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1995 J. Phys.: Condens. Matter 7 5891

(http://iopscience.iop.org/0953-8984/7/29/016)

J. Phys.: Condens. Matter 7 (1995) 5891–5899. Printed in the UK

The magnetic domain effect in the local canted spin ferrite $Zn_{0.5}Co_{0.5}Fe_{2-x}Cr_xO_4$: a macroscopic and mesoscopic study

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Received 21 February 1995, in final form 4 April 1995

Abstract. AC susceptibility, zero-field-cooled (ZFC) magnetization and field-cooled (FC) magnetization have been reported for the $Zn_{0.5}Co_{0.5}Fe_{1.1}Cr_{0.9}O_4$ disordered ferrite system. A polarization analysis of the transmitted neutron beam in both ZFC and FC conditions has also been reported for $Zn_{0.5}Co_{0.5}Fe_{2-x}Cr_xO_4$ ($x = 0.9$ and 1.0) systems. The low-field AC susceptibility shows a broad peak at a temperature (well below the Néel temperature) where a strong irreversibility between the ZFC and FC curves starts. The presence of a ferrimagnetic-like domain structure over the entire temperature range (below the Néel temperature) is confirmed from the presence of significant depolarization up to 12 K, the lowest measured temperature. The observed features of χ_{AC}, magnetization and neutron depolarization measurements have been analysed using a model of thermally activated domain wall movement of ferrimagnetic arrangement of local canted spins.

1. Introduction

Spinel ferrites constitute an important class of magnetic materials. The spinel structure consists of a close-packed FCC cage of oxygen ions with two interstitial sites of tetrahedral (A) and octahedral (B) site symmetries. The metal ions occupy these A and B sites and the magnetic structure depends upon the type of magnetic ion residing on the A and B sites and the relative strengths of the inter-sublattice interactions J_{AB} and intra-sublattice interactions J_{AA} and J_{BB}. Generally, all the three exchange integrals J_{AA}, J_{BB} and J_{AB} are negative with $|J_{AB}| \gg |J_{BB}| > |J_{AA}|$. Thus, the orientation of the A-site moment is antiparallel to the B-site moment with the AA and BB exchange bonds remaining unsatisfied. Further, as spinels offer the possibility of selective magnetic dilution of A and B sites, one finds a rather rich variety of magnetic behaviours [1–7] in this family. Various types of magnetic ordering ranging from ferrimagnetism, antiferromagnetism, local canted spin (LCS) to semi-spin-glass, spin-glass, etc, have been observed [1]. A quantitative phase diagram was worked out by Villain [8] that predicts a ferrimagnetic-to-semi-spin-glass transition as a function of the magnetic ion concentration on the A and B sites. Recent low-field magnetization, AC susceptibility and Mössbauer measurements by Muraleedharan *et al* [9] down to 80 K on $Zn_yCo_{1-y}FeCrO_4$ led to the conclusion that the ferrimagnetic phase disappears and spin-glass freezing is observed at low temperatures. On the other hand, a microscopic neutron diffraction study on the same disordered ferrites $Zn_yCo_{1-y}FeCrO_4$ ($y = 0.45$, 0.50 and 0.55) showed the existence of long-range ferrimagnetic ordering of the longitudinal components S_z of the spins and disorder of the transverse components S_t of the spins for all three compositions. It was found that the A-site moments are not very different from

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0953-8984/95/295891+09$19.50

their corresponding free-ion values, whereas the B-site moments are substantially smaller than their estimated free-ion values, suggesting that the B-site moments are highly non-collinear. Moreover, for $y \geqslant 0.50$ the long-range ferrimagnetic order of S_z was found to coexist with short-range correlation in S_t at low temperatures [10]. The neutron diffraction measurements carried out on $Zn_{0.5}Co_{0.5}Fe_{2-x}Cr_xO_4$ with $x = 0.9$ and 1.1 over a limited temperature range 100–300 K [11] showed that the effect of a slight increase in magnetic Cr-ion concentration on the B site is similar to that produced by an increase in diamagnetic Zn-ion concentration at the A site.

In view of the foregoing situation, we decided to perform AC susceptibility χ_{AC}, magnetization and neutron depolarization measurements to arrive at a better understanding of the nature of magnetic ordering in these disordered ferrites. In our earlier paper the detailed magnetization study of $Zn_yCo_{1-y}Fe_{2-x}Cr_xO_4$ with $x = 1.0$, $y = 0.45$, and with $x = 1.0$, $y = 0.50$, has been reported [12]. The magnetization measurements revealed that these disordered spinels exhibit local spin canting behaviour. In this paper, we present the results of macroscopic χ_{AC}, zero-field-cooled (ZFC) magnetization and field-cooled (FC) magnetization measurements of an $x = 0.9$, $y = 0.5$, sample. We have also carried out our study on a mesoscopic length scale, namely neutron depolarization measurements on both $x = 0.9$, $y = 0.5$, and $x = 1.0$, $y = 0.5$, samples over the temperature range 12–294 K.

2. Experimental details

The present work has been carried out on the same samples (prepared using the wet chemical method) as were used in the earlier neutron diffraction studies [10, 11].

The real part of χ_{AC} was measured on the $x = 0.9$ polycrystalline sample using a mutual inductance bridge at 280 Hz and about 2 Oe RMS field with the sample mounted on the cryotip of a closed-cycle helium refrigerator. The ZFC and FC magnetization measurements were carried out on the $x = 0.9$ sample using a commercial Faraday balance. Measurements were made on a powder sample which was compacted in the form of a pellet. The following procedures were used for ZFC and FC magnetization measurements. In ZFC measurements the sample was cooled from room temperature to 10 K in zero field. A field of 50 Oe was applied at 10 K, and then the ZFC magnetization measurements were carried out in the heating cycle after an adequate pause at each temperature for thermal stability. For the FC case, on the other hand, the sample was first cooled from room temperature to 10 K in the presence of a 50 Oe field (the measuring field used in the ZFC case) and then measurements were carried out (keeping the field on) in the heating cycle as in the ZFC case.

The one-dimensional neutron depolarization measurements were carried out using a neutron polarization analysis spectrometer at Dhruva reactor, Trombay ($\lambda = 1.201$ Å). A detailed description of the spectrometer has been given in an earlier report [13]. The depolarization measurements were performed with the incident neutron beam polarized along the $-z$ direction (vertically down) with a beam polarization of 98.83(1)%. The transmitted neutron beam polarization was measured along the $+z$ direction. A standard RF π flipper was used before the sample for flipping the incident neutron spin. A flat rectangular aluminium sample holder with an effective thickness of 4 mm was used for depolarization studies. The powder samples used were in the form of compressed pellets. The sample was placed in the neutron beam in such a way that the propagation direction of the polarized neutron beam remained along the thickness of the flat sample. The beam size was restricted within the size of the sample pellets. The measurements were carried out over the temperature range 12–300 K using a closed-cycle helium refrigerator with a temperature accuracy of better

than 0.1 K. The ZFC and FC depolarization measurements were carried out using the same procedures as described for the ZFC and FC magnetization measurements. In all cases, the external magnetic field (on the sample) was applied along the $-z$ direction using a small electromagnet. A field of 5 Oe was applied on both the samples.

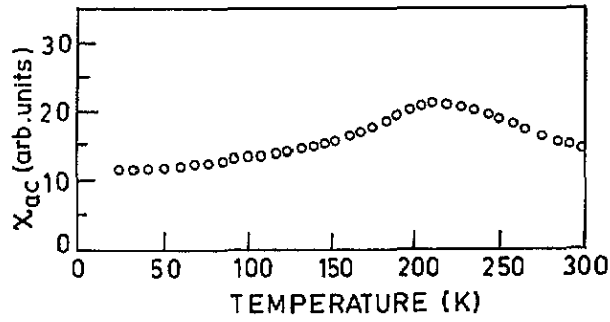

Figure 1. The temperature dependence of the real part of the AC susceptibility for $x = 0.9$ sample.

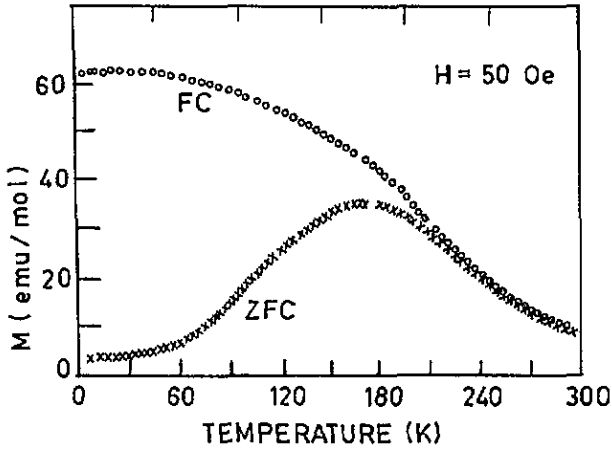

Figure 2. ZFC and FC magnetization as a function of temperature for the $x = 0.9$ sample with $H_{external} = 50$ Oe.

3. Experimental results and data analysis

Figure 1 shows the temperature dependence of the χ_{AC} measurements for the $x = 0.9$ sample. It shows a broad peak at around 220 K which is well below the Néel temperature of this composition (the estimated Néel temperature for this composition is above 300 K [11]). It is to be noted that the observed χ_{AC} curve is asymmetric. The low-field magnetization data for the $x = 0.9$ sample under FC and ZFC conditions are shown in figure 2. There is a strong irreversibility between the ZFC and FC curves which starts at around 220 K. It is to be noted

that the weak irreversibility starts right from 295 K, the highest measured temperature. The ZFC curve shows a broad maximum at about 168 K, while the FC magnetization continuously increases until about 36 K; thereafter it remains almost constant. The ZFC curve shows asymmetric behaviour as also seen in the χ_{AC} data (figure 1).

Before presenting the experimental results of our neutron depolarization study, we briefly recall the theory of neutron depolarization in various magnetic systems. The theory of neutron depolarization was first given by Halpern and Holstein [14]. The theory was developed further by several workers [15–17]. Later, Mitsuda and Endoh [18] derived the wavelength-dependent transmitted polarization $P(\lambda)$. Neutron depolarization is a mesoscopic probe. It can measure the spatial magnetic inhomogeneity on a length scale, say, from 100 Å to a few thousand ångströms. In an unsaturated ferromagnet or ferrimagnet, the magnetic domains exert a dipolar field on the neutron polarization and depolarize the neutrons owing to the Larmor precession of the neutron spins in the magnetic field of domains. $P(\lambda)$ can be written in the most general for as

$$P(\lambda) = \left(\left\langle \frac{B_{\parallel}^2}{B^2} \right\rangle_B + \left\langle \frac{B_{\perp}^2}{B^2} \right\rangle_B \langle \cos(cB\delta\lambda) \rangle_\delta \right)^N \tag{1}$$

where $B_{\parallel}$ and $B_{\perp}$ are the components of the magnetic induction B of a domain parallel and perpendicular, respectively, to the direction of incident neutron polarization $(-z)$, δ is the mean domain size and λ is the neutron wavelength. The constant c is related to the neutron gyromagnetic ratio g ($c = gm/2\pi\hbar = 4.63 \times 10^{-10}$ Oe^{-1} Å^{-2}) and N is the average number of the domains along the path of neutrons ($N = d/\delta$, where d is the sample thickness). The angular brackets $\langle\ \rangle_B$ and $\langle\ \rangle_\delta$ represent the ensemble average over the local induction B in each domain and the domain size, respectively.

It is clear from equation (1) that, in each ferromagnetic domain, the spin component parallel to the induction B does not precess whereas the component perpendicular to B does. The precession angle for a neutron of wavelength λ, travelling a distance δ in a field B is $\phi_\delta = (4.63 \times 10^{-10}\ \text{Oe}^{-1}\text{Å}^{-2}) B\delta\lambda$. As the neutron depolarization technique probes the magnetic inhomogeneity on a mesoscopic length scale [19–22] a magnetic inhomogeneity on an atomic scale—as in true spin-glass state—has no effect on the neutron polarization. In a true spin-glass phase the spins are randomly frozen in space on a microscopic length scale and, as a result, the magnetic induction averages out to zero on a mesoscopic length scale. Hence no depolarization is found in true spin-glass systems. Similarly no depolarization is expected in a paramagnetic state because the temporal spin fluctuation is too fast (10^{-12} s or faster) for the neutron polarization to follow the variation in the magnetic field B acting on the moving thermal neutron.

Figures 3 and 4 show the temperature dependences of ZFC and FC transmitted beam polarization for both the ferrites. For the $x = 0.9$ sample, both ZFC transmitted polarization and FC transmitted polarization show a continuous drop below about 285 K and attain their constant values below about 35 K. As a striking result, unlike the macroscopic χ_{AC} and/or low-field ZFC magnetization results, the mesoscopic depolarization data do not reveal any transition or anomaly at any temperature over the measured temperature range. However, differences are observed between the ZFC and FC depolarization data right from 294 K. The irreversibility between ZFC and FC depolarization increases with decrease in temperature. It is to be noted that at 294 K the measured polarization (with sample) was found to be slightly smaller than that measured without the sample. For the $x = 1.0$ sample the ZFC curve deviates from the FC curve right from 294 K (figure 4). The ZFC polarization decreases with decreasing temperature and reaches a plateau at around 40 K. However, at

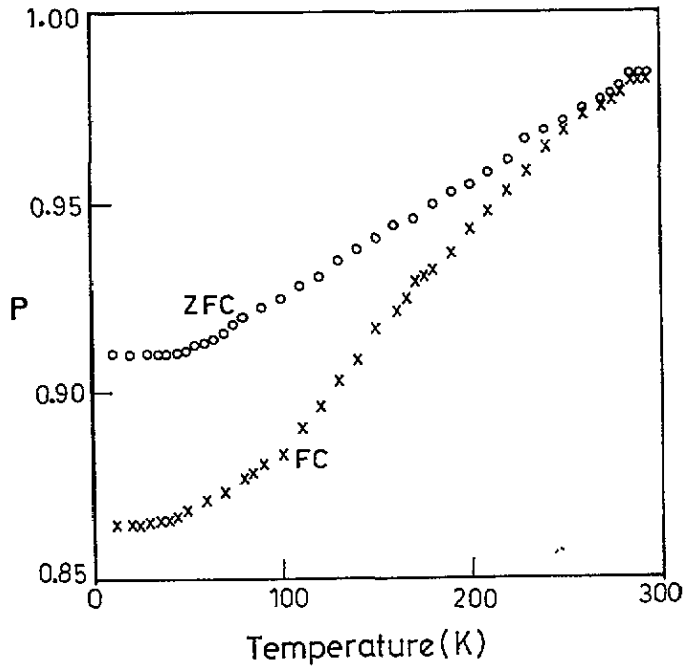

Figure 3. ZFC and FC polarization P versus temperature measured in a 5 Oe field for the $x = 0.9$ sample.

lower temperatures (below about 30 K) the polarization increases. The FC depolarization curve shows almost the same behaviour as in the ZFC case. It is to be noted that for both the samples the FC method shows a higher depolarization than that obtained from the ZFC method.

4. Discussion

The strong irreversibility between the ZFC and FC magnetization observed below 220 K (figure 2) occurs at a temperature which matches with the temperature where a broad peak in the χ_{AC} curve has been observed (figure 1). The appearance of such a broad peak in the χ_{AC} curve below $T_N(> 300$ K) is normally taken as a signature of spin freezing. For the $x = 1.0$ sample, similar χ_{AC} and ZFC–FC magnetization behaviours have been reported in [12]. We may recall here that such a broad peak in the χ_{AC} curve and differences between ZFC and FC magnetization have been observed in spin-glass or spin-glass-like materials [23, 24] and also in LCS ferrites [25, 26], amongst others. Low-field ZFC and FC magnetization measurements are often used to study spin-glass or spin-glass-like phases. However, for systems where long-range order is involved, the contribution can arise from domains, domain walls and from disorder. In LCS systems the ZFC–FC branching behaviour has been interpreted in terms of domains, i.e. as a consequence of the temperature variation in the hysteresis loop [1]. As mentioned before, the neutron diffraction study reported on the $x = 0.9$ sample [11] over a limited temperature range 100–300 K and on the $x = 1.0$ [10] sample over 5–300 K showed long-range ferrimagnetic ordering of longitudinal spin components. The neutron diffraction study gives the microscopic understanding of spin correlations in these ferrite

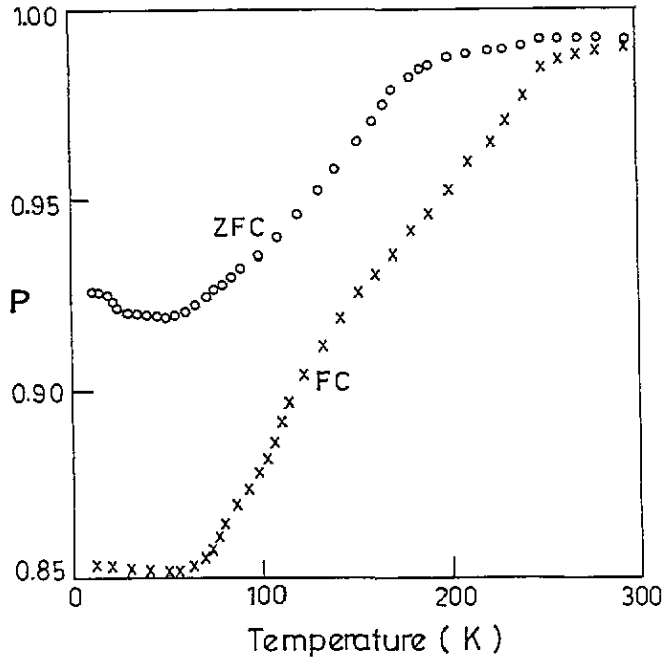

Figure 4. ZFC and FC polarization measured as a function of temperature in a 5 Oe field for the $x = 1.0$ sample.

systems. However, the question of the origin of the observed features in the macroscopic studies, namely χ_{AC} and ZFC–FC magnetization (figures 1 and 2) remains to be answered. In order to understand the macroscopic behaviour of these ferrites the mesoscopic neutron depolarization results provide help [19–22].

For both the $x = 0.9$ and the $x = 1.0$ samples the presence of a ferrimagnetic-like domain structure is confirmed from the presence of significant depolarization up to 12 K, the lowest measured temperature (figures 3 and 4). For the $x = 0.9$ sample a continuous drop in both the ZFC and the FC transmitted polarization right from room temperature (the highest measured temperature) up to about 35 K clearly indicates that the ferrimagnetic order parameter increases with decrease in temperature. The saturation behaviour of the ferrimagnetic order parameter is evident below 35 K as P attains its constant value below this temperature. It is to be recalled that ZFC and FC magnetization (for this composition) also saturate below about the same temperature. The difference between the ZFC and the FC depolarization increases with decrease in temperature until about 35 K (below which a constant difference is maintained). There is no indication of breakdown of ferrimagnetic correlation for the $x = 0.9$ sample at any temperature. The decrease in depolarization observed for the $x = 1.0$ sample below 30 K can arise from either a decrease in the effective internal fields and/or a decrease in the average domain size. A decrease in the effective internal fields can arise either from a decrease in the ferrimagnetic ordering at low temperatures or because of a different variation in the magnetizations of A and B sublattices. In fact, a neutron diffraction study on these ferrites shows different temperature responses of the individual tetrahedral site and octahedral site moments [10]. An increase in the canting angle of randomly canted spins (LCS structure) would also produce a decrease in ferrimagnetic ordering [1, 7].

The existence of magnetic domains over the entire temperature range for both the samples is evident from our depolarization study. This observation is consistent with the neutron diffraction results, namely a long-range ferrimagnetic order of the S_z components of spins. The observed short-range correlation of transverse spin components at 20 K for the $x = 1.0$ sample as seen by neutrons has not provided any evidence in our depolarization study. This can be understood in the following way. As the transverse spin components are correlated on a short length scale compared with the domain size, the transverse field seen by neutron spin is vanishingly small. As a result the depolarization is mainly determined by the longitudinal spin component [20].

The observed irreversibility between ZFC and FC depolarization clearly tells us that the domain mobility strongly depends upon the cooling process of the samples. It is interesting to note that in the FC case a higher depolarization is observed than in the ZFC case. In a normal situation, one would expect more depolarization in the ZFC case than in the FC case as, when sample is cooled in the absence of a field, the domains are more random and as a result the effective internal field (transverse to the neutron polarization) is high. From our study it is apparent that the domain growth mechanisms are different in the ZFC and the FC cases. When the sample is cooled in the presence of an external field, it helps the domains to grow. For our depolarization measurements a small field of 5 Oe was applied, which lies in the rising part of the virgin curve of magnetization versus field. In particular, the initial slope of the M–H curve is determined by the dynamics of the domain motions. At this low field, favourably oriented domains grow in size [27]. So a higher depolarization is expected from larger domains. It should be mentioned that our samples contain Co^{2+} ions, and this introduces uniaxial random anisotropy [28]. In the FC case the cooling field can induce a large unidirectional anisotropy so that very large domains can be maintained. For both samples the ZFC–FC branchings are found right from room temperature, the highest measured temperature. This observation supports the LCS-type behaviour of these ferrites, since in LCS ferrite systems one would expect branching right from T_N [1]. For the $x = 0.9$ sample we find a one-to-one correspondence between the strong irreversibility of ZFC–FC depolarization and low-field magnetization at around 220 K and a broad peak in the χ_{AC} curve at around the same temperature. We note here that for the $x = 1.0$ sample such correlations have not been found. This may be due to the strong field-dependent ZFC–FC magnetization–depolarization branching effects in this system. In fact it has been seen that the temperature at which the branching between the ZFC–FC magnetization occurs strongly depends on the field applied to the sample [12].

The above discussion shows that the decrease in the susceptibility and low-field ZFC magnetization observed below about 220 K and 140 K for the $x = 0.9$ (figures 1 and 2) and for the $x = 1.0$ [10, 12] samples, respectively, does not result from a breakdown of ferrimagnetic correlation or a transition to any spin-glass-like phase but can be related to magnetic domain effects. Here it should be mentioned that for the $x = 1.0$ sample the appearance of the χ_{AC} peak at around 140 K was taken as the signature of a phase transition from an unstable ferrimagnetic to a cluster spin-glass by Muraleedharan *et al* [9]. In our recent hysteresis measurements of the $x = 1.0$ sample [12] the temperature dependence of domain and domain wall motion is clearly seen. The coercive field H_C was found to be in the form of $A\exp(-T/T_0)$. The temperature dependence of domain and domain wall motion is very clear from the double-exponential behaviour of H_C as a function of temperature. The existence of two values of T_0 for the $x = 1.0$ sample indicated that there are two activation barriers for the domain wall pinning which has a natural explanation within the framework of the LCS structure [1]. Such an exponential temperature dependence has previously been observed in LCS ferrite systems [25, 29, 30].

The observed broad asymmetrical peak in the χ_{AC} curve (figure 1) and also in the low-field ZFC magnetization (which have been also observed for other diluted ferrites [31,32]) can be attributed to effects arising from uniaxial random anisotropy.

5. Summary and conclusions

We have performed χ_{AC}, low-field ZFC and FC isofield magnetization measurements on $Zn_{0.5}Co_{0.5}Fe_{1.1}Cr_{0.9}O_4$ ferrite. ZFC and FC neutron depolarization measurements have been performed on $Zn_{0.5}Co_{0.5}Fe_{2-x}Cr_xO_4$ ($x = 0.9$ and 1.0) ferrites. The observed features of χ_{AC}, magnetization and neutron depolarization measurements have been ascribed to a model based on thermally activated domain wall movement in a LCS arrangement. In this model, the broad hump in the χ_{AC} curve well below the Néel temperature and irreversibility between low-field ZFC and FC magnetization are not signature of a phase transition but a kinetic freezing process of magnetic domains.

Acknowledgments

It is a pleasure to thank Dr K R Rao and Dr B A Dasannacharya for their interest and encouragement in this work.

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