Journal of Magnetism and Magnetic Materials 449 (2018) 552–557

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

Search for the elusive magnetic state of hexagonal iron: The antiferromagnetic $Fe_{71}Ru_{29}$ hcp alloy

C. Petrillo [a], P. Postorino [b], A. Orecchini [a,*], F. Sacchetti [a]

[a] Dipartimento di Fisica e Geologia, Università di Perugia and Istituto per l'Officina Materiali of CNR, Via A. Pascoli, I-06123 Perugia, Italy
[b] Dipartimento di Fisica, Università di Roma Sapienza, P. A. Moro, I-0185 Roma, Italy

ARTICLE INFO

Article history:
Received 26 June 2017
Received in revised form 21 October 2017
Accepted 24 October 2017

Keywords:
Magnetic state of hcp iron
Neutron diffraction
Volume of magnetic states

ABSTRACT

The magnetic states of iron and their dependence on crystal structure represent an important case study for the physics of magnetism and its role in fundamental and applied science, including geophysical sciences. hcp iron is the most elusive structure as it exists only at high pressure but, at the same time, it is expected to be stable up to very high temperature. Exploring the magnetic state of pure Fe at high pressure is difficult and no conclusive results have been obtained. Simple binary alloys where the hexagonal phase of Fe is stabilized, offer a more controllable alternative to investigate iron magnetism. We carried out a neutron diffraction experiment on hcp $Fe_{71}Ru_{29}$ disordered alloy as a function of temperature. Fe in the hexagonal lattice of this specific alloy results to be antiferromagnetically aligned with a rather complex structure and a small magnetic moment. The temperature dependence suggests a Néel temperature $T_N = 124 \pm 10$ K, a value consistent with the low magnetic moment of $1.04 \pm 0.10\ \mu_B$ obtained from the diffraction data that also suggest a non-commensurate magnetic structure with magnetic moments probably aligned along the c axis. The present data provide evidence for magnetic ordering in hcp Fe and support the theoretical description of magnetism of pure Fe at high pressure.

1. Introduction

Despite decades of experimental and theoretical work, understanding the phase diagram and the magnetic state of iron continues to be a central topic of magnetism. In particular, the discovery of the hexagonal compact phase of iron at high pressure over 60 years ago [1] has driven a large body of investigations of the magnetic state associated to hexagonal iron. Indeed, reproducing the phase diagram and the magnetic state of iron as a function of the crystalline structure is a test bed for theoretical approaches like [2]. The iron phase diagram calculated by [3] describes three different structural phases: α-Fe (bcc) at low pressure and temperature, γ-Fe (fcc) at low pressure and high temperature, and ϵ-Fe (hcp) at high pressure with a consequently higher number density. The three phases correspond to different magnetic states with however very similar cohesive energies, which makes first principle calculations always a challenging task. An interesting, although not exhaustive, analysis on the lattice stability is reported in [4] where the intrinsic complexity of Fe structures is discussed. Here, we remind that the observation of the hcp phase of iron at high pressure was readily followed by the discovery that ferromagnetism disappears as soon as the *compact* hexagonal phase is reached [5].

A direct, unambiguous experimental identification of the magnetic state of hexagonal iron is not yet available, since Mössbauer spectroscopy by [6,7] and X-ray magnetic circular dichroism by [8] (XMCD) provide somehow contradictory results, since suggesting a non-magnetic phase for hcp iron whereas supporting the presence of magnetic fluctuations up to fairly high pressure, as shown by [8]. On the contrary, theoretical calculations of the hcp phase of iron at moderately high pressures [2,9,10] clearly support the existence of a magnetic state, at least at zero temperature. Also, compact structures, namely fcc and hcp, usually favor ferromagnetic ordering while the stability of the antiferromagnetic phase, characterized by frustrated magnetic moment distributions, implies a complex arrangement of the magnetic moment directions. A detailed description of the delicate competing mechanisms giving rise to a magnetically ordered structure in the hcp phase is provided by [2] where calculations support the formation of a collinear orthorhombic magnetic structure. Other structures, including non-collinear, have been considered by [9,10] and more exotic

* Corresponding author.
E-mail address: andrea.orecchini@unipg.it (A. Orecchini).

https://doi.org/10.1016/j.jmmm.2017.10.093
0304-8853/

structures, not tested yet theoretically, could be also possible. A collinear structure seems to be favored by [10], which provides also an explanation for the negative result of the Mössbauer experiments [6,7]. Indeed, the calculation results in a negligible hyperfine field because of a cancellation of core and valence electron contributions.

On a general ground, we observe that the atomic volume compression following a pressure increase, tends to favor an antiferromagnetic against a ferromagnetic structure, and a further decrease of the volume is expected to cancel out any magnetic ordering. Indeed, at larger volumes the electron kinetic energy is reduced, which can compensate the energy increase due to the rise of the Fermi energy caused by the presence of a larger number of electrons in the majority-spin band. This qualitative interpretation is backed by the results of the calculated equation of state [10] where the non-magnetic state is characterized by a volume smaller than the antiferromagnetic state.

The direct study of the magnetic ordering of hcp Fe can be efficiently performed by neutron or also X-ray diffraction experiments as the absence of ferromagnetism, in principle, enables for an easy identification of the magnetic reflections even with a fairly small intensity. Due to the weakness of X-ray magnetic scattering, x-rays are an efficient experimental tool when single crystals are available. Neutron diffraction can be adequate for this sort of investigation although the needed very high pressures still represent a strong limitation.

Given the large uncertainty on the nature or even on the existence of magnetic ordering in ϵ-Fe, and the outlined experimental boundaries, we planned a neutron diffraction experiment on a properly chosen alloy with hcp structure at a high Fe concentration. This approach was widely employed in past studies to get information on the magnetic properties of the fcc phase of Fe by extrapolating the results towards 100% Fe concentration. Unfortunately, the hcp phase of iron rarely stabilizes in binary random alloys. Examining the likely binary systems, Fe-rich Fe-Ru alloys were the best choice because of the hcp phase stabilizing at a relatively low Ru concentration with a consequently low contribution of Ru to the magnetic state of the alloy. Therefore, we decided to use the Fe-Ru alloy at about 30% atomic Ru concentration where a good stability of the hcp phase is expected, given that the hcp phase boundary is observed at about 1500 K and 24% Ru concentration[11]. At this alloy composition, the atomic volume and the lattice parameter ratio c/a are close to the corresponding data for pure ϵ-Fe, obtained by extrapolating the data from Refs. [12,13] to zero pressure. The structural characteristics of the chosen alloy system make it an adequate candidate to simulate the ϵ-Fe phase in the much easier accessible low-pressure region.

Long ago the magnetic structure of $Fe_{80}Ru_{20}$ alloy was investigated by neutron diffraction [14], although the experiment, because of the weakness of the neutron signal, was only capable to suggest the existence of an antiferromagnetic phase with an associated very small magnetic moment. Mössbauer spectroscopy [14], on the other hand, provided further indications on the onset of a possible antiferromagnetic order below 100 K.

Taking advantage of the highly improved experimental technique and instrumentation, we started the search for the iron magnetic state in the hcp environment by a neutron diffraction experiment on the selected hcp Fe-Ru alloy, which would provide direct information on the magnetic structure of the alloy and give clues to unveil the nature of the pure ϵ-Fe hcp phase. It is well established that the magnetic state of iron plays a role on the actual electron–electron interactions also in the regions of high temperature and high pressure where a magnetic state is not stable. We believe this picture applies also to the hcp phase of iron at high temperature, which can have an impact on the study of the iron behavior in the inner Earth core [15–17].

2. Experiment and data analysis

The alloy of nominal composition $Fe_{70}Ru_{30}$ was obtained by Goodfellow Cambridge Ltd. (UK). Structure and composition of the received sample were further tested by in–house measurements: X-ray fluorescence analysis confirmed negligible levels of impurities and showed the presence of Fe and Ru only. Density measurements on the samples prepared for the neutron diffraction experiment were carried out to determine the composition by comparison with the tabulated lattice parameters reported by [18] at room temperature. Data obtained on several pieces showed a good uniformity of the sample. The actual composition was found to be $Fe_{71}Ru_{29}$ with an accuracy largely better than 1%. Series of X-ray diffraction measurements at 10 K were performed to verify the crystal structure of the sample, and they confirmed the hcp single-phase for the alloy with a very small amount (less than 0.1%) of α-Fe. Additional room temperature neutron diffraction measurements also established the single-phase nature of the present sample. The absence of the α-Fe phase was also proven by magnetic measurements. In conclusion, the preliminary characterization measurements confirmed the hcp phase of the sample with an almost negligible residual contribution from α-Fe precipitates. To complete the characterization of the sample, the lattice parameters were measured using the Co K_α radiation to avoid the Fe fluorescence. It was found $a = 2.590$ Å, $c = 4.167$ Å and no evidence for structural transitions down to 10 K. Further, the study of Ref. [19] on artificial Fe/Ru superlattices reported quite complex structures, which called for a careful analysis of the diffuse scattering as it would appear in both X-ray and neutron diffraction spectra. Indeed, diffuse scattering was found to be always flat, which is a typical behavior for a random alloy, and this result confirmed the hcp phase of the present sample with a random distribution of the two atoms at the lattice sites.

The experimental value of the c/a ratio obtained from the present X-ray measurements at 10 K on the $Fe_{71}Ru_{29}$ sample, i.e. $c/a = 1.609$, is reported in Fig. 1 against the c/a data of the Fe-Ru alloys at room temperature and normal pressure from [18]. This value is slightly different from $c/a = 1.624$ obtained by extrapolating the data of [18] to zero Ru concentration, and closer to $c/a = 1.606$ that is the zero pressure extrapolated value of the room temperature c/a data for pure hcp Fe [12]. The observed value of the c/a ratio, not far from the ideal closed packed value $c/a = \sqrt{8/3} \simeq 1.633$,

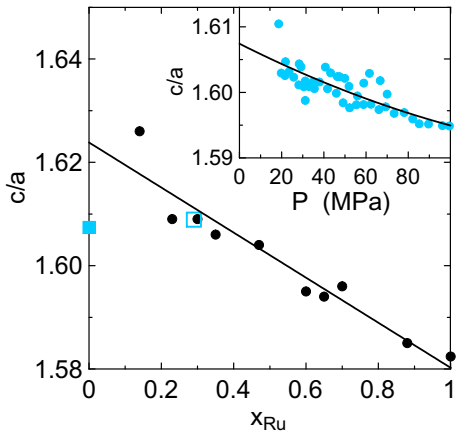

Fig. 1. Room temperature, normal pressure, c/a ratio plotted as a function of Ru concentration (black dots) from Ref. [18]. The full line is a linear fit to the data, which provides an extrapolated value $c/a = 1.624$ at zero Ru concentration. The blue empty square is the present data measured at 10 K for the 29% Ru alloy, while the full blue square is the hcp pure Fe data from Ref. [12]. The inset shows the c/a ratio of pure hcp Fe at 15 K as a function of the pressure [13].