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Journal of Alloys and Compounds 452 (2008) 140–142

Journal of ALLOYS AND COMPOUNDS

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High frequency collective excitations in molten Fe/Ni alloys studied by inelastic neutron scattering

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Received 18 September 2006; received in revised form 1 December 2006; accepted 1 December 2006
Available online 20 January 2007

Abstract

The spectra of liquid 85%Fe5%Ni10%S ($T_m = 1650$ K) and liquid 85%Fe15%Ni have been studied by means of inelastic neutron scattering. Our aim was to explore at high frequencies some observed anomalies as reported from ultrasound studies. Contrary to the behavior of the pure liquid-metals, the phase velocity of the observed excitation for the sulfur-containing sample increases with temperature while their damping decreases. On the other hand, data of the binary Fe/Ni alloy do not show such an anomalous behavior.
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Keywords: Inelastic neutron scattering; Collective dynamics

1. Introduction

The available evidence from seismological sources as well as relevant planetological data measured by spacecraft probes [1] point towards the metallic liquid nature of the outer cores of several planetary bodies. The current knowledge of their composition identifies light alloying elements as necessary ingredients in addition to Fe and Ni to explain a wealth of seismic data [2]. Liquid Fe and FeNi alloys as well as those of the same mixture with the addition of elements such as O, Si or S have being extensively investigated, especially at high temperatures and pressures [3], trying to emulate the conditions of planetary interiors.

From tests on Earth models against shock-wave pressure-density and compressibility data at high pressure, Birch et al. [2] pointed out that the outer liquid core of the Earth was less dense by about 10% than bulk iron within the 133–330 GPa pressure range. At pressures of 330–364 GPa, a density close to that of pure iron matches models of the Earth [4]. To account for this change in density, the presence of a light element in the FeNi alloys is assumed. Among the possible candidates, special attention was paid on FeNi sulfide alloy.

Our interest on these molten alloys was awaken from a paper by Nasch et al. [5] that has reported a highly anomalous behavior of the ultrasonic sound velocity $c_v(T)$ and attenuation $a(T)$ in the mixture 85%Fe5%Ni10%S for temperatures above melting (T_m =1650 K) up to 2000 K under its saturated vapor pressure. In fact and contrary to data for the pure liquid-metal components [6], the sound velocity for such a sample increases with temperature with a rate of $\mathrm{d}c/\mathrm{d}T = 0.625\,\mathrm{m\,s^{-1}\,K^{-1}}$at 2000 K. This figure is to be compared with the decrease of the sound velocity with temperature for pure elements [6]. On the other hand, the quantity actually reported in Ref. [5], which is inversely proportional to the attenuation per wavelength, decreases with increasing T at a rate which can be estimated as $0.033\,\mathrm{K^{-1}}$. Hydrodynamically, the main contributions to acoustic attenuation are the longitudinal viscosity and a heat-conduction term. The former quantity comprises bulk and shear viscosities. Again, the temperature dependence of the viscosity of the pure metals decreases with increasing temperature [6]. On such a basis the existence of some form of microscopic aggregation is postulated as a plausible explanation for the observed acoustic anomaly [5]. In fact, some electronic properties of the pure liquid components are shown to be deeply affected by the presence of elements such as

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doi:10.1016/j.jallcom.2006.12.148

Si or S [7], something which 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 breakup of these units with increasing temperature will explain the increase in sound velocity as well as the anomalous behavior of the attenuation.

2. Experimental details

Two samples with compositions $\mathrm{Fe_{0.85}Ni_{0.15}}$ and $\mathrm{Fe_{0.85}Ni_{0.05}S_{0.10}}$ were prepared by the Metallurgical Laboratory, Centro Atómico Bariloche, Argentina. The alloys were prepared from high-purity Fe, Ni and FeS in an arc furnace, on a water-cooled copper hearth, using nonconsumable electrodes under a 350-Torr Ar atmosphere. The samples were held within an Alumina container of 35 mm width and of 3 mm thickness. These dimensions were calculated in order to have ~20% the incoming neutrons scattered and/or absorbed by the sample account made of the neutron scattering and absorption cross sections of the studied samples, $\sigma_s = 12.61$ barns and $\sigma_{abs} = 2.84$ barns, respectively for the FeNi sample, and $\sigma_s = 10.21$ barns and $\sigma_{abs} = 2.32$ barns, respectively for the FeNiS sample. Both samples were studied within the liquid state. The liquid was obtained by heating the sample up to its melting point, inside a Nb furnace. The experiment was carried out on the hot three axis spectrometer IN1, at the Institut Laue Langevin (ILL). The optimal conditions yielding maximum flux and relatively high resolution in energy transfers were found to be those employing a Cu(3 3 1) monochromator and a Cu(4 0 0) analyser, using horizontal collimations of $20'$–$20'$–$20'$–$20'$. The experiment was carried out at a constant final wavevector $k_f = 8.5$ Å^{-1}. The energy-resolution for this configuration was a Gaussian of 4.1 meV, full width at half maximum. The isothermal sound velocities of liquid FeNi and FeNiS have been estimated from the low-Q region of the structure factors $S(Q)$ and the values are 3242 and 2741 m/s, respectively. All the excitations were reached when working at this k_f. The sample was placed inside a vacuum box (pressure $\lesssim 10^4$ mbar) preventing scattering from air. The sample was heated up to ~1750 K at a rate of 450 °C/h. Melting was monitored as Bragg peaks from the crystalline sample disappeared from elastic scans which yield a rough estimate of the static structure factor, $S(Q)$. When melting was achieved a broad liquid peak appeared at $Q \simeq 3$Å^{-1}, which corresponds to the first diffraction peak of the liquid [9]. Several scans at constant Q versus energy transfer were carried out from 0.6 up to 1.4 Å^{-1} for the FeNi sample and up to 1.1 Å^{-1} for the FeNiS sample. Above $Q = 1.1$ Å^{-1} the excitations were overdamped in both samples.

3. Experimental results

After performing the corresponding corrections (direct beam and instrumental background subtractions), the measured data $I(Q, \omega)$ can be written as,

$$I(Q, \omega) \propto S(Q, \omega) \otimes \Re(Q, \omega) + b, \tag{1}$$

where $\Re(Q, \omega)$ is the spectrometer resolution function defined by a Gaussian of standard deviation of 1.74 and b is a background term. The dynamical structure factor $S(Q, \omega)$ contains the information of the liquid dynamics and can be modeled in term of a quasielastic contribution (central part of the spectrum) and a purely inelastic one,

$$S(Q, \omega) = S_{\mathrm{q.el}}(Q, \omega) + S_{\mathrm{inel}}(Q, \omega). \tag{2}$$

The quasielastic part, $S_{\mathrm{q.el}}(Q, \omega)$, provides information of the stochastic processes and has two contributions, one arising from the mass diffusion and the other from the paramagnetic contribution. The widths of the latter contribution were obtained after the fitting procedure, giving values between ~50 meV

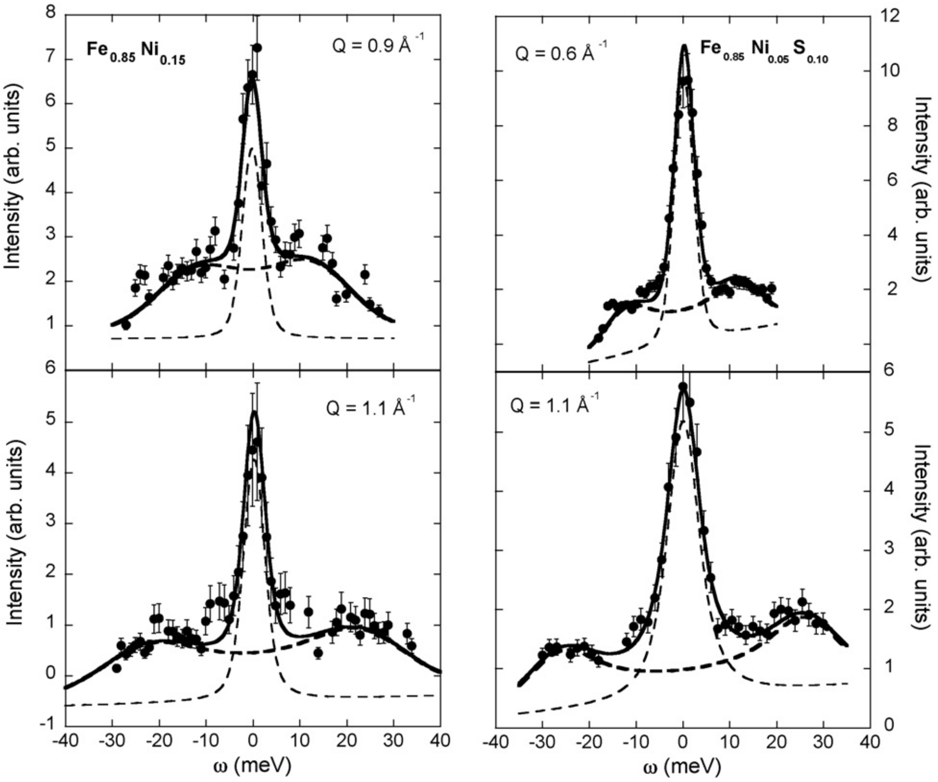

Fig. 1. Several fitted spectra for liquid FeNi and FeNiS. Experimental data are shown by solid symbols. The model instensities $I(Q, \omega)$ are described by the solid line. The quasielastic component centered at the elastic line is shown by the thick dotted line. The inelastic component is shown by the thin dotted line.

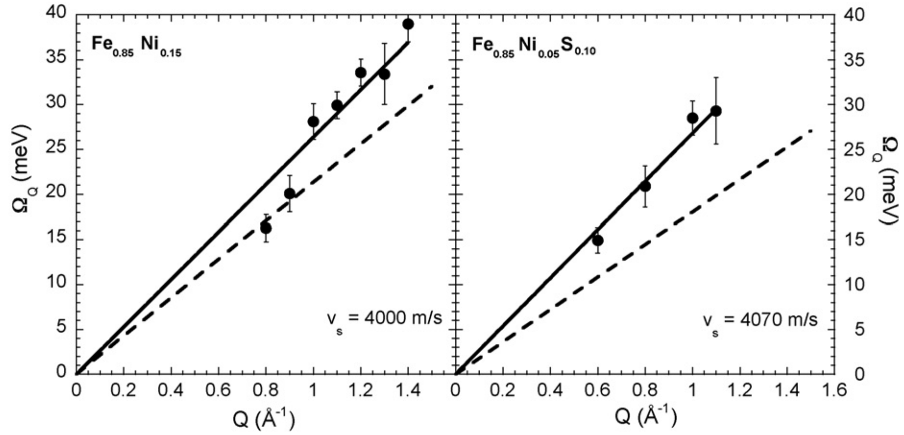

Fig. 2. Dispersion curves for liquid FeNi and FeNiS. Solid symbols represent the frequency of the phonon excitations. The solid lines show fits to the wave-vector dependences described in the text. The dashed lines show the hydrodynamic linear dispersion.

for the lowest wave vector measured and ∼150 meV for the highest Q value. These values agree with those obtained by Tajima et al. [8] and contribute to the measured spectra as a constant background. The inelastic contribution, $S_{\text{inel}}(Q, \omega)$, contains information about collective dynamics and is modeled in terms of a damped harmonic oscillator (DHO). Fig. 1 shows a set experimental and fitted spectra, where the excitations can be clearly seen at both sides of the elastic line.

From the wavevector dependence of the parameters obtained after fitting the experimental results with Eq. (2), ω and Γ, the excitation velocity and the damping coefficient are obtained ($\omega(Q) = vQ$ and $\Gamma(Q) = DQ^2$). Fig. 2 shows the dispersion curves for FeNi and FeNiS and from there an estimate of the excitation velocities of 4000 and 4070 m/s were obtained for FeNi and FeNiS respectively. Linear hydrodynamic sound is expected to follow a law $\Omega_Q = c_T Q$ with c_T the isothermal sound velocity. These values have been estimated from the low-Q of the structure factors $S(Q)$. In both cases the hydrodynamics regime is approched from below, that agrees with the behavior of the excitations frequencies of molten 3d metals, known as positive dispersion. From the ratios Ω_Q/Γ_Q it is inferred that the region of propagating density oscillations extends up to ∼1 Å^{-1}. The lifetimes estimated as $2\pi/\Gamma_Q$ for the lowest accesible wave vector $Q = 0.8$ Å^{-1} as $\tau = 2\pi/\Gamma_Q$ give figures of ∼0.44 and ∼0.42 ps which translates into mean free paths of ∼17.6 and ∼17.1 Å for FeNi and FeNiS, respectively.

The neutron scattering technique samples the high-frequency sound velocity

$$c_\infty = \sqrt{\frac{3k_B T}{M} + \frac{3\omega_E^2 R_0^2}{10}}$$

where R_0 stands for the position of the main peak of $g(r)$ and ω_E is the Einstein frequency. Setting the value of c_∞ to the measured values, one gets for the Einstein frequency values of 18.9 and 19.3 meV for FeNi and FeNiS, respectively.

4. Conclusions

The $S(Q)$ static structure factors reported in Ref. [9] have shown some indications pointing towards the fact that that the sulfur-containing sample has well-defined Fe–S bonds possibly of a partially covalent character. However, no evidence of sulfur clustering within the Fe–Ni matrix was found there [9].

Here we show that both compounds sustain well-defined collective excitations and show quite similar dispersion curves and therefore sound propagation, despite the differences observed on the structure factor and the densities referred above. The result gives further support to the inference made in Ref. [9] indicating the absence of any significant clustering of sulfur. If clustering would take place within the nanometer scale we would expect to find a significantly larger damping term for the sulfur-containing sample since such clusters will be strong scatterers of the high-frequency sound waves.

In summary, data here reported on show rather small differences in the elastic behaviour of FeNi and FeNiS molten alloys. The small increase in the values found for the sound velocity, that are translated into the Einstein frequencies could be understood as resulting from the presence of the light particle, a phenomenon that has been well charaterized for binary metallic mixtures [10].

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