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Magnetic properties of Zr doped Y_9Co_7

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Abstract. Detailed measurements of magnetization and ac susceptibility at low temperatures of 1% Zr-substituted Y_9Co_7 are presented. All results are indicative of itinerant weak ferromagnetism with $T_c \sim 9{\cdot}5$ K. The zero-field magnetizations follow T^2 or $T^{4/3}$ behaviour as in the Ni-substituted system. The estimated critical exponents are $\beta = 0{\cdot}38 \pm 0{\cdot}03$, $\gamma = 1{\cdot}16 \pm 0{\cdot}05$. It is argued that the main effect of the non-magnetic Zr-substitution in Y_9Co_7 is to stabilize the ferromagnetic ordering by suppressing the 'hopping' of Co atoms along the c-axis sites of the hexagonal structure.

Keywords: Magnetic superconductor; Y_9Co_7; ac susceptibility; magnetization; critical exponents.

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1. Introduction

The intermetallic compound Y_9Co_7 has unusual magnetic and superconducting properties. It has been emphasized by Sarkissian (1986) that these properties at low temperatures can be explained in terms of the hopping mechanism proposed by Yu and Anderson (1985) for A15 superconductors. The Y_9Co_7 is a strongly interacting spin fluctuation system, which co-exists with superconductivity below the temperature $T^*(\leqslant 5{\cdot}5\,\mathrm{K})$ and does not order magnetically, but it becomes superconducting at $T_S \leqslant 2{\cdot}7$ K. The absence of long range order has been shown by many experimental techniques such as small angle neutron scattering, neutron depolarisation, μ ESR, and the absence of spontaneous magnetization as predicted by virgin magnetization curves (see references in Sarkissian 1986). Further the properties of Y_9Co_7 are sensitive to disorder and alloying. For example substitution (up to 2000 ppm) of rare-earth elements like Gd or nonmagnetic elements (Sc, Lu) at Y sites and the transition metals Ni, Mn and Ti at Co sites suppress the superconductivity and magnetism (Sarkissian 1982; Grover and Sarkissian 1983). Ranganathan and Thummes (1987) recently, explained the saturation behaviour in resistivity using a diffraction model, the s–d scattering model for the substituted compounds, to compare with A15 superconductors. Here we report the low field magnetization experimental results at very low temperatures $0{\cdot}125\,\mathrm{K} \leqslant T \leqslant 10\,\mathrm{K}$ and low frequency, low field ac susceptibility results of 1% Zr-substituted sample. The particular choice of the Zr-substituted sample stems from the fact that Zr does not have local moment, unlike Gd which gives ferrimagnetic ordering around 18 K in $(Y_{0{\cdot}95}Gd_{0{\cdot}05})_9Co_7$ (Grover and Sarkissian

1983). Further the 1% Zr sample does not show any superconductivity down to 125 mK unlike Ni-substituted sample ($T_s \leqslant 0{\cdot}5$ K) (Sarkissian and Tholence 1984). Thus a systematic study of magnetization at very low temperatures is possible in the 1% Zr sample, because of the absence of superconductivity, and this enables us to throw more light on the magnetism.

2. Experimental methods

The sample ($m = 127{\cdot}9$ mg) consisted of a polycrystalline thin stick ($\phi = 1{\cdot}2$ mm, $l = 10$ mm) which was prepared by Dr H E N Stone at Imperial College, London, UK by arc melting and annealing. The details of the preparation will be presented elsewhere. The 1% Zr-substitution has been nominally made for Co in the parent Y_9Co_7. It is apparent that the results would not be different even if the replacement is attempted for Y. The low field ac susceptibility was measured at a field $H_{\mathrm{rms}} \sim 1{\cdot}5$ Oe and frequency 24 Hz, by a standard mutual inductance bridge. For the same sample the magnetization was measured in the field up to 2000 Oe, in the temperature range 0·125 K – 9 K by an extraction principle. The very low temperature was obtained by an adiabatic demagnetization. The field was applied along the sample to minimise the demagnetization effect.

3. Results and analysis

It has been shown that the impurity substituted Y_9Co_7 (Ni, Fe, Gd, etc.) shows long range order (Sarkissian 1982; Sarkissian and Tholence 1984). We found that Zr-substituted Y_9Co_7 dealt with in this paper is a ferromagnet unlike Y_9Co_7 which is a spin fluctuation system. Hence we have carried out the analysis to estimate the critical exponents γ and β. One of the most direct and accurate methods to find the critical exponents γ and the initial susceptibility, χ_0 comes from ac susceptibility experiments. By definition initial susceptibility is $\chi_0 = [\partial M/\partial H]_{H=0}$. Since $\chi = \chi' + i\chi'$, it follows that at low field in ac susceptibility experiments the χ' component approaches χ_0, χ'' being the small quantity at low frequency. Figure 1 shows the ac susceptibility (χ' and χ'') measured at 24 Hz, 1·5 Oe. For the temperature just above T_c,

$$\chi_0(T) = \Gamma(t)^{-\gamma}, \quad t > 0, \tag{1}$$

where Γ is the critical susceptibility amplitude and $t = (T - T_c)/T_c$. The alternative form of (1) is (Kouvel and Fisher 1964)

$$f(T) = \chi_0^{-1}(T)[\mathrm{d}\chi_0^{-1}(T)/\mathrm{d}T]^{-1} = \frac{T - Tc}{\gamma}, \tag{2}$$

The plot $f(T)$ vs T as shown in figure 2(a) with $T_c = 9{\cdot}50 \pm 0{\cdot}05$ K and $\gamma = 1{\cdot}16 \pm 0{\cdot}05$ for the best linear fit close to T_c.

Figure 3 shows the general features of Arrots plots for Zr sample in the temperature range 0·125 K–9 K just below T_c in the whole range of the applied field 0–2000 Oe. These data were taken after cooling in zero field. The well-defined and parallel lines were obtained for the field 400 Oe onwards. We have not plotted certain other

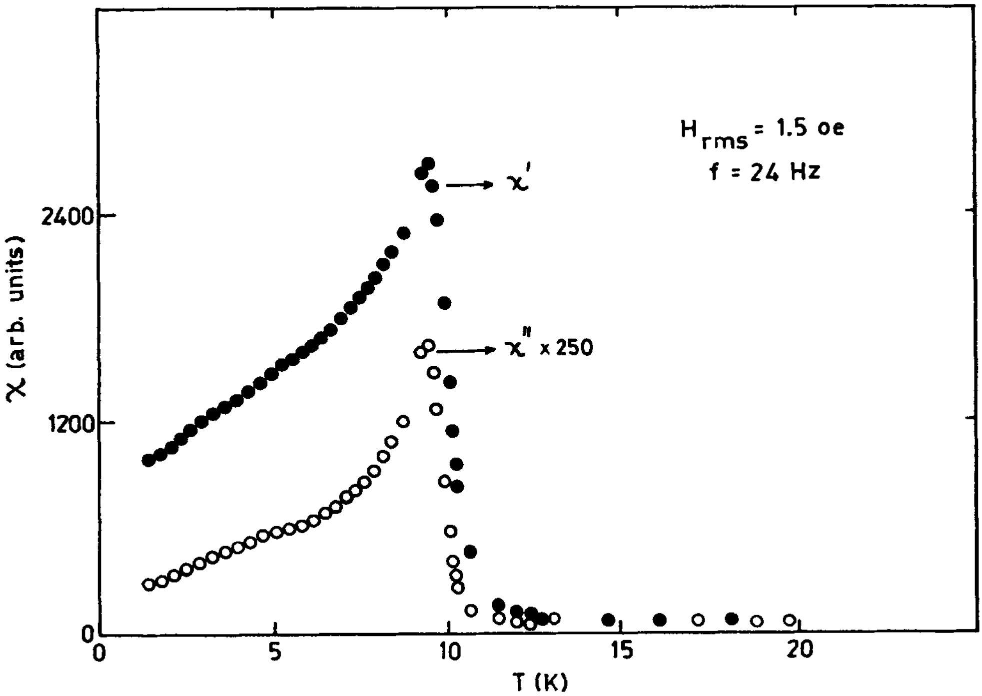

Figure 1. ac susceptibilities χ'(●) and χ''(○) as a function of temperature for Zr-substituted sample.

temperature data to avoid over-crowding in figure 3. The hysteresis curve at 4·2 K is shown in figure 4. The magnetization extrapolated to zero field from the Arrots plot $M(0, T)$ can be written as for $T < T_c$

$$M(0, T) \propto [(T_c - T)/T_c]^{\beta}. \tag{3}$$

The straightforward determination of the critical exponent is to use a double logarithmic plot of (3) if we have a well predetermined T_c. However to check the T_c deduced from χ (ac) data, we adopted the method of Kouvel and Fischer (1984) where $M_s(\mathrm{d}Ms/\mathrm{d}T)^{-1}$ (in our rotation $M_s(T)$ is represented by $M(0, T)$ is plotted against temperature resulting in straight lines. The inverse slope gives β and the intercept gives T_c. These results are shown in figure 2(a) where $\beta = 0{\cdot}38 \pm 0{\cdot}03$, $T_c = 9{\cdot}46 \pm 0{\cdot}05$ K which is in agreement with T_c deduced from χ(ac) data.

Furthermore to study the nature of magnetism in the Zr sample, it may be useful to compare the $M(H)$ results with the mean-field theory and the self-consistent renormalization theory of spin fluctuations as in $Y_9(Co_{0{\cdot}97}Ni_{0{\cdot}03})_7$ (Sarkissian 1984). The field and temperature dependence of the magnetization for the weak itinerant ferromagnetism in the Stoner model of single particle excitations can be written as, (Edwards and Wohlforth 1968).

$$M^2(H, T) = M^2(0, 0)\left[1 - \left(\frac{T}{T_c}\right)^2 + \frac{2\chi_{0H}}{M(H, T)}\right] \text{for } 0 < T < T_F \tag{4}$$

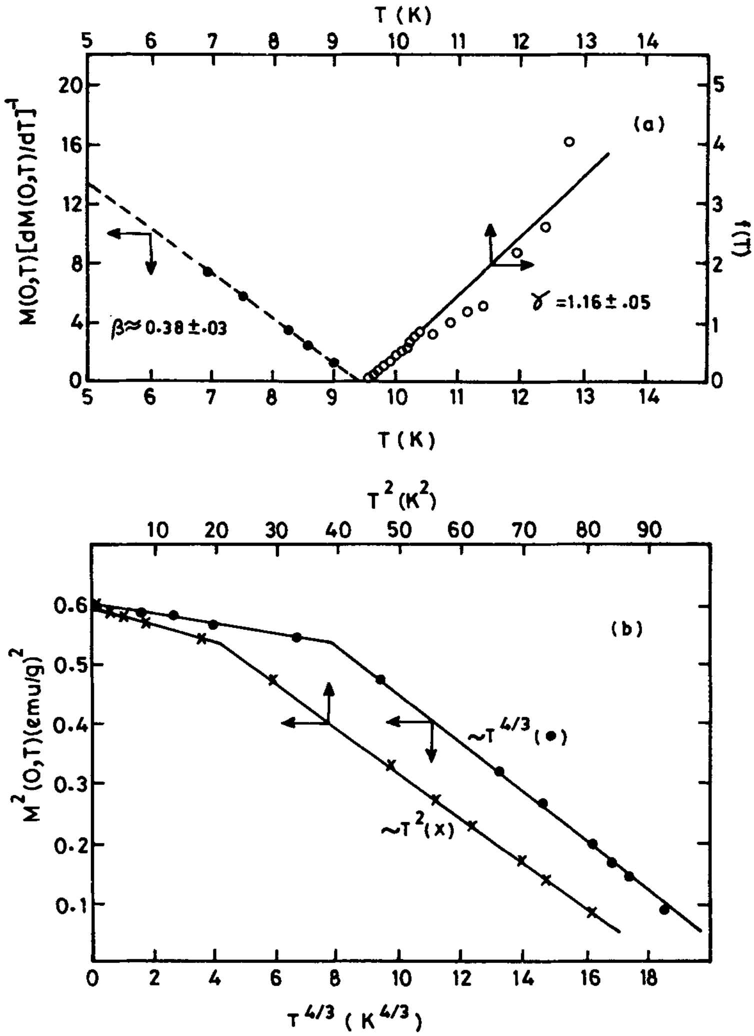

Figure 2. (**a**) Estimation of critical exponents from the magnetization and ac susceptibility data (see text). (**b**) Temperature dependence of the magnetization, $M(O, T)$.

$$M^2(0,T) = M^2(0,0)\left[1-\left(\frac{T}{T_c}\right)^2\right],$$

$$= \frac{M^2(0,0)}{T_c^2}(T_c^2 - T^2).$$

This can be written as proportionality only in the form

$$M^2(0,T) \sim T_c^2 - T^2. \tag{5}$$

Moriya (1979) showed that due to temperature variation of spin density fluctuations in itinerant electrons the $M^2(H)$ near T_c varies as $T_c^{4/3} - T^{4/3}$.

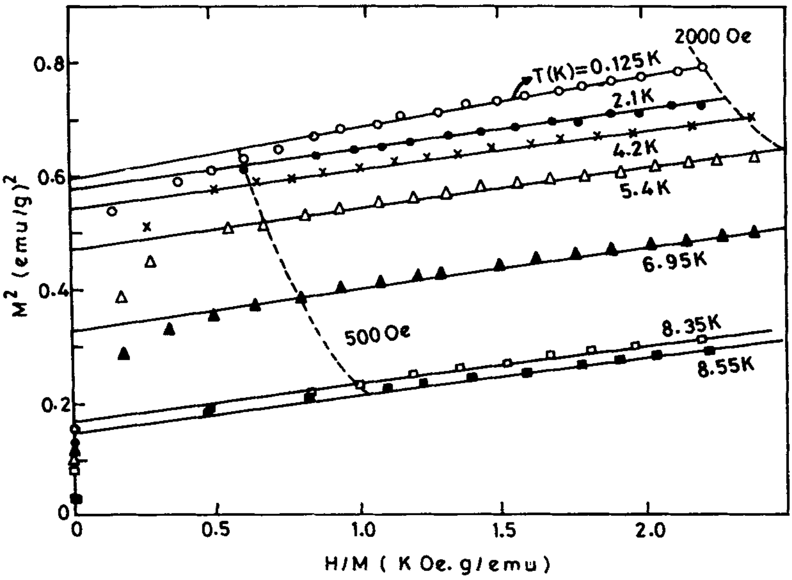

Figure 3. M^2 versus H/M isotherms.

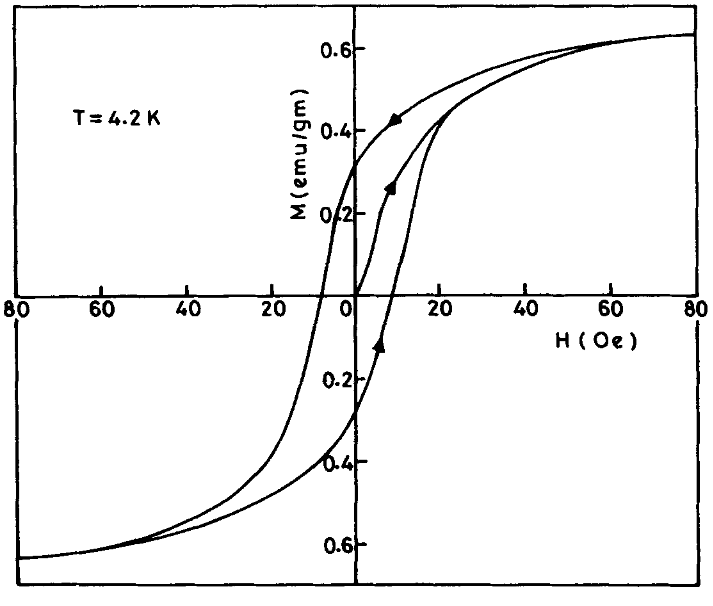

Figure 4. Magnetic hysteresis at 4·2 K.

$$M^2(0, T) \sim T_c^{4/3} - T^{4/3}. \tag{6}$$

From (5) and (6), it follows that as $T \rightarrow T_c$

$$M^2(0, T) \propto (T_c - T) \tag{7}$$

i.e., $M(0, T) \propto (T_c - T)^\beta$ with $\beta = 1/2$.

This value of $\beta = 1/2$ is the conventional mean-field value. Figure 2(b) shows the variation of $M^2(0, T)$ with T^2 or $T^{4/3}$. From our plot it is difficult to distinguish whether T^2 or $T^{4/3}$ is the best fit with $M^2(0, T)$.

4. Discussion

The critical exponents β and γ for Zr-substituted sample derived from low field ac susceptibility and magnetization results are $\beta = 0{\cdot}38 \pm 0{\cdot}03$, $\gamma = 1{\cdot}16 \pm 0{\cdot}05$ which is different from the respective mean-field values 0·5 and 1·0. But the value of β is close to the value seen in many magnets (i.e., $\beta = 0{\cdot}35$). Focussing next on the magnetization, we found that our $M(0, T)$ data are in good agreement with those reported by Yamaguchi and Nishihara (1986) in the high field range ~40 kOe with $T_c \sim 9{\cdot}9$ K. The magnetization of the 1% Zr sample is larger than in Y_9Co_7 and in $Y_9(Co_{0{\cdot}97}Ni_{0{\cdot}03})_7$. For example the typical value of $M(0, T)$ at 4·2 K in the Ni sample is 0·032 emu g^{-1} and in the present study it is 0·738 emu g^{-1} as against 0·730 reported by Yamaguchi and Nishihara (1986). The $M^2(0, T)$ vs T^2 or $T^{4/3}$ plots seem to follow the same trend as in the Ni-substituted sample. The origin for the change in slopes of the two lines at about $T^2 = 20$ K $T^{4/3} = 8$ in figure 2(b) is not clear to us. However, as in any ferromagnets the deviation of $M^2(0, T)$ with T^2 or $T^{4/3}$ fit at low temperatures is possible and this can be due to domain wall formation.

At present it is not clear whether the Zr in Y_9Co_7 replaces the Y or Co sites. X-ray powder diffraction studies confirmed the hexagonal crystal structure as that of Y_9Co_7, but the relative intensities of the diffraction lines could not have been used to reveal the sites of Zr in the structure. Chemical considerations such as electronegativity and atomic sizes suggest the preferential substitution of the Y by Zr. Nevertheless, this substitution might not be restricted to Y alone but could well occur for the crystallographically different Co sites (Lemaire *et al* 1969; Yvon *et al* 1983). The detailed structure analysis about the position of Zr in Y_9Co_7 is beyond the scope of the present work. However, it is probably helpful for the ensuing discussion to assume the partial replacement of *c*-axis Co sites by Zr atoms. We would like to emphasize that such substitution may result in the disruption of the potential Co sites along the *c*-axis and hence presumably the formation of an asymmetric potential well for these Co atoms, as opposed to the symmetric potential well which was proposed for Y_9Co_7 (Sarkissian 1986). Sarkissian has argued that in Y_9Co_7 for temperatures of the order of T^*, the *c*-axis Co hopping rate is small compared with the effective *d*-level width of the Co spin, such that spin fluctuations dominate this temperature region. At lower temperatures, on the other hand, the hopping rate becomes larger, which in turn will broaden the *d*-level width of the Co spin, thereby tipping the balance to superconductivity.

It is therefore helpful to interpret the observed magnetic ordering in Zr-substituted Y_9Co_7, in terms of the reducing effects of the *c*-axis Co atom hopping rate in the asymmetric potential well mentioned above. Arguments similar to that of Yu and Anderson (1985) indicate that in contrast to the symmetric potential well, the hopping rate for an atom in an asymmetric well is always smaller. Intuitively, for the present system it is necessary to assume that the effective Co atom hopping probability vanishes at zero temperatures, i.e., Co atoms will be effectively localized in one well or the other and thereby the width of their *d*-level is reduced. This feature leads to destruction of the phase coherence necessary for the superconductivity to occur, and this will always tend to favour magnetic ordering.

5. Conclusion

We have made the following observations from the low field χ(ac), magnetization experiments of Zr-substituted Y_9Co_7 at low temperatures (i) the estimated critical exponents are $\beta = 0{\cdot}38 \pm 0{\cdot}03$, $\gamma = 1{\cdot}16 \pm 0{\cdot}05$ (ii) zero field magnetization $M^2(0, T) \sim T^2$ or $T^{4/3}$ arising from spin fluctuations as in the Ni-substituted samples. From our measurements alone it is difficult to determine whether the best fit is for T^2 or $T^{4/3}$. However, it may be useful to describe $M(H)$ in terms of Moriya's spin fluctuations theory. Zr-substitution causes a reduction in the hopping rate of Co atoms along the c-axis sites and the system stabilizes ferromagnetic ordering at $T_c = 9{\cdot}5$ K in contrast with Y_9Co_7.

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