Experimental report

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Council: 4/2011

Title: Ferromagnetic-NSE study of the low-frequency spin-dynamical signatureof the INVAR effect in Fe65Ni35

Research area: Physics

This proposal is a new proposal

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Samples: Fe65Ni35

Instrument	Requested days	Allocated days	From	To
IN15	8	0		
IN11	8	7	08/11/2012	15/11/2012

Abstract:

The origin of the INVAR effect - near zero thermal expansion around room temperature in certain ferromagnetic alloys - is still not properly understood. Although the phenomenological two state model proposed by Weiss, where thermal population between two different spin states of high and low volumes can be used to explain the curious thermal expansion, there has been no direct observation to corroborate the theory. Recently many studies have involved the use of electronic structure calculations using many different techniques, many of which infer that disorder, either in the magnitude of the local moments, or in the degree of collinearity plays a role in the phenomena observed in these systems. The proposed experiment seeks to probe low-frequency spin-dynamics in INVAR alloy (Fe65Ni35) in order to verify an interesting spin-dynamical signature of the INVAR effect, recently seen in muon spectroscopy studies.

I. INTRODUCTION

In 1897 C. E. Guillaume established that face-centred-cubic (fcc) alloys of iron and nickel with a concentration of ∼35% at. % nickel exhibit an anomalously small thermal expansion over a wide range of temperature[1]. He considered the expansion of these alloys to be *invariable* and hence this effect has since become known as the INVAR effect. This effect has since been observed in various ordered and random alloys and in some metallic glasses - all of which are ferromagnetic[2]. There is a wide range of applications in which INVAR alloys are used because of this useful property; for example in the manufacture of precision scientific instruments, temperature regulators and microwave resonators. Despite many years of study of the INVAR effect a clear understanding of the mechanism behind this effect is still lacking. INVAR behaviour is clearly related to metallic ferromagnetism[2,3]. Below the Curie temperature (T_c) typical coefficients of linear expansion observed in INVAR alloys have a value $\alpha \simeq 2.1 \times 10^{-6}$, while in their respective paramagnetic phases α increases by one order of magnitude. An early attempt at a theoretical description of the INVAR effect is the so–called 2γ–state model due to Weiss[3]. This model assumes the co–existence of two near degenerate spin–states in f.c.c. iron (γ-Fe): a high spin (HS), high volume state and a low spin (LS), low volume state. Accordingly, thermal spin–excitations from the HS state (labelled γ_1) to the LS, γ_2 state leads to a loss of magnetisation on increasing temperature with an associated volume contraction which counteracts phononic thermal expansion.

Electronic band theory calculations confirm the main idea of the 2γ–state model. First–principles calculations of γ-Fe, randomly ordered $Fe_{65}Ni_{35}$and ordered Fe_3Ni clearly show the existence of two stable magnetic states, a low-spin, low-volume (LS) and a high-spin, high-volume (HS) state[4–6]. In particular Entel *et al.* predicted a change in the relative occupancy between the anti–bonding t_{2g} majority spin states and the non-bonding e_g minority spin states in favour of the latter as the temperature increases[4]. This results in the contraction of bonds, thereby counteracting thermal expansion. However, experimental confirmation of the existence of two spin states at ambient pressure in any INVAR material is, so far, lacking. There is some evidence of closely space spin–states in some metallic ferromagnets at high pressure. Recent X-ray magnetic circular dichroism (XMCD) measurements on $Fe_{72}Pt_{28}$ revealed that the system undergoes a spin–state transition at an applied pressure of 4 GPa (40 kbar)[7,8]. Other X-ray diffraction measurements have shown that the non-INVAR metallic ferromagnet Pd_3Fe exhibits INVAR properties at high pressure[9]. However, precise measurements of the magnetic form factor (magnetisation distribution in k-space) in $Fe_{65}Ni_{35}$ INVAR using polarized neutron diffraction[10,11] in addition to magnetic X-ray Compton scattering experiments[12] show that the fraction of unpaired electrons with e_g symmetry remains constant in a range of temperature from 100 K - 600 K, contradicting the theoretical results of Entel *et al.*[4] and effectively ruling out the 2γ–state model as a candidate description of the INVAR effect.

In the mid 1980s, there was an effort by theorists such as Moriya and co-workers to attempt to improve the theoretical description of finite temperature properties of metallic magnets - which are traditionally badly described by simple Stoner models - using so-called self–consistent–renormalisation (SCR) theory[13]. Here, instead of there being two near–degenerate electronic states available to the system, spin fluctuations give rise to a manifold of continuously varying electronic states, resulting in a smoothly varying local magnetisation $\langle M^2_{\mathrm{loc}}(T)\rangle$ which increases monotonically as a function of temperature, and details of which temperature variation depending on the structure and the occupation of the bands. This temperature variation of $\langle M^2_{\mathrm{loc}}(T)\rangle$ then leads to a magneto–volume effect consistent with INVAR behaviour. This theory received some experimental confirmation from Ishikawa *et al.* [14] who used neutron scattering to directly observe quasi–elastic magnetic neutron scattering associated with incoherent spin–fluctuations in the ordered state of $Fe_{65}Ni_{35}$, although that study did not observe spin–fluctuations in Fe_3Pt.

Further modelling of the temperature dependence of the thermal expansion coefficient from magnetostriction measurements[15,16] using SCR theory showed a remarkable level of agreement, though it was argued - notably by Wohlfarth[17] that the description of the pressure dependence of the Curie temperature in these alloys was less successful. Motivated by the research of the excitations responsible of the INVAR effect, Ishikawa et al. performed inelastic neutron scattering measurements on the INVAR alloys $Fe_{65}Ni_{35}$ and Fe_3Pt and on non-INVAR $Fe_{50}Ni_{50}$. They observed that in INVAR $Fe_{65}Ni_{35}$ and Fe_3Pt spin wave excitations explain only about a half of the temperature decrease of the magnetization while this discrepancy is absent in non-INVAR $Fe_{50}Ni_{50}$[18,19]. On the basis of their results they suggested that the variation in amplitude of the local magnetic moment and then the INVAR effect may be due to the presence in these alloys of some *hidden (undetected) excitation.* Nevertheless, to–date no other source of magnetic excitations which may be responsible for the INVAR effect have been observed. Stoner excitations appear at too high an energy ($\simeq$ 100 meV) to be responsible for the INVAR effect[19–22], while longitudinal spin–fluctuations are observed only in $Fe_{65}Ni_{35}$ and not in Fe_3Pt[14].

More recent theoretical studies suggest that the INVAR effect is related to thermal magnetic disorder. Two main models of magnetic disorder have been proposed; the disordered local moment (DLM) picture[23–27] and a model incorporating non–collinear magnetic structures[28]. Schilfgaarde *et al.* find in INVAR concentrations of Fe–Ni alloys a magnetic structure characterized, even at zero temperature, by a continuous transition from a ferromagnetic state at high volumes to a disordered non-collinear configuration at low volumes[28]. This non-collinearity gives rise to anomalies in the binding energy volume dependence curve which is directly related to the thermal expansion coefficient through the bulk modulus and Grüneisen constant. Extensive polarized neutron diffraction measurements have been undertaken to look for non–collinear (and hence transverse) magnetism in $Fe_{65}Ni_{35}$ but no sign of non–collinear ferromagnetism is found[29]. However, an indication of the presence of non–collinear moments has been confirmed experimentally at low momentum transfers[30] in $Fe_{65}Ni_{35}$. On the basis of this observation Menshikov *et al.* concluded that in $Fe_{65}Ni_{35}$, non–collinear inhomogeneities are present on a 10 - 15 Å length scale. They suggested a model magnetic structure characterised by the occurrence of static longitudinal spin fluctuations embedded in a ferromagnetic matrix[31]. Recent ab initio electronic structure calculations based on the disordered local moment (DLM) approach, give a good description of the INVAR effect in $Fe_{65}Ni_{35}$[27], Fe–Pt[26] and R-Co_2 with R= Dy, Ho[24]. These studies indicate that thermal magnetic disorder (modelled as Ising spin–flips in a local moment picture) leads to INVAR behaviour. However, these models are generally simplistic - assuming fully localised moments, and often localised and randomised defects. More importantly, the DLM picture is lacking experimental justification (beyond the reproduction of the anomalous $\alpha(T)$ behaviour).

In this study, we report on efforts to look for low–frequency spin–fluctuations in $Fe_{65}Ni_{35}$ INVAR alloy using zero– and longitudinal–field muon spin relaxation (ZFμSR and LFμSR) and ferromagnetic neutron spin–echo (FMNSE) measurements. Our motivation is to look for low frequency spin–fluctuations associated with either disordered local moments or with disordered clusters proposed by Menshikov and co–workers[30,32]. The μSR technique is uniquely sensitive to small amplitude magnetic inhomogeneities with fluctuation rates on the GHz timescale. FMNSE has inherently lower sensitivity due to limitations of neutron beam flux, but is able to probe GHz timescale magnetisation dynamics, while simultaneously distinguishing a characteristic length scale for the spin–fluctuations.

II. EXPERIMENTAL PROCEDURE

The samples were prepared by melting appropriate quantities of starting materials with purity of 99.99 in an argon–arc furnace. The as melted ingots were then annealed at 800 C for 72 hours followed by a slow cool. The stoichiometry of the samples was verified by performing energy dispersive fluorescence analysis using a commercial scanning electron microscope. For the FMNSE experiment a $Fe_{65}Ni_{35}$ sample with a mass of $\sim$ 100 g, was studied using the spin–echo spectrometer IN11 at the Institut Laue-Langevin, Grenoble. A saturating vertical field of 1 T was applied to align the magnetic domains in the sample and hence preserve the neutron polarization. The temperature dependence of the intermediate scattering function $S(Q,t)/S(Q,0)$ was measured using neutron wavelength of $\lambda = 5.5$ Å at a scattering angle $2\theta = 4°$.

III. RESULTS

The intermediate scattering function $S(Q,t)/S(Q,0)$ with $Q \simeq 0.1$ Å^{-1} measured from our FMNSE study is plotted in Fig. 1 for three temperatures; 200 K, 320 K and 400 K. The advantage of spin–echo neutron spectroscopy over conventional neutron spectroscopy is that the technique directly measures the time–dependent spin–spin autocorrelation function $S(t)$ over a range of so–called *Fourier times* associated with the precession field in the spectrometer (see for example the review of Ehlers[33]). In the FMNSE configuration, IN11 is able to measure over approximately one decade of time between 0.25 and 2.6 ns, and is therefore sensitive to spin–fluctuations of that order. The data shown in Fig. 1 were corrected for instrumental resolution by dividing the data using a low temperature run measured at 5 K. In Fig. 1 we see that $S(t)$ starts to decrease at long Fourier times above $\sim$1 ns indicating the presence of nanosecond timescale spin–fluctuations in $Fe_{65}Ni_{35}$. While this is in the upper reaches of the available time–range on IN11, it is within the time–resolution of the instrument, and we note that the characteristic spin–fluctuation rate increases systematically with temperature. In order to give a quantitative estimate of the timescale of the observed spin–fluctuations, the data were fitted to a stretched–exponential function, $S(t)/S(0) = \exp\left[-(t/\tau)^{\beta}\right]$. We find relaxation times τ^{β} of $\sim$22 ns, $\sim$34 ns and $\sim$45 ns at 400 K, 320 K and 200 K respectively. Since these spin–fluctuations are measured at a momentum transfer of $Q \simeq 0.1$ Å^{-1} we can associate them with spin–clusters of approximately 10 Å in extent. While the statistical quality of the measured $S(t)$ does not permit a robust fit, the observed lineshape is evidently strongly non–exponential in form.

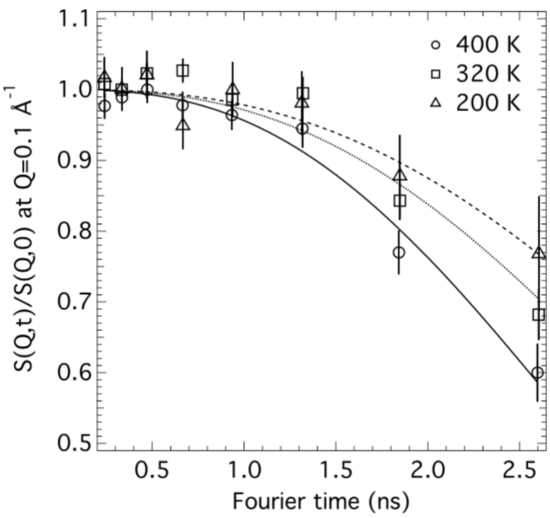

FIG. 1: The normalised intermediate scattering function $S(Q,t)/S(Q,0)$ with $Q \simeq 0.1$ Å^{-1} measured on $Fe_{65}Ni_{35}$ using the IN11 spin–echo spectrometer as a function of temperature. These show evidence of slow spin–fluctuations in the ordered ferromagnetic state. Lines are fits to a stretched–exponential decay in order to loosely quantify the relaxation time.