Journal of Alloys and Compounds 303–304 (2000) 232–238

Journal of ALLOYS AND COMPOUNDS

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Iron magnetism in cubic Laves phase itinerant ferromagnets

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Abstract

The cubic Laves phase compounds form a wide class of magnetic materials with important applications. Starting some 20 years ago the heavy rare-earth iron materials (REFe$_2$) were studied with neutron scattering. The high T_C of these materials is a consequence of strong Fe–Fe interactions, but the intrinsic anisotropy is provided by the RE–Fe interaction. The situation is more complex for itinerant systems such as CeFe$_2$ and UFe$_2$, in which a strong hybridization occurs between the f states of the Ce or U ions and the 3d electrons of Fe. In these materials there is no observable response that can be associated with the f states, but the Fe spin waves are substantially modified. For example, their spin–wave stiffness is enhanced in UFe$_2$, whereas it is reduced and antiferromagnetic (AF) fluctuations are found in CeFe$_2$. Doping CeFe$_2$ with a small amount of Co stabilizes the AF ground state, but it can be quenched with a modest magnetic field, and this leads to a large magnetoresistance. We review briefly neutron inelastic scattering measurements on single crystals of YFe$_2$, UFe$_2$, CeFe$_2$, and Co-doped CeFe$_2$.

Keywords: Itinerant magnets; Cerium; Uranium; Neutron inelastic scattering

PACS: 75.20Hr; 75.40Gb

1. Introduction

The study of the spin waves of the REFe$_2$ (RE=Tb, Ho, Er) cubic Laves phase compounds over a number of years [1] has presented a clear picture of the microscopic exchange interactions in these materials, which has been useful in designing their industrial applications, for example, in magneto–acoustic coupling and in magneto–optical recording devices [2]. The basic separation of the localized 4f electrons and the itinerant 3d states allows one to consider the high T_C (>500 K) as a consequence of the strong Fe–Fe exchange (the distance between Fe atoms in this structure is close to that in pure Fe), whereas the Fe–RE interaction provides the anisotropy, essentially because of the large spin–orbit coupling experienced by the 4f states. For the rare-earth ions the direct 4f–4f interaction is negligible, but they sense the magnetism of each other and the Fe states through interactions via the 5d states. In this sense the "standard model" for rare-earth magnetism works [3]. The lighter rare earths, Pr and Nd do not form in the cubic Laves phase with Fe, but both Ce and U do — some of the properties of these compounds, along with that of YFe$_2$ are given in Table 1. Although there had been interest in CeFe$_2$ previously, this increased considerably after theoretical predictions by Eriksson et al. [4] claimed that the Ce 4f states would be itinerant, so that the magnetism would be different from that found previously in the REFe$_2$ compounds. About the same time (the late 1980s) both theoretical [5] and experimental work [6] on UFe$_2$ showed that it too should be regarded as an itinerant system, with a strong hybridization between the 5f and 3d electrons. Since that time, many experimental techniques have focused on the static ground-state properties of both CeFe$_2$ and UFe$_2$ and there is a reasonable agreement between theory and experiment. As yet, however, there have been no theoretical studies addressing the dynamical properties of these materials. The present paper gives a brief review of the experimental work performed over the last 6 years to characterize such dynamical properties of these itinerant systems with strong f–d hybridization. Naturally, we hope that these studies will stimulate theo-

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0925-8388/00/$ – see front matter
PII: S0925-8388(00)00664-2

Table 1
Information on the 3 Laves phases ferromagnets (all with the C15 fcc crystal structure, symmetry *Fd3m*) studied by inelastic neutron scattering[a]

	Fe	YFe_2	$CeFe_2$	$Ce(Fe_{0.93}Co_{0.07})$	UFe_2
a_0 (Å) (RT)	2.8665	7.370	7.304	7.274	7.057
d (Fe–Fe) Å	2.48	2.61	2.58	2.57	2.50
T_C (K)	1043 (2)	545 (5)	235 (5)	210(2)	165 (5)
$\mu_{Fe}(\mu_B)$	2.20 (4)	1.5 (1)	1.2 (1)	1.1(1)	0.6 (1)
ΔE (meV)	<0.1	0.21(5)	0.25(3)	0.15(6)	0.40(5)
D (meV-Å^2) $T=100$ K	325 (10)	250 (12)	155 (5)	110(3)	440 (30)
J (meV) (~±15%)	24.0	24.4	19.4	15.2	117

[a] In this structure each Fe has six nearest Fe neighbors. Pure Fe, which is bcc with 8 nearest Fe neighbors, is added for comparison. T_C is the Curie temperature, μ_{Fe} is the magnetic moment on the Fe site, and ΔE is the ferromagnetic spin–wave gap at the zone center, $q=0$. The spin–wave stiffness constant D (see text) is shown for 100 K. The final row gives the deduced exchange between the Fe moments. Standard deviations in parentheses refer to the least-significant digit.

retical advances with which the experimental results can be compared.

2. Ferromagnetic iron spin waves

The spin waves in Fe are well known, but for comparison we prefer also to have the results from YFe_2. This has the advantage that it is the same cubic Laves phase structure as the compounds of interest, and, of course, Y does not carry a magnetic moment. We note in Table 1 that the Fe–Fe exchange in YFe_2 is the same as that in pure Fe, so that the lower T_C and the reduced spin–wave stiffness compared to pure Fe are simply a consequence of the smaller magnetic moment on the Fe site, the reduced coordination, and the difference in interatomic spacing. In Fig. 1 we show three panels representing the dispersion curves for the iron spin wave as measured in YFe_2, $CeFe_2$, and UFe_2. One can see from the slopes of the thick solid lines, that the spin–wave stiffness for these three compounds are different, but before examining these in more detail we need to make one additional point.

When we started these experiments we anticipated observing some kind of inelastic response associated with the rare-earth (or actinide) ion. To return to the heavy $REFe_2$ systems discussed in the introduction, such a RE response consists of a dispersionless (crystal-field like) mode that is a consequence of the RE ion sensing the strong molecular-field exchange field of the surrounding Fe ions. This mode has no dispersion because there is almost no direct RE–RE interaction. Furthermore, because it is an out-of-phase (optic like) mode, it may be measured conveniently around the [002] zone center in the Brillouin zone (BZ) since in-phase modes do not around this position. However, in our first experiments with UFe_2 we found no evidence of any significant response around the [002] zone center [7]. Further work on $CeFe_2$ confirmed that no discrete mode from the rare-earth element could be observed [8]. This absence of any bark in the night (for those who remember Sherlock Holmes!) is important, but it is also useful to recall intensity limitations. One reason for no observed signal could simply be that (as a first approximation) it is proportional to S_{RE}, where S_{RE} is the spin associated with the rare earth. This quantity is small for $CeFe_2$, and even smaller for UFe_2 [6], so that one might explain this as just an intensity problem. The lowest energy acoustic-like mode in these materials is the Fe spin wave because $S_{RE}<2S_{Fe}$, (where S_{Fe} is the Fe spin) [7]. What is surprising is that we have been unable to detect the mode associated with the in-phase precession of both the rare-earth and Fe moments. This contribution should be visible especially around the [220] as at this position the Fe structure factor is zero. The most likely explanation for the absence of these modes is that, because they involve the f states, the excitations are strongly damped and thus broad, and hence weak. It is always difficult to establish whether there will be enough weight of any broad and damped response falling into the resolution ellipsoid of the triple-axis spectrometer for the excitation to be observed above background. A further possibility is that these modes are at much higher energy, although approximate estimates [7] suggest that this is unlikely as the overall anisotropy is small. We may then return to the Fe spin wave response, and Fig. 1, with the knowledge that is the only-observed response in the system.

It is evident from comparing YFe_2 and UFe_2 in Fig. 1, that the spin–wave stiffness of UFe_2 is greater than that in YFe_2. This is shown more clearly in Fig. 2(a), in which we plot the low-energy part against q^2 to give straight lines that are proportional to the spin–wave stiffness. We write

$$E=\Delta E+D(1-\beta q^2)q^2+\ \ldots \tag{1}$$

where ΔE is the gap, D is the spin–wave stiffness, and we take $\beta \sim 1$ following the work on iron. Here we are interested only in the term in Dq^2. The spin–wave gap, ΔE, is small and comparable for all these materials (see Table 1). It is also consistent with the small gaps associ-

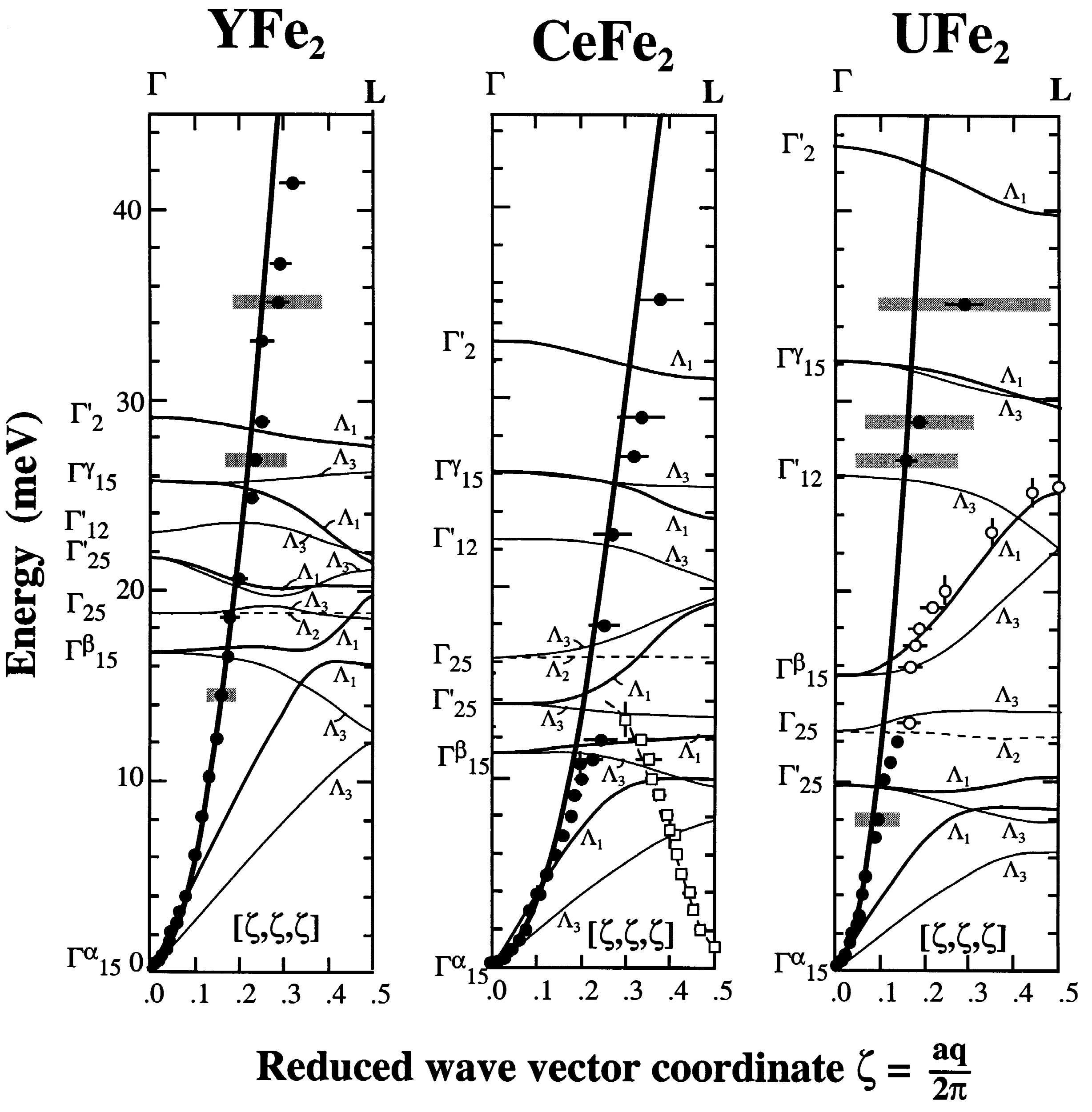

Fig. 1. The dispersion curves at $T=100$ K for the three compounds YFe_2, $CeFe_2$ and UFe_2 as a function of distance across the Brilloiun zone in the direction [111]. The phonons are drawn as thin solid lines. The thick solid lines give the dispersion of the magnetic Fe spin. The open squares in the center panel (taken at 15 K) represent the dispersion of the antiferromagnetic fluctuations observed in $CeFe_2$ (with a gap of ~1 meV), and the open circles in the case of UFe_2 represent the mixed magnon–phonon mode that is thought to exist.

ated with itinerant systems (as long as large orbital moments are not present). Thus, the first surprise is that, despite the small moments on the both the U and Fe sites in UFe_2, and its low T_C, the spin–wave stiffness is actually larger than found in pure Fe. Furthermore, we find its dependence on reduced temperature much stronger than that found in elemental Fe. There are two further points to be made about UFe_2. The spin waves appear to interact with a longitudinal optic phonon of symmetry Γ_{15} and over the energy region from ~12 to ~ 20 meV it is difficult to measure the excitations. At higher energies the magnetic excitations are again observed, but they are broad. There is not the space to discuss this here; full details are given in Ref. [9]. Unfortunately, the definitive experiment of actually proving the magnon–phonon interaction, which involves using polarization analysis of scattered neutrons did not succeed because of intensity limitations and the relatively high energy transfer involved. That there is a strong electron–phonon interaction in UFe_2 may be also seen from the analysis of the phonon force constants [10].

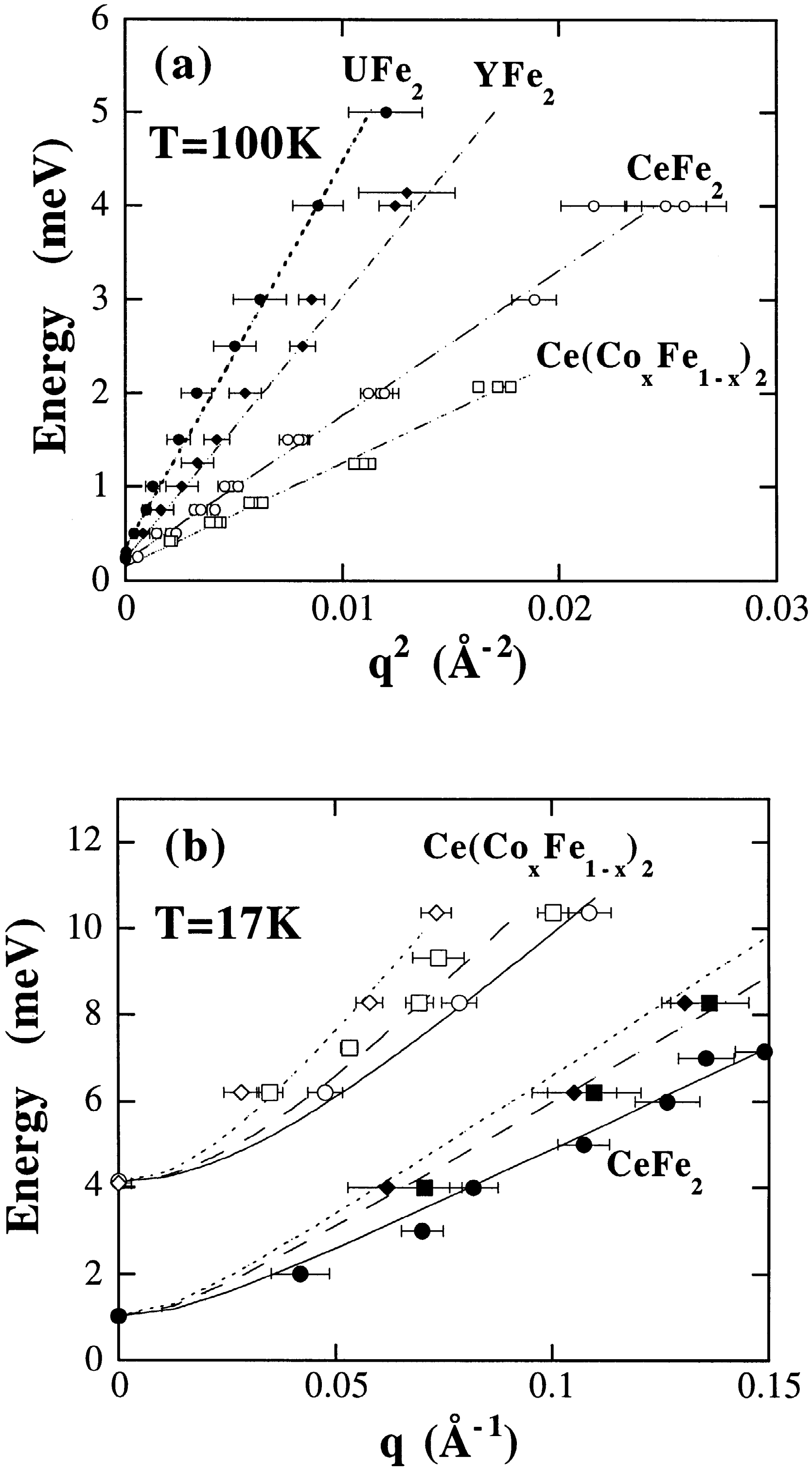

Fig. 2. (a) E vs. q^2 to illustrate the ferromagnetic interactions in these materials. The gaps at $q=0$ of all these materials are comparable. The slopes give the spin–wave stiffness, D in Eq. (1). (b) The equivalent plot for the antiferromagnetic fluctuations. Note the much large gap in the case of the doped compound. The different symbols represent different directions.

Compared to the other Laves phase materials, the phonon force constants for UFe_2 are anomalous, and this may reflect the unusual electronic structure of this material.

3. Antiferromagnetic fluctuations

As shown in Fig. 1 (middle panel) the intrinsic ferromagnetism of $CeFe_2$ is actually accompanied by antiferromagnetic fluctuations. The dispersion of these away from the L point (1/2, 1/2, 1/2) in the BZ is shown in the same middle panel of Fig. 1 as open squares. It is important here to again emphasize the unusual nature of these fluctuations — they arise, as does the intrinsic ferromagnetism — from the Fe moments. Moreover, efforts to determine their magnitude as compared to the known ferromagnetic Fe moment of 1.2 μ_B lead to a question of the dynamic range of the AF fluctuations. It is certainly possible to plot their dispersion, as shown in Fig. 2(b), but their intensity as a function of temperature gives an unusual curve — see Fig. 3(a). In fact, these AF fluctuations have a temporal aspect so that the component observed will depend on the dynamic window employed. In Ref. [8] we estimate that at low temperature within a time window of ±20 GHz there is a component of ~0.05 μ_B. As the temperature is increased the fluctuations become faster (this is consistent with the enlargement of the effective AF gap as shown in Fig. 3(b) as a function of temperature), but they also become more short range in extent. Because it is sensitive to such short-range interactions the AF fluctuations affect Mössbauer measurements [8] even at the highest temperatures, although this was not recognized in the earlier experiments [11].

Pure $CeFe_2$ is certainly close to an AF instability. This has been known for at least 10 years, although the nature of the instability was previously unclear. In a series of experiments on polycrystalline samples, the late Bryan Coles and his students got close to characterizing these effects [12]. This early work also established that doping the Fe site with almost any element led to stable antiferromagnetism. Since that discovery [13], a great deal of work has been reported [14]; perhaps the most interesting of which concerns the observation of giant magnetoresistance in some of these compounds [15].

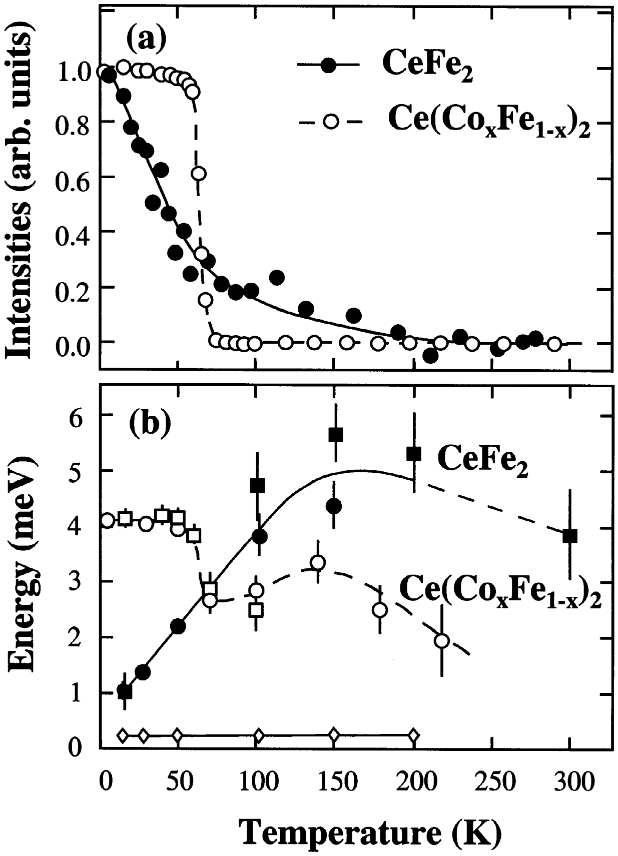

Fig. 3. Properties associated with antiferromagnetism in the pure (solid symbols) and $x = 0.07$ samples (open symbols): (a) Intensity of AF signal. In the pure sample this is the signal obtained in a ±20 GHz energy window with a cold source 3-axis spectrometer. For the doped samples the signal is that of the AF Bragg reflection. (b) For the pure sample the gap tends to decrease as T is lowered. The diamonds represent the small (and T independent) ferromagnetic gap. For the doped sample the gap of the AF fluctuations is roughly constant in the ferromagnetic state but increases abruptly at the discontinuous transition into the AF state, and stays at 4 meV at low T.

4. Doped $CeFe_2$ and AF order

Following the trend discussed above we have recently obtained (again from the group at Ames) a large single crystal of 7% Co doped $CeFe_2$. We show in Fig. 3(a) the intensity of the (1/2, 1/2, 1/2) magnetic zone center point as a function of temperature. The doped material shows a discontinuous transition from ferromagnetism to ordered antiferromagnetism. This transition is also accompanied by a rhombohedral distortion. In agreement with Kennedy et al. [16] we find a rhombohedral angle in the AF state of 90.31° compared to their value of 90.26° for both the 15 and 20% Co-doped $CeFe_2$. Furthermore, on cooling into the AF state there is a relative volume contraction of 0.18%.

The phase diagram of the system as a function of H and T is shown in Fig. 4. The $T_N = 66$ K with $H = 0$ fixes the Co concentration at $x = 0.07(1)$. The T_C of this material is ~210 K. In Fig. 5 we show constant-E scans (at an applied field of $H = 2.9$ T for all panels) taken with an energy transfer of 5 meV. This energy transfer is above the gap of 4 meV in the antiferro-magnetic state. The top panel is in the supposed ferromagnetic state (where there is no structural distortion). There are two peaks at $\xi = 1.12$ and 1.88 that correspond to the ferromagnetic spin waves emanating from the [111] and [222] BZ centers, respec-

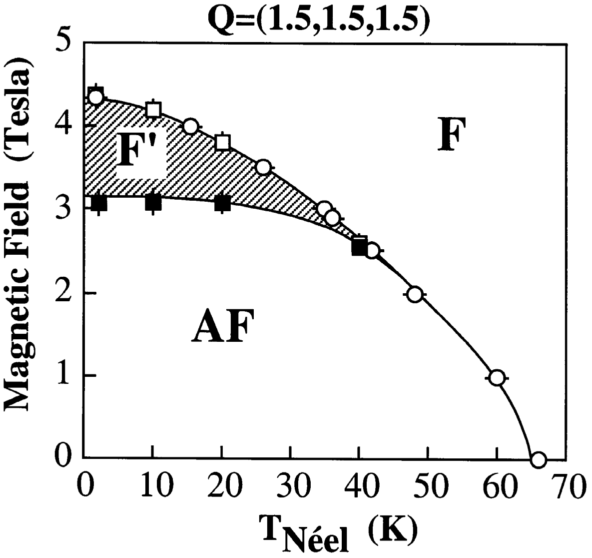

Fig. 4. Phase diagram for the 7% Co doped CeFe$_2$ sample. The Curie temperature is 210 K. Shown is the strong H dependence of T_N and the unusual phase labeled F′. This must be accessed by field cooling the sample. In this F′ state both long-range ordered ferro- and antiferromagnetism are found.

tively. The signal from the [222] is stronger because it has a larger Fe structure factor. However at $\xi=1.5$ there is extra intensity, and this corresponds to the AF fluctuations that are observed in pure CeFe$_2$. Thus in the ‘‘ferromagnetic’’ state the doped CeFe$_2$ materials closely resemble pure CeFe$_2$. The center panel corresponds to the situation found with zero-field cooling. Here the state is purely AF. There is a strong signal at $\xi=1.5$ from the AF state and no sign of the ferromagnetic spin waves (the small signal at $\xi=1.88$ is from a LA phonon — this can be verified by going to higher BZs and noting that the phonon intensity is proportional to Q^2). Moreover by field cooling (for $2.5<H<4.3$ T) a mixed ferro- and antiferromagnetic phase (indicated by F′ in Fig. 5) is found. In this state there is no long-range AF (but fluctuations) and a clear ferromagnetic signal; in addition there is no rhombohedral distortion. The lower panel in Fig. 5 is representative of this state. In this regime zero-field cooling results in the AF state. For $H>4.3$ T the F state is obtained whatever the cooling conditions.

There is an additional interesting aspect of the AF state in the doped CeFe$_2$ material. The gap is large [see both Figs. 2(b) and 3(b)] at 4 meV, but the weight of the antiferromagnetic spin waves may not be distributed uniformly over the high frequency region. In fact most of the weight of this AF response is centered around 4–6 meV. Again, this is an aspect where theoretical guidance would be particularly useful. Some interesting comments have been made by Khowash [17], but these focus on density-of-state arguments, whereas we probably require much more detailed considerations of $S(Q,\ \omega)$.

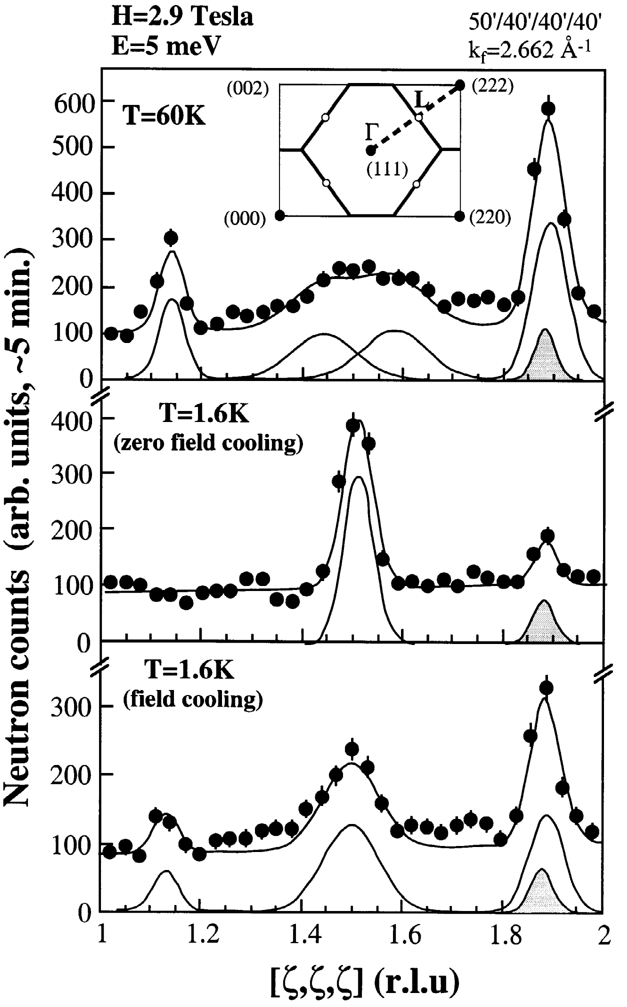

Fig. 5. Data obtained on the doped sample by performing constant-E scans across the Brilloiun zone in the [111] direction (see insert) with an applied field of $H=2.9$ T and a constant energy transfer of 5 meV. The lines represent Gaussians fitted to the various contributions. The top panel shows spectra in the F state. The two peaks at $\xi=1.12$ and 1.88 arise from the ferromagnetic spin waves, and the intensity around $\xi=1.5$ is from the AF fluctuations. The middle panel shows the AF state obtained by zero-field cooling, even at $H=2.9$ T. The strong peak at $\xi=1.5$ is the AF spin wave. The small peak near $\xi=1.88$ is an LA phonon. Lower panel — field cooling the sample to achieve the same condition as the middle panel, but now showing the F′ state.

5. Conclusions

The study of excitations in the hybridized systems CeFe$_2$, the 7% Co-doped CeFe$_2$, and UFe$_2$ have shown an interesting range of behavior that is quite different from that encountered, and largely understood, in the heavy rare-earth Laves phases. UFe$_2$ shows enhanced ‘‘ferromagnetic’’ behavior, as evidenced by the increase in the Fe spin–wave stiffness, even if the T_C and the Fe moments are substantially reduced. There is also an important electron–phonon interaction in this material. In CeFe$_2$, on the other hand, antiferromagnetic fluctuations are observed, with a concomitant weakening of the Fe spin–wave stiffness. On doping pure $CeFe_2$ the AF state is stabilized, but the AF state is quite different — there is both a significant rhombohedral distortion and a relatively large spectral gap (4 meV). Surprisingly, however, a field as small as ~4.5 T can destroy this AF state. This situation was already noted by Wada et al. [18] in an 8% Co-doped sample when they analyzed the magnetization data of Ali and Zhang [19]. An even earlier theoretical paper by Moriya and Usami [20] draws attention to the possible co-existence of F and AF states in itinerant magnets.

There has been great interest in the magnetic moment associated with the Ce atom in both pure and doped $CeFe_2$. Despite a number of dichroism studies (in the F state), which give contradictory results [21], we believe the polarized-neutron study of Kennedy et al. [22] to be the most reliable, and this claims that the moment on Ce in $CeFe_2$ is $<0.2\ \mu_B$. One possibility in the doped compound is that the Ce moment becomes localized and large — this would certainly explain the anisotropy evident in the AF state (arising from spin–orbit coupling) and the lattice distortion. On the other hand, no such Ce moment was found by Kennedy et al. [16] in earlier studies. The small energies differences involved between these ground states are reminiscent of the work on γ-Fe, in which there are a number of spin configurations close in energy [23]. Another possibility is that the electronic instability involves a change in the orbital occupation at the Fe site on cooling into the AF state. In this respect, the complex orbital occupation suggested in Ref. [22] is interesting.

We hope this work encourages both theory and further experimental work on these interesting materials.

Acknowledgements

This work has stretched over a period of at least 6 years and we wish to thank our co-authors of Refs. [7–10] for their considerable assistance in these endeavors. For the recent (unpublished) experiments on doped $CeFe_2$ we thank Bernard Hennion and Arno Hiess for their able assistance at Saclay and ILL, respectively. Finally, it is a pleasure to acknowledge close collaboration with Paul Canfield and his group at Iowa State University and Ames Laboratory for providing the excellent single crystals of YFe_2, $CeFe_2$ and the doped material. GHL acknowledges stimulating discussions with Bruce Harmon of Iowa State University.

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