Spin glass behaviour in the $Co_{2-x}Zn_xTiO_4$ compound

M. N. KHAN, S. AL-DALLAL, A. MEMON, A. AHMED
Department of Physics, University of Bahrain, PO Box 32038, Bahrain, Arabian Gulf

A.c. susceptibility measurements were carried out on the disordered spinel system $Co_{2-x}Zn_xTiO_4$ ($0 < x < 1$) between 10 and 80 K. Our measurements show three peaks in the χ versus T curve for Co_2TiO_4 and $CoZnTiO_4$ compounds. In both compounds two peaks are very close to each other, indicating that the Néel and semi-spin glass temperatures are very close. A third peak indicates the presence of the semi-spin glass to spin glass transition. In $Co_{1.5}Zn_{0.5}TiO_4$ only one peak is observed which indicates spin glass ordering at 26 K. Furthermore, the A-site canting present in Co_2TiO_4 and $CoZnTiO_4$ has a collinear and magnetic structure, indicating strong A–B coupling. X-ray analysis indicated that compounds of the system $Co_2Zn_xTiO_4$ synthesized with cubic symmetry. From transport properties it was found that the activation energy and thermoelectric coefficient decrease with increasing concentration of Zn in the system. The mobility of the system calculated from infrared measurements is typically of the order of 10^{-9} cm^2 V^{-1} s^{-1}.*

1. Introduction

Concerning the open questions of the transition of spin-glass to a ferrimagnet which occurs in a number of systems when the concentration is varied, and that of the behaviour of samples just on the ferromagnetic side of the critical concentration, a.c. susceptibility, X-ray, electrical conductivity, thermoelectric power and infrared measurements of the system $Co_{2-x}Zn_xTiO_4$ are reported with a view to investigating the spin glass behaviour. The d.c. magnetization measurements [1] showed the disordered spinel ferrite Co_2TiO_4 (cation distribution $Co^{2+}[Co^{2+}Ti^{4+}]O_4^{2-}$) to be a re-entrant ferrimagnet.

Some researchers [2–4] have shown that it is possible to have three phase transitions (ferro/ferri/antiferromagnetic state), namely the paramagnetic state $T_C \Leftrightarrow T_N$, T_{M1} (mixed phase 1) and T_{M2} (mixed phase 2). Although many examples of re-entrant behaviour are available, only a few systems are known in which the three transition temperatures $T_C(T_N)$, T_{M1} and T_{M2} were determined experimentally. We have reported magnetic hysteresis studies and structural and transport properties of various chalcogenides and spinel systems [5, 6].

2. Experimental procedure

Starting from very pure stoichiometric CoO, ZnO and TiO$_2$, these compounds were prepared in appropriate molar proportions in acetone. The pellets of these compositions were prepared using poly(vinyl acetate) as a binder. Pellets were first slowly fired at 773 K for 20 h in order to remove the binder and then fired at

1173 K for 80 h. The samples were cooled slowly in air at a rate of 50 K h^{-1}.

This sequence was repeated until sharp X-ray diffraction (XRD) peaks were obtained, then the samples were characterized and indexed in terms of single-phase cubical spinel structures. XRD analysis was carried out with a Philips type PW 1050/70 diffractometer using nickel-filtered CuK_α radiation at $1°(2\theta)$ min^{-1} from 10 to 90°.

The electrical conductivity was measured using a Hewlett–Packard 4140 B-Pa current meter with a sensitivity of the order of 10^{-15} A. The faces of each pellet were coated with a thin layer of conducting silver paste and measured from 300 to 500 K using the two-probe technique.

The infrared spectra were recorded at room temperature (Perkin–Elmer 683) from 4800 to 400 cm^{-1}. Thermoelectric power measurements for the system were carried out from room temperature to 573 K by sandwiching a thick pellet between the Cu–contantan thermocouples and the potential difference generated was recorded with a microvoltmeter.

The a.c. susceptibility measurements were carried out using a two-phase lock-in amplifier with a sensitivity of 100 mV, drive frequency of 20 kHz and with a.c. amplitude of 0.7 V (r.m.s.) The offset of two amplifiers for the background and sample run was removed using special features (such as auto-function of the lock-in amplifier).

3. Results and discussion

Fig. 1 shows the plot of a.c. susceptibility, as a function

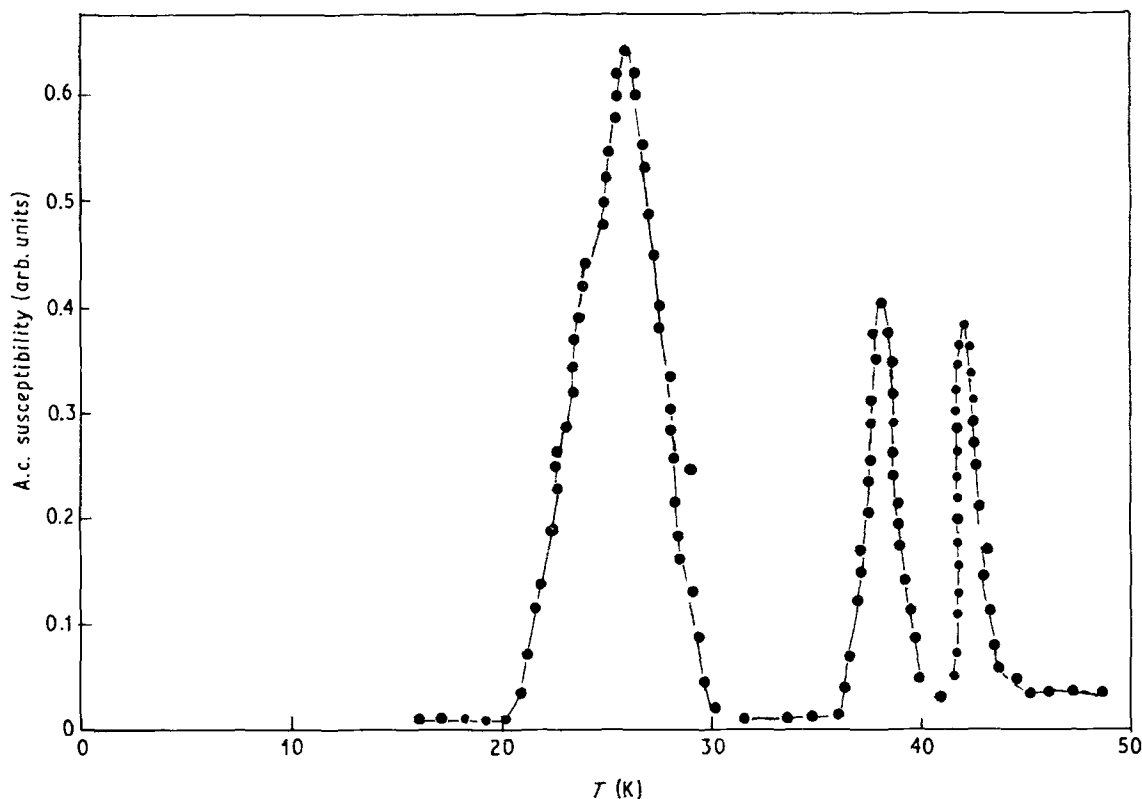
Figure 1 A.c. susceptibility versus temperature for Co_2TiO_4.

of temperature for the compound Co_2TiO_4 of the system $Co_{2-x}Zn_xTiO_4$. It is clear from the figure that the Néel temperature and semi-spin glass ordering temperature lie very close to each other, at around 38 K. Due to the superimposition of these peaks, usually observed in spin glasses, an extra peak (third peak) was noted for the first time in the Au–Fe system by Kleiman et al. [7]. They attributed the third peak either to the freezing of loose spin or to the change randomness of frozen spins. This does not seem to be the case with Co_2TiO_4, which means that the third peak observed by us at 26 K shows the transition from the semi-spin glass to the spin glass state. At this temperature even the spins that were ferrimagnetically ordered along the longitudinal direction were also frozen randomly. The reason for attributing the transition to the pure spin glass freezing can be given as that the spins in Co_2TiO_4 are highly canted since we have two sublattices in the spinel structure where the magnetic ions exist and it is unlikely that spins at both sites would freeze at the same temperature. It would depend on the degree of frustration in the spins at A and B sites. This frustration would be different depending on the canting angles. Villain [8] showed that the canted local spin induces a long-range spin canting and therefore we suggest that very weak interactions due to long-range canting of spin would exist in such a compound and it is likely that freezing of the moments of the A and B sites would take place at different temperatures. This behaviour can be understood from the theory of replica-symmetry breaking as suggested by Gabay and Toulouse [3]. The compound $Co_{1.8}Zn_{0.2}TiO_4$ has been reported to be antiferromagnetic with collinear spin structure by neutron

diffraction studies carried out by Gavoille and Hubsch [9].

The results of our a.c. susceptibility measurements of the compound $Co_{1.5}Zn_{0.5}TiO_4$ for the system $Co_{2-x}Zn_xTiO_4$ with $x = 0.5$ are shown in Fig. 2. We observed only one transition due to spin-glass ordering in this compound at 26 K. This temperature is the same as the spin-glass freezing temperature observed in Co_2TiO_4. The compound $CoZnTiO_4$ of the system $Co_{2-x}Zn_xTiO_4$ with $x = 1.0$ exists with a collinear spin structure unlike Co_2TiO_4. The a.c. susceptibility, χ, versus T plot for $CoZnTiO_4$ is shown in Fig. 3. It can be seen from this plot that three transitions are present in this compound. Like Co_2TiO_4 in this compound, the Néel temperature and semi-spin glass transition temperature are very close. We can attribute these three peaks to the paramagnetic-to-ferromagnetic (at 45 K), ferromagnetic-to-semi-spin glass (at 41 K) and semi-spin glass-to-spin glass (at 61 K) transitions. Since the spin arrangement in this compound is collinear, no extra transitions are observed. The three peaks observed in this compound could be explained by the Gabay and Toulouse [3] replica-symmetry means field theory of vector spin glass as was applicable to Co_2TiO_4 and $Co_{1.5}Zn_{0.5}TiO_4$.

The results of conductivity measurements as a function of temperature in the range 300–573 K for the system $Co_{2-x}Zn_xTiO_4$ are shown in Fig. 4. The temperature dependence of d.c. conductivity is exponential and could be described by

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

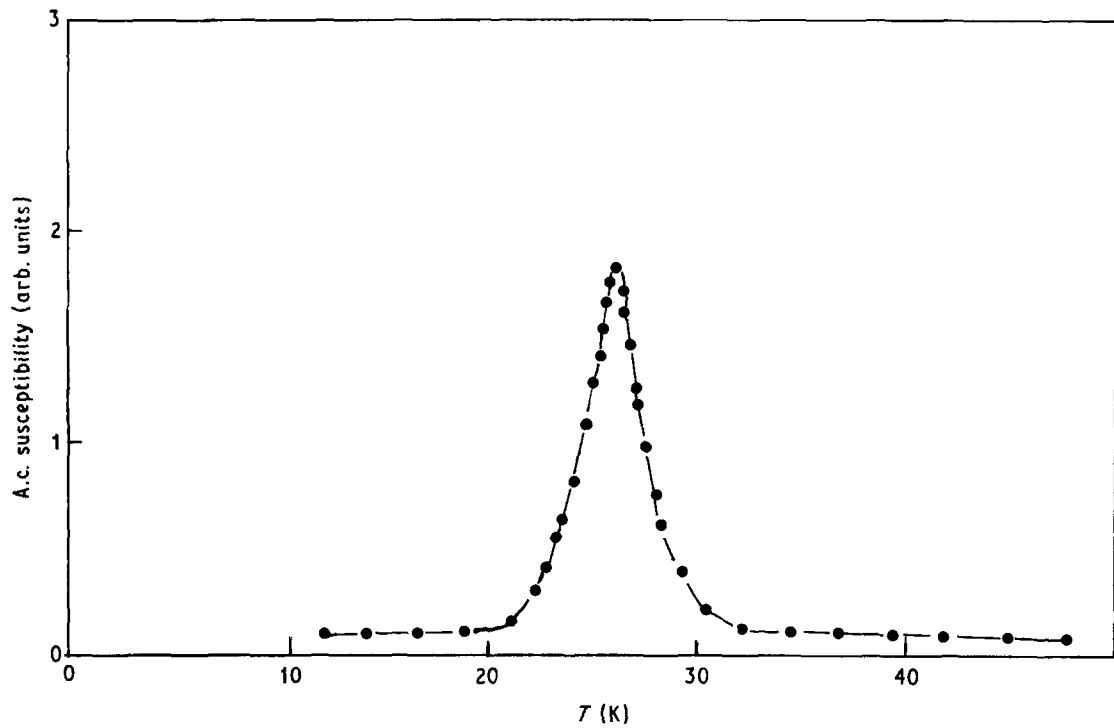The values of the activation energy, ΔE, above 300 K

5677

Figure 2 A.c. susceptibility versus temperature for $Co_{1.5}Zn_{0.5}TiO_4$.

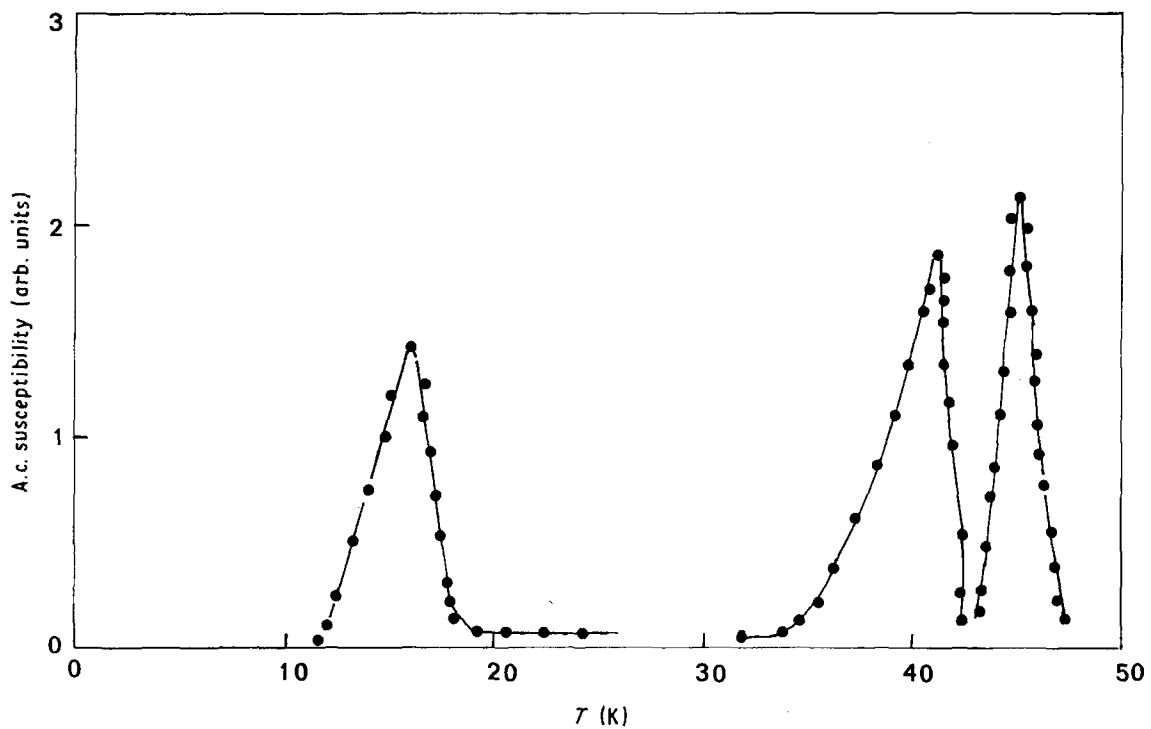*Figure 3* A.c. susceptibility versus temperature for $Co_1Zn_1TiO_4$.

are summarized in Table I. It is seen from this table that the activation energy increases as the concentration of Zn increases. In the following an attempt is made to justify the increase in activation energy for conduction in the system studied. Actually, $Zn^{2+}d^{10}$-orbitals have lower energy and are more contracted than $Co^{2+}d^{7-}$ orbitals, so increasing the content of Zn will result in a greater activation energy for the

TABLE I Values of the lattice constant a, activation energy ΔE and thermoelectric coefficient c of the spin glass system $Co_{2-x}Zn_xTiO_4$

Compound	a (nm)	ΔE (eV)	c ($\mu V K^{-1}$)
Co_2TiO_4	0.8425	0.79	275
$Co_{1.5}Zn_{0.5}TiO_4$	0.841	0.83	195
$CoZnTiO_4$	0.8421	0.88	-64
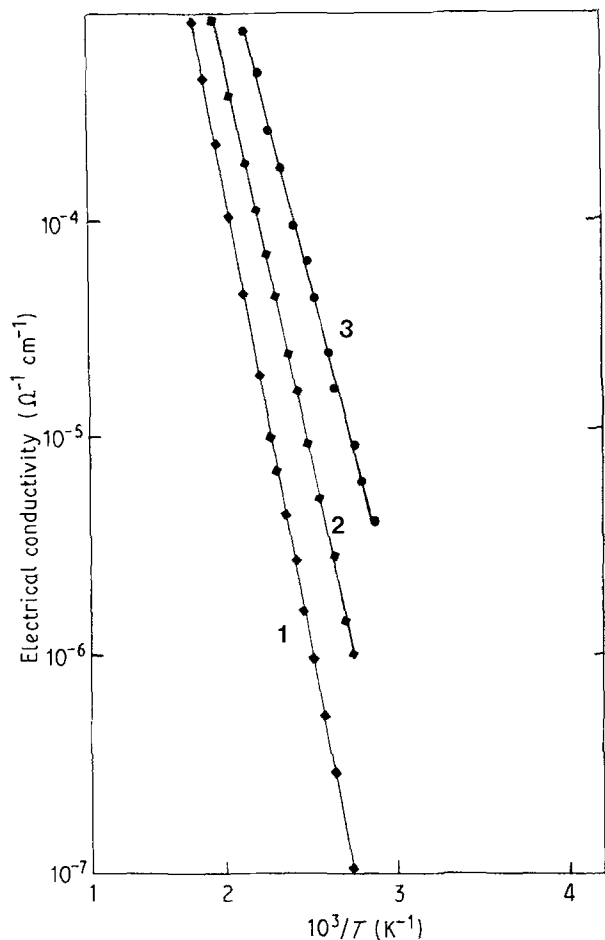
Figure 4 Electrical conductivity against reciprocal temperature for various compounds.

Figure 5 Plot of ΔV against ΔT for the spin glass system $Co_{2-x}Zn_xTiO_4$.

Figure 6 Infrared absorption for Co_2TiO_4.

mobility of charge carriers, resulting in a decrease in the conductivity. Furthermore, the high activation energy for d.c. conductivity is due to the presence of different types of cations at the B-site, such as $Co^{2+}[Co^{2+} + TiO_4]O_4^{2-}$ in Co_2TiO_4. Another somewhat simple but plausible explanation for the increase in activation energy could be ascribed to the different possible oxidation states that are due to mixed ions with possible pairing of mixed ions in the form of oxygen-bridged associates as explained in [10].

Linear plots of thermal e.m.f., ΔV, developed across the samples as a function of the temperature difference, ΔT, are given in Fig. 5. The values of the thermoelectric coefficient, α, for the compound having $0 < x < 0.5$ indicate p-type semiconduction whereas negative values of α for the compound having $x = 1.0$ point to n-type semiconduction. The p-type conduction is a co-balt-rich formation which is shown as

$$Co^{2+} + Co^{3+} \rightleftharpoons Co^{3+} + Co^{2+}$$

where the motion of Co^{3+} ions in the lattice can be visualized as a motion of holes. It is clear from Table I that with increasing concentration of Zn^{2+} ions in the lattice the thermoelectric coefficient values decrease and the compounds with $x = 1.0$ show n-type conduction. This may be attributed to the electron exchange hopping mechanism. It was proved experimentally [11] that volatilization of zinc occurs during the firing process in most zinc-rich compounds and the cation
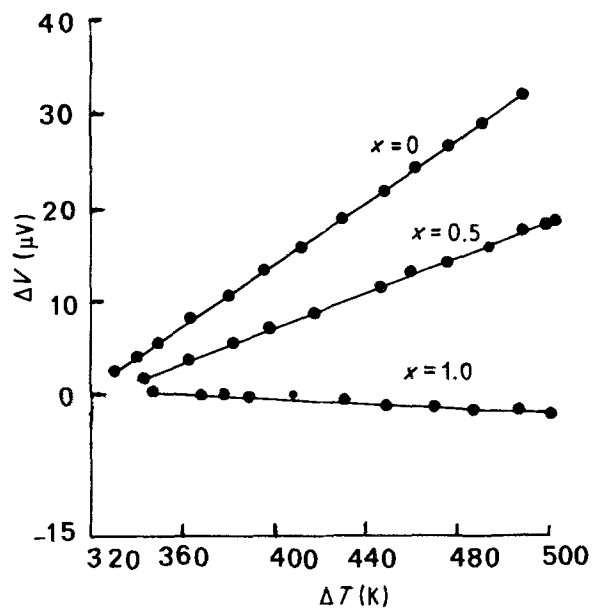
vacancies are created at tetrahedral (A) sites. As a result small numbers of octahedral (B) sites cation (Co) may go to A sites, creating holes at B sites and hence the compounds having $0 < x < 0.5$ show p-type conduction. Infrared studies indicate the presence of two strong absorption bands at 500 and 600 cm^{-1} as shown in Fig. 6. However, the band at 600 cm^{-1} was considered for calculating the mobility using

$$\mu = \left(\frac{ed^2\nu}{kT}\right)\exp(-\Delta E/kT) \qquad (1)$$

where ΔE is the average activation energy, k is the Boltzmann constant, d is the jump length and ν is the lattice frequency.

The mobility, μ, can be calculated using Equation 1 as postulated by Heikes and Johnston [12]. The mobility value as calculated for our system was found to be of the order 10^{-9} cm^{2}V^{-1}.

References

1. J. HUBSCH and G. GAVOILLE, *Phys. Rev.* **B26** (1982) 3815.
2. N. SAKMOTO, *J. Phys. Soc. Jpn.* **17** (1962) 1799.
3. M. GABAY and G. TOULOUSE, *Phys. Rev. Lett.* **47** (1981) 201.
4. D. M. CRAIG, D. SHERRINGTON and M. GABAY, *ibid.* **49** (1982) 158.
5. M. N. KHAN, A. VENKATACHALACHALAM, A. AHMED and V.S. DARSHANE, *J. Mater. Sci.* **25** (1990) 595.
6. M. N. KHAN, A. MEMON, C. A. HOGARTH, A. AHMED, B. A. MULLA and V. S. DARSHANE, *Phil. Mag.* **B62** (1990) 103.
7. R. N. KLEIMAN, I. MAARTEMSE and G. WILLIAMS, *Phys. Rev.* **B26** (1982) 5241.
8. J. VILLAIN, *Z. Phys.* **B33** (1979) 31.
9. G. GAVOILLE and J. HUBSCH, *J. Magn. Mater.* **36** (1983) 89.
10. M. N. KHAN, ASHFAQ AHMED and V. S. DARSHANE, *J. Mater. Sci.* **24** (1989) 2615.
11. L. K. LEUNG, B. J. EVANS and A. J. MORIH, *Phys. Rev.* **88** (1973) 29.
12. R. R. HEIKES and W. D. JOHNSTON, *J. Chem. Phys.* **26** (1957) 582.