form-factor contributing to

$S(Q)$ at large Q values, or as an identifiable peak appearing at about 2 Å in the static correlation function. This finding is in apparent contrast with the conjecture of formation of long aggregates of “molecular” S and their break down with increasing temperature as a main mechanism to explain ultrasound data [2]. On the other hand, our results are in line with first-principles calculations [6], where no tendency to polymerisation of S was found.

Our data show that relevant structural details of alloys suspected to be present within the Earth's outer core can be derived by means of neutron diffraction. This opens the way for future experiments using isotopic substitution in order to derive first hand experimental information on the partial pair correlation functions. The present data suggests rather well defined Fe–S bonds, possibly of a covalent character, although the binding strength does not seem to be high enough to consider such units as “molecules”.

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