Ru–INDUCED LOSS OF LONG-RANGE MAGNETIC ORDER IN a$-Fe_{90-x}Ru_xZr_{10}$

D. H. Ryan,

Physics Department, McGill University,

3600 University St., Montreal, Quebec H3A 2T8, Canada

J.M. Cadogan

School of Physics, The University of New South Wales,

Sydney, NSW 2052, Australia

Zin Tun

AECL, Chalk River Laboratories,

Chalk River, Ontario K0J 1J0, Canada

Abstract

Mössbauer spectroscopy, magnetisation, susceptibility and neutron depolarisation have been used to investigate the loss of long-range ferromagnetic order in a$-Fe_{90-x}Ru_xZr_{10}$. Our depolarisation results show a rapid reduction in domain size from $1.6\mu m$ to $0.4\mu m$ as x increases from 0 to 2, with no evidence for long-range order in either depolarisation or magnetisation data for $x \geq 3$. Furthermore, for x=1 and 2, we observe a clear break in the temperature dependence of $< B_{hf} >$ which may be associated with the ordering of transverse spin components in these partially frustrated alloys.

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Introduction

Iron-rich amorphous Fe–Zr alloys exhibit a rich variety of magnetic behaviour as a result of partially frustrated exchange interactions [1]. This frustration arises through the distance dependence of the direct exchange interaction ($\mathcal{J}(r)$) coupled with short Fe–Fe contacts in the glass which lead to significant numbers of antiferromagnetic (AF) bonds that compete with the dominant ferromagnetic (FM) interactions. Essentially all additions (*e.g.* hydrogen) or substitutions for Fe by other 3d transition elements or metalloids lead to an increase in ordering temperature, even when accompanied by a reduction in magnetisation [2]. The substituents act by shifting the balance between FM and AF interactions either by contributing strong FM couplings, as with Co, or by expanding the lattice, as with H, and reducing short Fe–Fe contacts. The one clear exception to this rule is Ruthenium, which leads to an immediate and rapid reduction in both T_c and the magnetisation when added to a$-Fe_{90}Zr_{10}$ [3,4]. Indeed, the only other element that comes close to the –30 K/at% effect on T_c is iron itself. The reduction in T_c appears to be accompanied by a loss of long-range magnetic order, and susceptibility measurements suggest that a$-Fe_{87}Ru_3Zr_{10}$ may be a spin glass (SG), with a T_g of 84K, down from a T_c of 230K in the Ru–free alloy.

We report here magnetisation, Mössbauer and neutron depolarisation measurements aimed at determining the nature of the Ru-induced changes in the magnetic order of a$-Fe_{90-x}Ru_xZr_{10}$. Our results confirm the destruction of magnetic order and show that by $x = 3$, no long-range ferromagnetic order is present above 2K.

Experimental Methods

The alloys were prepared by arc-melting the appropriate ratio of pure elements (Fe: 99.95%, Zr: 99.5% and Ru: 99.9% pure) under Ti-gettered argon to yield $\sim 2\,g$ ingots. Melt-spinning was carried out under a partial pressure of Helium onto a copper wheel at 50 m/s. Absence of crystallinity was confirmed using Cu$-K_\alpha$ powder x-ray diffraction and room temperature Mössbauer spectroscopy.

A LakeShore susceptibility system with a closed-cycle fridge was used to record χ_{ac} *vs.* T down to 12K. Magnetisation data up to 7 Tesla were obtained using both a LakeShore MPMS. and a Quantum Design PPMS. Mössbauer measurements were made on a constant acceleration spectrometer with a 1GBq ^{57}Co**Rh** source calibrated using an $\alpha-$Fe foil. Samples were mounted in a vibration-isolated closed-cycle fridge for spectra at temperatures down to 12K.

Neutron depolarisation data were obtained using the DUALSPEC triple-axis spectrometer at AECL, Chalk River. Initial polarisations of ~95% at λ =0.237 nm were achieved with Cu_2MnAl

single crystals as polariser and analyser. Measurements were made between 2 and 300K in a 1 mT guide field, on single 5mm lengths of 20μm thick ribbons.

Results and Discussion

χ_{ac} measurements show a steady reduction in T$_c$ and evolution from ferromagnetic behaviour to a spin glass like cusp with increasing Ru content. While there is an abrupt change between $x = 2$ and $x = 3$, the cusp for the $x = 3$ sample is far more rounded than that of the $x = 4$ and it is possible that some FM order is present. Magnetisation at 2K shows a decrease with increasing x and an increase in high-field slope, consistent with a loss of collinear order. These results are in complete accord with earlier work [3,4].

The temperature dependence of the average hyperfine field (derived from Window fits [5]) in Fig. 2 shows an abrupt change between $x = 2$ and $x = 3$. For $x \leq 2$, the onset of magnetic splitting exhibits conventional FM behaviour and corresponds to the point where χ_{ac} rises from zero (Fig. 1), however for $x \geq 3$ the onset occurs at the peak in χ_{ac}, as it does in spin glasses. This suggests that the SG–FM boundary may lie between $x = 2$ and $x = 3$. Further indications of a significant change in magnetic order at this Ru content comes from modified Arrott plots, which yield ordering temperatures consistent with our other measurements for $x \leq 2$, but show no sign of order or spontaneous moment for $x \geq 3$, strongly suggesting that this system is a spin glass for $x > 2$. The ordering temperatures determined in this work are summarised in Fig. 3.

The clearest evidence for the disappearance of long-range order comes from the neutron depolarisation data shown in Fig. 4. For $x = 0$ we observe conventional ferromagnetic behaviour [6]: a rapid depolarisation of the neutron beam on cooling through T$_c$. The curve is well fitted assuming a constant domain size, with a domain magnetisation that follows a modified Brillouin function [7]. Ordering temperatures for $x = 0$, 1 and 2 agree with values determined by other methods. The depolarisation caused at T=0 decreases rapidly with increasing Ru, far more so than either the magnetisation or $< B_{hf} >$ (a measure of the total iron moment), we attribute this to a rapid reduction in domain size from 1.64$\pm$0.01 μm at $x = 0$ to 0.4$\pm$0.1 μm by $x = 2$. For $x \geq 3$ no depolarisation is observed at any temperature, ($\Delta P < 5 \times 10^{-4}$) and we can rule out the presence of ferromagnetic correlations on a length scale greater than 10nm. We conclude that for $x \geq 3$ the system is a spin glass.

For x =1 and 2, there is also a striking recovery in the depolarisation below about 80K. The simplest explanation for this would be a reduction in one or both of the domain size or the domain magnetisation. Magnetisation curves exhibit only a monotonic increase on cooling, allowing us to rule out contributions from this source, however we have no independent measure of the domain sizes and so are unable to determine whether or not domain size changes occur. Comparison with the Mössbauer data for the $x = 1$ sample raises another possibility. In the limit of small domains ($< 10\mu m$ for these materials) the polarisation goes as $P = \exp(-\alpha\lambda^2)$ [6] where the factor α depends on the domain size, sample thickness and the mean square domain magnetisation perpendicular to the neutron polarisation, $< B_\perp^2 >$. For a random assembly of domains this last term is just $2B^2/3$, while for a thin sheet with its plane parallel to the neutron polarisation direction and domains oriented in the plane by demagnetisation fields, we get $B^2/2$. The Mössbauer spectra also contain information on spin directions through the intensity of lines 2 and 5, and for the $x = 1$ sample we observed a change in spin directions from largely perpendicular to the ribbon plane above 80K, to more random below. If we incorporate this behaviour into the calculation of $< B_\perp^2 >$, then we are able to fit the data for the $x = 1$ sample with a consistent parameter set for both the Mössbauer and depolarisation data. While this consistency is suggestive, the actual domain distribution can be highly strain dependent, and differential thermal contraction can change the strain pattern on cooling. In order to unambiguously separate domain size changes from reorientations we need to measure the depolarisation signal for neutrons polarised along three orthogonal directions. Development of these modifications for the DUALSPEC spectrometer are currently underway.

Closer examination of $< B_{hf} >$(T) in Fig. 2 for $x = 1, 2$ reveals a clear break in slope near 80K. We emphasise that this break in slope is not caused by the change in the intensity of lines 2 and 5 discussed above. Firstly, the change in intensity starts about 15K above the break in $< B_{hf} >$(T). Secondly, forcing a constant intensity in line 2 and 5 degrades the fit quality, but does not eliminate the break in slope. The observed temperature dependence is well fitted by a combination of a modified Brillouin function and a linear term that appears only below the break temperature. T_{br} While this linear behaviour cannot continue to T=0, it does give an excellent description of the data (within 0.5%). The form of the additional term was suggested by examination of the difference between the data and a Brillouin function fitted only to the high temperature (T$\geq$ 90K) region. While no break is apparent in the $x = 0$ data, the same Brillouin function plus linear term also fits well but yields a T_{br} that is not significantly different from zero. The break points, shown in Fig. 3, lie below, but close to the ordering temperatures of the $x \geq 3$ samples. This might suggest that we are seeing two-phase behaviour, with a FM component that disappears with increasing x and is gradually replaced by a 80K SG phase that dominates for $x \geq 3$. However $< B_{hf} >$(T) is not linear in T for $x \geq 3$, rather it follows the same modified Brillouin function found for $x < 3$. Furthermore, we detect no indication of two-phase behaviour in other measurements: (i) Magnetisation curves show no change in form on heating through the break temperature. (ii) The width of the hyperfine field distribution increases gradually on cooling and does not exhibit the sharpening expected when an additional component orders. (iii) $< B_{hf} >$(0 K) does not change dramatically between $x = 2$ and 3, the difference is only 1 Tesla, even though the linear term, which we might associate with the SG phase, never contributes more than 5 Tesla and should be the only component present at $x = 3$.

An alternative, uniform, description of the system is provided by bond frustration [1]. Increasing numbers of frustrated bonds lead to reduced T_c and magnetisation, and to the appearance of a second transition (T_{xy}) below which non-collinear order develops. T_c and T_{xy} merge at high frustration levels and the system becomes a spin glass. Such a picture has been used to account for the magnetic properties of a$-Fe_xZr_{100-x}$ and is fully consistent with the phase diagram in Fig. 3 if T_{br} is identified with T_{xy}. The only remaining question is why Ru additions lead to an increase in exchange frustration. A simple appeal to atomic packing fails because Ru is larger than Fe. The increase in the numbers of short Fe–Fe distances that follow from replacing a large Zr atom by a smaller Fe has been used to explain increasing frustration in a$-Fe_xZr_{100-x}$ [1], however, for Ru such an argument would predict a reduction in frustration. Similarly, we cannot appeal to antiferromagnetically coupled Ru-moments as isolated Ru atoms do not carry a moment in Fe [7], nor would such isolated AF moments cause the frustration needed to drive the system towards spin glass ordering [8]. One possible mechanism might be that the changes in the density of states associated with Ru additions act so as to change the crossover point in $\mathcal{J}(r)$ so that the distance at which the Fe–Fe exchange interaction switches from FM to AF is increased and more bonds become frustrated.

Acknowledgments

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Figure captions

Figure 1 χ_{ac} measurements on a$-Fe_{90-x}Ru_xZr_{10}$ showing the reduction in T$_c$ and the evolution towards a spin glass like cusp with increasing Ru content.

Figure 2 Average hyperfine field ($< B_{hf} >$) versus temperature for the five alloys studied here. The onset for x=3 corresponds to the peak in χ_{ac} shown in Fig. 1 suggesting spin glass ordering. Note also the clear break in slope for $< B_{hf} >$(T) in the cases of x=1 and 2. Lines are fits described in text.

Figure 3 Ordering temperatures (T$_c$) for a$-Fe_{90-x}Ru_xZr_{10}$ derived from χ_{ac}, Mössbauer spectroscopy and neutron depolarisation. Also shown as open squares, is T$_{br}$, the break points in $< B_{hf} >$(T) for x=1 and 2 (see text).

Figure 4 Neutron depolarisation data for a$-Fe_{90-x}Ru_xZr_{10}$ obtained on cooling (∇) and heating ($\Box$) in the guide field of 1mT. Data for the $x = 4$ sample were omitted as they show the same absence of change apparent for the $x = 3$. Solid lines are fits described in the text.

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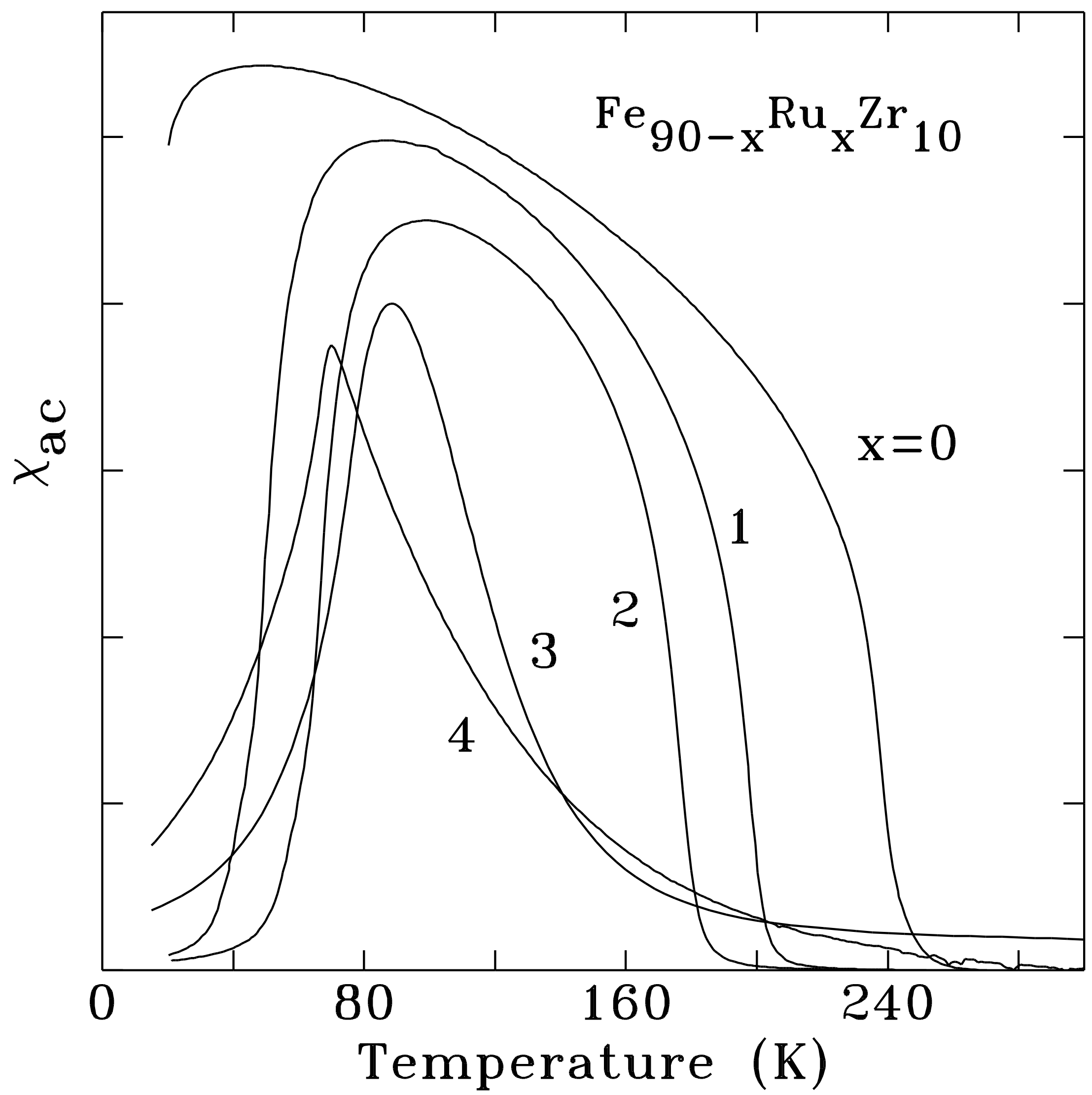

Figure 1: Ryan, Cadogan and Tun, MMM96 CD–08

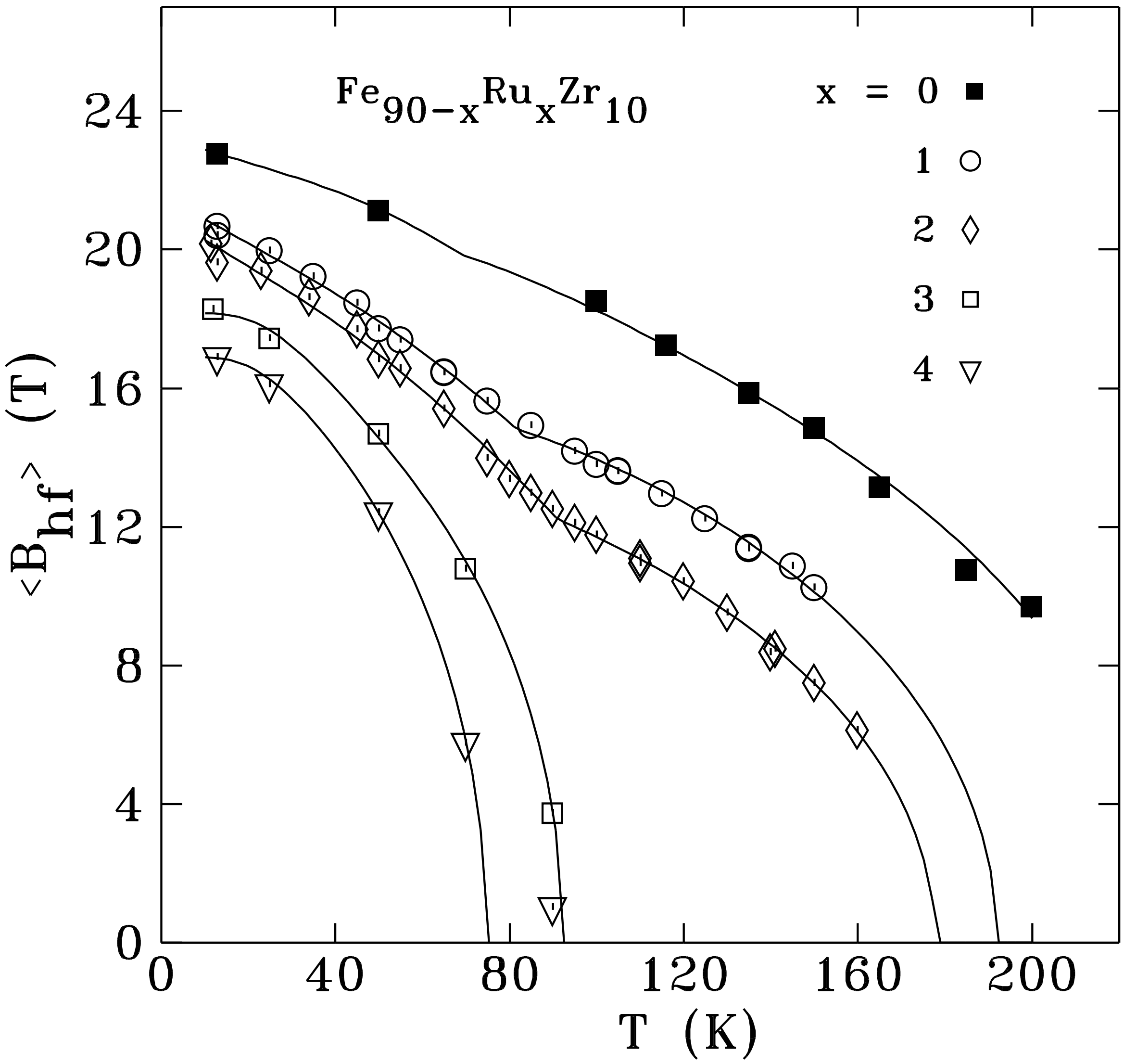

Figure 2: Ryan, Cadogan and Tun, MMM96 CD–08

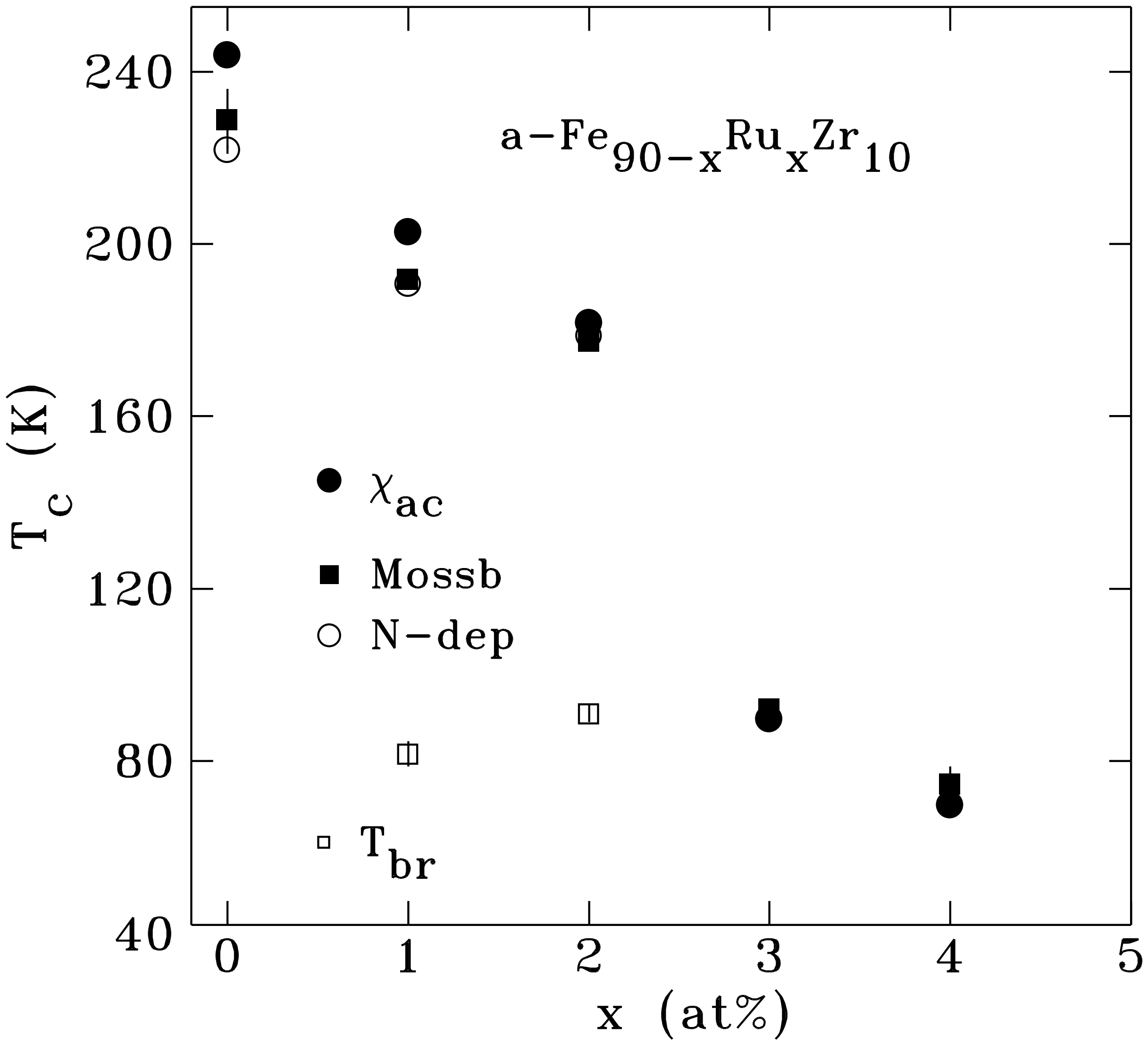

Figure 3: Ryan, Cadogan and Tun, MMM96 CD–08

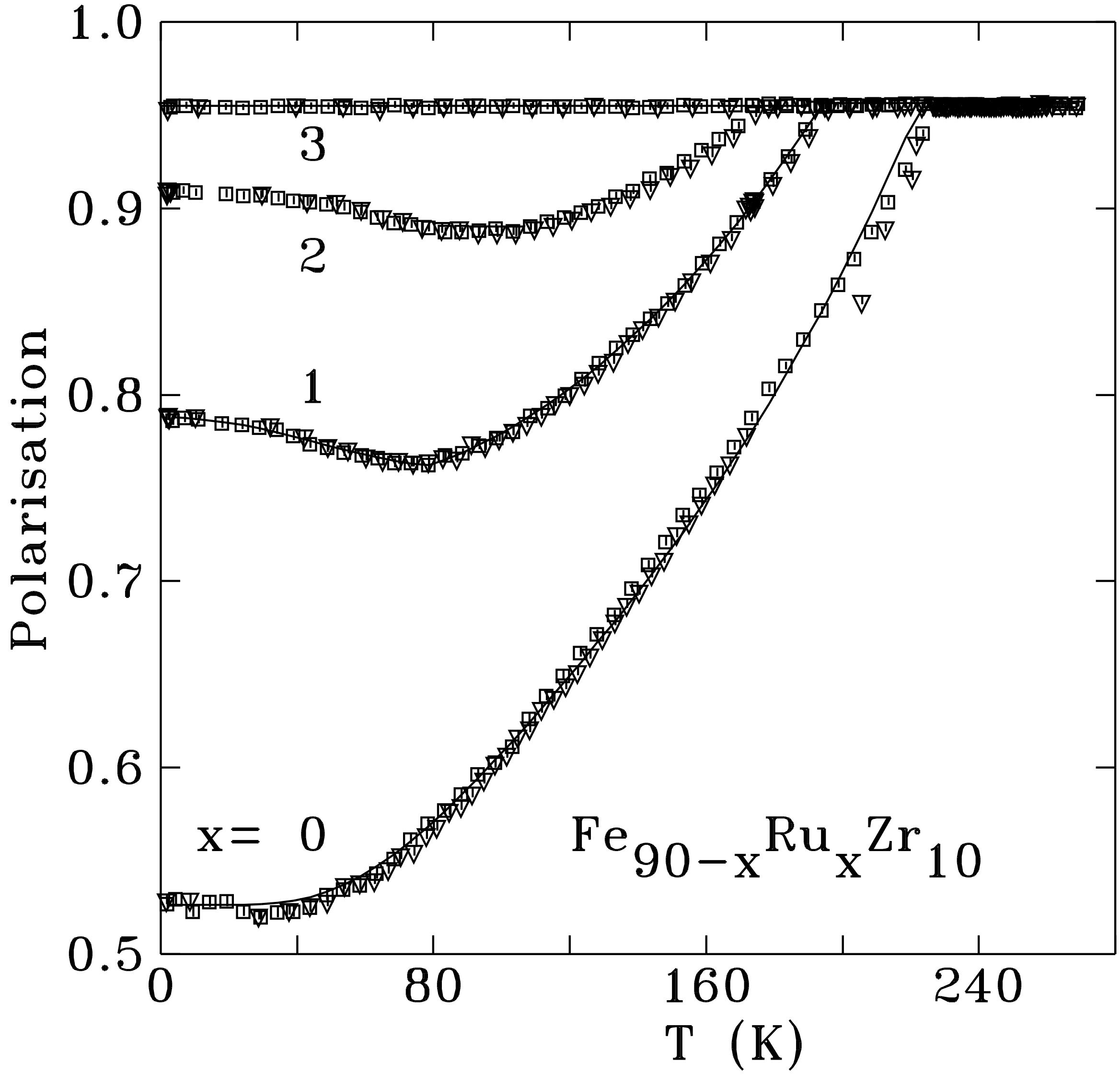

Figure 4: Ryan, Cadogan and Tun, MMM96 CD–08