Pramāṇa – J. Phys., Vol. 35, No. 4, October 1990, pp. 377–381. © Printed in India.

Unusually large shift in low-temperature susceptibility peak of $Fe_{2\cdot8}Ti_{0\cdot2}O_4$ with frequency

C RADHAKRISHNAMURTY, S D LIKHITE and R NAGARAJAN
Tata Institute of Fundamental Research, Bombay 400005, India

MS received 23 July 1990; revised 10 August 1990

Abstract. The temperature dependence of magnetic susceptibility, χ, of titanomagnetites ($Fe_{3-x}Ti_xO_4$, $0 \leqslant x \leqslant 0{\cdot}2$) at different frequencies in the range of 13 Hz to 117 kHz is reported. Whereas the position of the χ-peak of Fe_3O_4 at 120 K shows no significant shift over this frequency range, that of $Fe_{2\cdot8}Ti_{0\cdot2}O_4$ shifts from 70 K at 13 Hz to 115 K at 117 kHz. This seems to be the first observation of such large shift in the position of a χ-peak with frequency reported for any magnetic material. Generally, for ferrites, a χ-peak observed at low-temperatures is attributed to the occurrence of an isotropic point (temperature at which first order anisotropy constant $K_1 = 0$) associated with change in crystal structure. In such a case a shift in χ-peak with frequency is not expected normally. Thus, the observed large shift in the position of χ-peak with frequency is an unusual phenomenon and some of its repercussions are discussed.

Keywords. Titanomagnetites; magnetic susceptibility; anisotropy constant; isotropic point.

PACS No. 75·30

1. Introduction

The behaviour of magnetic materials is somewhat different when studied in low and high magnetic fields. Low field parameters, such as permeability (μ) or susceptibility (χ) are usually determined using AC techniques and generally at low frequencies (11 to 350 Hz). The results at such frequencies are presumed to be the same as those from DC methods. In the present context, one of the major features seen in the low field susceptibility of ferrites, particularly in magnetite (Fe_3O_4) is the occurrence of a peak attributed to the isotropic point of the material. Magnetite is cubic (inverse spinel) at room temperature and changes to orthorhombic structure below 119 K. The first order crystalline anisotropy constant, K_1, of magnetite is $-1{\cdot}10 \times 10^5$ erg/cc at 293 K (Bickford 1950) and it attains a value of $+1{\cdot}65 \times 10^6$ at 77 K (Bonstrom *et al* 1961), crossing zero value at 119 K, the isotropic point. At low frequencies a χ-peak of magnetite has been observed (Radhakrishnamurty *et al* 1981) at ~ 120 K, as expected. A small variation (about 10 K) in this value seems to occur with frequency, if all the reported results are carefully scrutinized and reinterpreted. For example, the χ-peak in the present study is at 13 Hz at 120 K, while the μ-peak has been reported to be at 130 K at 16 GHz (Bickford 1950). Such data are rare in the range from 10 Hz to 100 kHz for ferrites and rarer still are the studies on temperature dependence at low frequencies, though such investigations at frequencies > 1 MHz and above reaching up to GHz ranges are more common due to application aspects or ferromagnetic resonance studies. In view of the above, the temperature dependence of χ for titanomagnetites ($Fe_{3-x}Ti_xO_4$ with $0 \leqslant x \leqslant 1{\cdot}0$) at different frequencies has been investigated here. Due to recent intense activity in the area of high temperature superconductivity, commercial susceptibility meters covering the range 10 Hz to 120 kHz have now become available. We have used one such system manufactured by Sumitomo Heavy Industries Ltd of Japan, which can measure susceptibility in the frequency range 13 Hz to 120 kHz over the temperature interval 12 to 300 K.

2. Experimental

Titanomagnetites ($Fe_{3-x}Ti_xO_4$, with $0 \leqslant x \leqslant 1{\cdot}0$) were synthesized by a standard ceramic method and their bulk magnetic properties down to 77 K have been reported earlier (Radhakrishnamurty *et al* 1981). The $\chi - T$ investigations on the same polycrystalline powder samples, have been extended during the present investigation to five different fixed frequencies viz 13 Hz, 313 Hz, 5 kHz, 13 kHz and 117 kHz in the temperature interval 15 to 300 K.

3. Results

The low field susceptibility behaviour at 13 Hz and 117 kHz for Fe_3O_4 and for $Fe_{2\cdot8}Ti_{0\cdot2}O_4$ (hereafter abbreviated as TM0 and TM20 respectively, the number denoting the atomic percentage of Ti in Fe_3O_4) is shown in figure 1 as a function of temperature. An unusually large shift in the position of the χ-peak with frequency is easily discernible for TM20. $\chi - T$ curves at 13 Hz and 117 kHz only are presented in figure 1 to avoid crowding of data points. The following features are noteworthy.

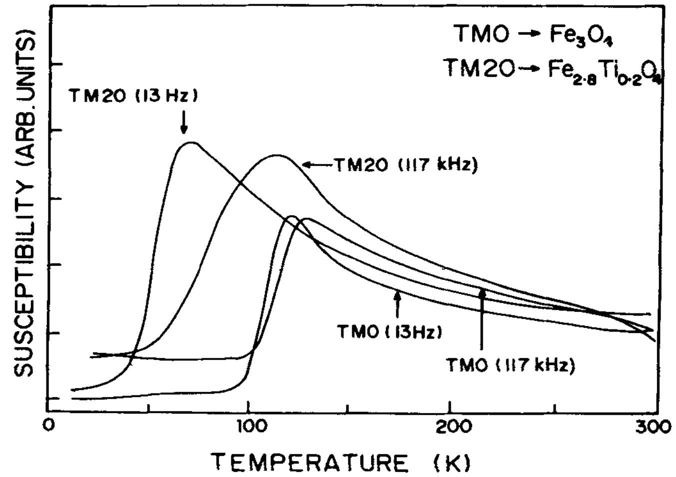

Figure 1. Susceptibility (χ) vs temperature (T) curves at two different frequencies, 13 Hz and 117 kHz for Fe_3O_4 (TM0) and $Fe_{2\cdot8}Ti_{0\cdot2}O_4$ (TM20). The Y-axis scale is arbitrary. The low magnetic fields used at the two frequencies differ and hence the amplitudes of the curves are not proportional. However, the samples were subjected to the same field at a given frequency. The important feature to be noted is the large shift of the χ-peak of TM20 with frequency.

1) The well documented μ-peak for TM0, which occurs at 120 K, is seen clearly in the $\chi-T$ curve at the same temperature.
2) The drop in χ below 120 K at 13 Hz for TM0 is quite sharp. This feature is retained at 117 kHz. The peak is shifted upwards by ~ 5 K, from 120 to 125 K, at 117 kHz.
3) For TM20, the shape of the χ-peak at 70 K observed at 13 Hz is almost akin to that of TM0 at 120 K.
4) At 117 kHz, the χ-peak of TM20 occurs at 115 K an upward shift by 45 K, from its value at 13 Hz which is quite unusual.
5) The peak of TM20 at 117 kHz is broad compared to the other peaks.

The $\chi-T$ curves for these two materials at other frequencies show very similar features.

4. Discussion

The magnetic and other properties of TM0 have been investigated and reported long ago, both in its single crystal form and also in polycrystalline powders in multidomain (MD) and single-domain (SD) states. Similar studies on TM20 have not been reported so far, which is a drawback in comparing its behaviour with TM0. However, the magnetic properties of these two materials are similar, though the actual values of various parameters differ slightly in the two systems (O'Reilly 1976; Radhakrishnamurty *et al* 1981). In view of this, a drastic difference in the magnetic behaviour between TM0 and TM20 is not expected, although the substitution of Ti does change some of the parameters marginally. Thus, the observed large shift of about 45 K in the χ-peak with frequency for TM20 and the small or no shift for TM0 is rather surprising and calls for a radically different explanation.

In conformity with literature, the χ-peak of TM0 at about 120 K, both at 13 Hz and 117 kHz, correspond to $K_1 = 0$. Being the crystallographic transition point, it is not normally expected to depend on frequency (consistent with the present observation) if one can overlook the small shift of ~ 5 K. As for the χ-peak of TM20 at the low-frequency of 13 Hz, it bears a good similarity in its shape to that of TM0. It may be noted that the isotropic point for TM10 determined by torque method has been estimated to be about 90 K (Syono 1965). This appears to suggest that the peak observed in TM20 at 70 K for 13 Hz could be due to its isotropic point. In that case the χ-peak of TM20 at 115 K for 117 kHz would have to be considered as arising from a totally different effect. One could consider the possibility that the χ-peak at the isotropic point of 70 K might have been masked, rendering it imperceptible, and a new χ-peak at 115 K emerges at 117 kHz perhaps due to some broad resonance effect of domain walls or single-domains, even at these low-frequencies. This is apart from the well documented resonances at very high frequencies (Rado *et al* 1950). It is also possible that even the χ-peak at 70 K in 13 Hz could be due to a similar effect and not due to an isotropic point. However, it should be noted that the value of K_1 determined by DC and AC methods (through ferromagnetic resonance) have been found to differ in certain cases (Bozorth *et al* 1955). This would imply that the magnetic response of the system is such that the effective anisotropy could be different at different frequencies and temperatures. In such a case, the isotropic point also appears to depend on the frequency. However, the above observation has been made from studies with a static (DC) method and at 24 GHz at only two temperatures 293 and

77 K and not many details of temperature dependence are known. More work needs to be done in this direction if such reasoning is to be applied to the observed large shift in the position of the χ-peak for TM20.

It was reported earlier (Radhakrishnamurty and Nanadikar 1979) that the χ-peak associated with an isotropic point of a magnetic material would be clearly observable when the grains are in an MD state, while the same will be suppressed if the grains are in SD state. Moreover, a narrow size range of single-domains with blocking temperatures well below the Curie point, T_c, might show a χ-cusp akin to that of spin glasses (Radhakrishnamurty *et al* 1979), but which is not related to the isotropic point of the material and is due to a single-domain to superparamagnetic transition arising from relaxation effects of magnetic moment of the clusters/grains. It is known that the χ-cusp of spin glasses does depend on the frequency and for conducting spin glasses the shift has been found to be about 1 K (Tholence 1980) while for insulating ones it is about 3 K (Tholence *et al* 1986) when the frequency is changed from 10 Hz to 10 kHz. However, it is to be noted that in the temperature region of our interest, the material TM20 is magnetically ordered ($T_c \approx 700$ K) and is in MD state as shown from hysteresis (Radhakrishnamurty *et al* 1981) and domain wall observations (Soffel *et al* 1982). Therefore, we believe that conventional relaxation mechanisms such as relaxation of cluster spins or spin glass freezing are not likely to be the cause of the observed shift. It is known that for MD materials, the main contribution to low field susceptibility is due to domain wall movements. Thus, it appears that the large shift in the position of the χ-peak with frequency found for TM20 is more likely to be related to some domain wall effect at low-frequencies. However, this is purely a conjecture and needs confirmation from other type of studies.

5. Conclusion

A large shift in the position of the susceptibility peak with frequency for $Fe_{2.8}Ti_{0.2}O_4$ has been found, whose exact mechanism remains to be understood.

Acknowledgements

The authors wish to thank Professors S S Jha, R Vijayaraghavan, Girish Chandra, M Barma and many other colleagues for their interest in the work, Shri C V Tomy and Dr Geetha Balakrishnan for valuable help in the experiments and Professor V Nagarajan for critical reading of the manuscript.

References

Bickford Jr L R 1950 *Phys. Rev.* **78** 449

Bonstrom D B, Morrish A H and Watt A K 1961 *J. Appl. Phys.* **32** 272S

Bozorth R M, Beatrice B, Cetlin J K, Merritt F R and Yager W A 1955 *Phys. Rev.* **99** 1898

O'Reilly W 1976 *Rep. Prog. Phys.* **39** 857

Radhakrishnamurty C and Nanadikar N G 1979 *Pramana – J. Phys.* **13** 413

Radhakrishnamurty C, Likhite S D and Nagarajan R 1980 *J. Magn. Magn. Mater.* **15–18** 195

Radhakrishnamurty C, Likhite S D, Deutsch E R and Murthy G S 1981 *Phys. Earth Planet. Inter.* **28** 433

Rado G T, Wright R W and Emerson W H 1950 *Phys. Rev.* **80** 273
Soffel H C, Deutsch E R, Appel E, Eisenach P and Petersen N 1982 *Phys. Earth Planet. Inter.* **30** 336
Syono Y 1965 *Jpn. J. Geophys.* **4** 71
Tholence J L 1980 *Solid State Commun.* **35** 113
Tholence J L, Yeshurun Y, Kjems J K and Wankyn 1986 *J. Magn. Magn. Mater.* **54–57** 203