Bull. Mater. Sci., Vol. 3, Number 2, July 1981, pp. 217-224. © Printed in India.

# Mossbauer and magnetic studies on the system $Fe_{3-x}Ti_xO_4$

R NAGARAJAN and C R K MURTY
Tata Institute of Fundamental Research, Bombay 400 005, India.

MS received 14 November 1980

**Abstract.** Mossbauer measurements have been made on the system $Fe_{3-x}Ti_xO_4$ for $1{\cdot}0 \geqslant x \geqslant 0$. This system is interesting in that it is expected to form a continuous solid solution over the whole range and also occurs naturally. Spectra taken at various temperatures between 300 K and 77 K show complex behaviour. The results can be understood in terms of disorder and consequent formation of superparamagnetic clusters which are supported by our earlier hysteresis and susceptibility studies at various temperatures. It appears that with increasing Ti content domain wall formation is inhibited resulting in effectively monodomain clusters. Considering the work reported by others, we suggest that Mossbauer spectra of multidomain material should show well-resolved magnetic hyperfine spectrum, even close to its $T_N$.

**Keywords.** Titanomagnetite; superparamagnetism; Mossbauer effect; susceptibility; hysteresis; magnetic studies.

## 1. Introduction

The system $Fe_{3-x}Ti_xO_4$, where $1{\cdot}0 \geqslant x \geqslant 0$, which is considered to be the solid solution of $Fe_3O_4$ (magnetite) and $Fe_2TiO_4$ (ulvospinel) and known as titanomagnetite (TM) series has been of interest for a long time in rock magnetism due to its occurrence in nature and also due to its complex magnetic properties (Nagata 1961). There have been several studies on the synthetic TM (Uyeda 1958; Syono and Ishikawa 1963; Banerjee and O'Reilly 1966). However, the importance of domain state in determining the bulk magnetic properties of this system and the role of Ti in deciding the domain state of the material have not been brought out in these studies. Recently Radhakrishnamurty and coworkers (Radhakrishnmurty and Deutsch and Radhakrishnamurty *et al* 1974, 1978) have shown that using their techniques of low-field susceptibility $\chi$ and high-field hysteresis measurements at different temperatures, it is possible to distinguish between the multidomain (MD), single domain (SD) and superparamagnetic (SP) states of any magnetic materials. It has also been shown by these methods that domain wall formation might be inhibited in $Fe_{3-x}Ti_xO_4$ when $x > 0{\cdot}2$ (Radhakrishnamurty and Nanadikar 1979) and as $x$ approaches $1{\cdot}0$ the material almost behaves like a spin glass from the point of view of thermal variation of $\chi$ (Radhakrishnamurty *et al* 1980). In this paper we examine the causes of this behaviour by combining the results of the microscopic technique of Mössbauer effect and bulk magnetic measurements.

## 2. Experimental

The TM samples were prepared by the conventional method (Uyeda 1958; Banerjee and O'Reilly 1966). Stoichiometric proportions of micropowders of highly pure $\alpha-Fe_2O_3$, $TiO_2$ and Fe were thoroughly mixed, sealed in evacuated quartz capsules, heated at 1300 K for 12 hr and then quenched. The samples were examined by x-ray diffraction to ensure that the reaction is complete and each of them was of a single phase.

Mössbauer measurements were made using a constant acceleration drive (Cohen *et al* 1963) in conjunction with a multiscalar analyser developed earlier (Nagarajan and Memon 1977). All the measurements were made with respect to $^{57}Co$ source in chromium matrix. Low temperature spectra were taken by keeping the sample in a cold finger-type cryostat. The performance of the Mössbauer system was checked from spectra of enriched $\alpha$-$Fe_2O_3$ standard absorber. We obtained a full width at half maximum of 0·5 mm/sec for the outermost lines, which is reasonable.

Magnetic measurements of $\chi$ and high-field hysteresis at different temperatures were carried out using the techniques described earlier (Radhakrishnamurty and Likhite 1970; Radhakrishnamurty *et al* 1971).

## 3. Results

Figure 1 shows some of the typical Mössbauer spectra. They are similar to those reported in literature (Banerjee *et al* 1967a, b) but spectra for $Fe_{2\cdot9}Ti_{0\cdot1}O_4$, referred hereafter as TM10, (and other members of this series are designated accordingly) and for TM20 are reported here for the first time. The low temperature spectra of TM10 and TM20 (figures 1a and 1b) are very similar to TMO, *i.e.*, magnetite (Sawatzky *et al* 1969). One can clearly see the hyperfine splitting due to at least two distinct components, one corresponding to 535 kOe and the other 515 kOe.

The room temperature (RT) spectrum of TM68 (figure 1c) is an unresolved broad spectrum, eventhough it is at about 100 K below its $T_N$($T_N$~400 K). The low temperature spectrum of TM68 (figure 1d) shows the expected hyperfine field of about 520 kOe, judging from the separation of the outermost lines. Normally, when the nucleus experiences an internal field of this magnitude, the hyperfine lines should have been well resolved as is the case for TM10 and TM20. However, this resolution is not seen in the spectrum which indicates that the material is not magnetically homogeneous. This will be discussed in detail later on.

TM80 is paramagnetic at RT and therefore shows no magnetic splitting (figure 1e). However, there is a quadrupole splitting and the lines are asymmetric. The asymmetry is attributed to the contribution of $Fe^{3+}$to the left-hand peak (Banerjee *et al* 1967b). Once again the low temperature spectrum (figure 1f) is magnetically split with a hyperfine field of about 480 kOe, but not well resolved, indicating magnetic inhomogeneity.

Figure 2 shows the $\chi$–$T$ curve and high field hysteresis loops at 77 and 300 K for TM20. As the sample goes from paramagnetic to ferrimagnetic region, $\chi$ sharply increases to a peak, known as Hopkinson peak, and then decreases gradually but only to a small extent upto 300 K and beyond that increases slightly. There is not much change in the shape of the hysteresis loops between 300 K and 77 K except for a small increase in the already small coercive field ($H_C$).

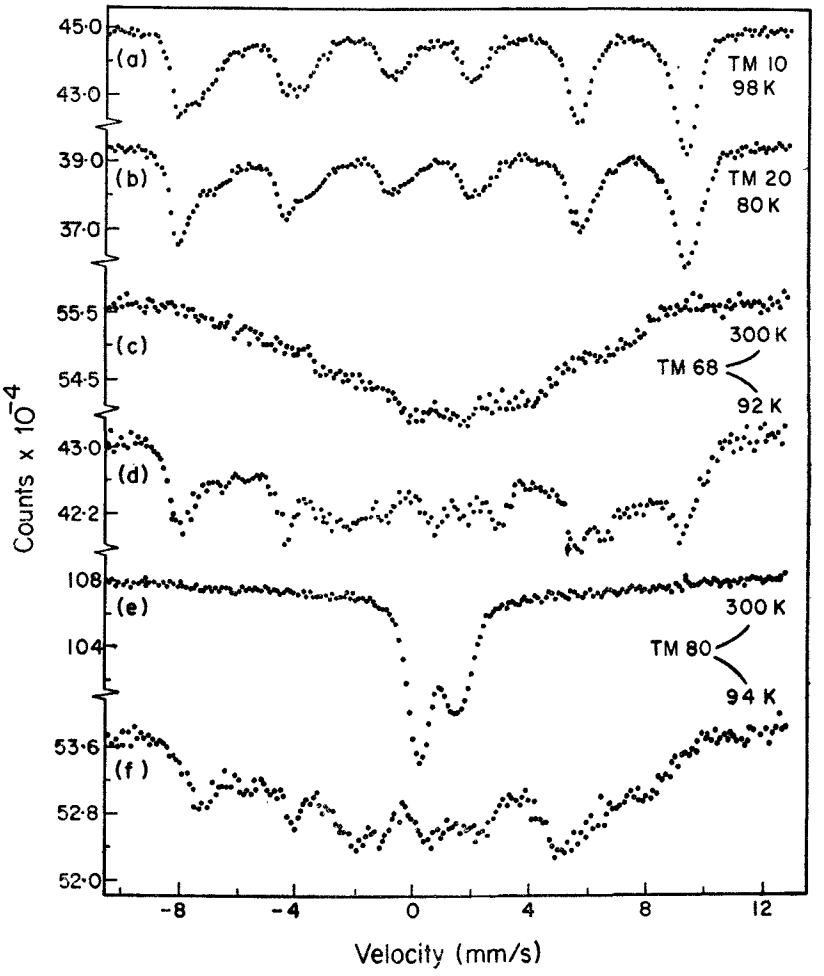


**Figure 1.** Mossbauer spectra for TM10 ($Fe_{2\cdot9}Ti_{0\cdot1}O_4$), TM20 ($Fe_{2\cdot8}Ti_{0\cdot2}O_4$) TM68 ($Fe_{2\cdot32}Ti_{0\cdot68}O_4$) and TM80 ($Fe_{2\cdot2}Ti_{0\cdot8}O_4$).

Figures 3a, b and c show the bulk properties for TM68. The essential difference in the $\chi$–$T$ curve of TM68 (figure 3a) with respect to that of TM20 (figures 2a), is a fall in $\chi$ after the peak value, as the temperature is lowered. Figures 3b and 3c show that there is a considerable increase in the $H_C$ at low temperature. Figures 3d, e and f show these properties for TM80. The effective width of the $\chi$–$T$ curve of TM80 is smaller than that for TM68 and the $H_C$ is much larger at 77°K. All these features can be understood on the basis of the domain state aspects of these materials as discussed below.

## 4. Discussion

Whenever there is ordering in any magnetic material, it is generally believed that it is in MD state with domain walls separating adjacent domains, except in special cases such as microfine particles where fine particle superparamagnetism is known

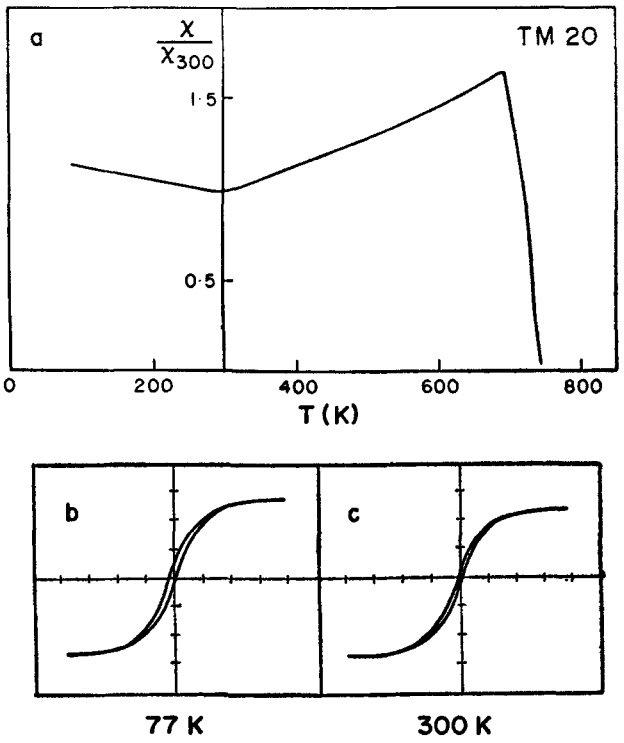


**Figure 2.** Susceptibility *vs* temperature curve and hysteresis loops for TM20 ($Fe_{2.8}Ti_{0.2}O_4$). Scale for b and c: X-axis, 1 division = 750 Oe; Y-axis, arbitrary.

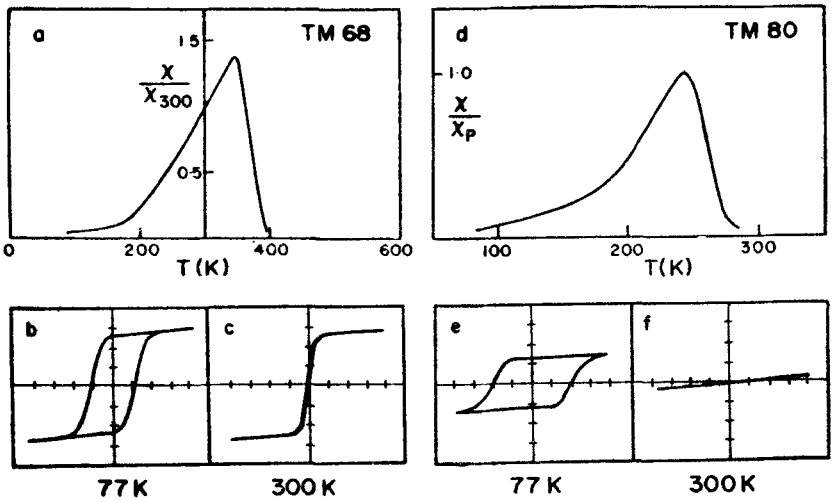


**Figure 3.** Susceptibility *vs* temperature curves and hysteresis loops for TM68 ($Fe_{2.32}Ti_{0.68}O_4$) and TM80 ($Fe_{2.2}Ti_{0.8}O_4$). Scale for b,c,e and f, X-axis, 1 division = 1200 Oe, Y-axis, arbitrary. The hysteresis loops are tracings of oscilloscope photographs and the shift of the loop, particularly in c was due to the beam spot not coinciding with the origin and has no other significance.

(Roggwiller and Kündig 1973). It has been shown (Radhakrishnamurty *et al* 1978; Radhakrishnamurty and Nanadikar 1979) that if a material is in MD state, then generally the hysteresis should be relatively independent of temperature with small $H_C$ and that $\chi$ should also be independent of temperature below the Hopkinson peak. If there is an isotropic point for the material, where the magnetocrystalline anisotropy constant ($K_1$) becomes zero, there will be a peak in $\chi$ at that temperature (Bickford 1950), which will be well defined only if the sample is in MD state (Radhakrishnamurty and Nanadikar 1979). It can therefore be inferred from figures 2a, b and c that TM20 satisfies these conditions and so it is very likely to be in MD state. It appears that for TM20 the isotropic point is below 77 K (which is yet to be confirmed), and hence one sees the small increase in $\chi$ near 77 K (figure 2a). Mössbauer spectrum of TM20 (figure 1b) also seem to confirm the presence of long range order as seen from the relatively narrow line shapes. Room temperature spectrum of TM20 (not shown) also maintains this degree of resolution. Therefore we believe that at RT also the long range order is preserved. It may be mentioned in this context that well-ordered materials like iron (Preston *et al* 1962) and magnetite (Häggström *et al* 1978) show well-resolved line shapes with narrow lines, except for reduction in hyperfine splitting, till their respective $T_C$ or $T_N$. On the other hand TM68 and TM80 do not conform to the MD behaviour but show SP-SD behaviour as per the above bulk magnetic data. This could be understood as follows.

If there are SP clusters, then they would behave as SD regions below the blocking temperature ($T_b$). $T_b$ depends on the individual cluster volume $v$, and is given by the equation

$$vJ_sH_c = 2kT_b$$

where $J_s$ is the saturation intensity and $k$ is the Boltzmann constant. Thus, for a sample with SP-SD mixture, as we go from paramagnetic to SP state by lowering the temperature, $\chi$ would increase but would fall off on further reduction in $T$ as more and more clusters go over to SD state as they go below their respective $T_b$. At the $\chi$-peak the number of clusters at their $T_b$ is maximum. The $\chi$ of an SD sample is much smaller than that for SP sample of the same material because $\chi$ depends inversely on $H_c$. The $H_c$ is large for SD, whereas it is almost zero for the SP sample (Bean 1955). This increase in $H_c$ is also seen experimentally (figures 3b and 3e), Thus the decrease in $\chi$ below the peak temperature is accounted for. The observed hysteresis loops at 77 K emphasises the fact that all the clusters in both TM68 and TM80 go over to optimum SD state at this temperature. Further, from the above facts one can show that the width of the $\chi$–$T$ curve depends on the range of the cluster sizes involved in the material. Therefore from figures 3a and d we infer that the range of the cluster sizes seem to be narrower for TM80 than that for TM68. We shall present the arguments later that this is to be expected.

Now the question arises as to what is the cause of this SP-SD behaviour and we believe that some clues could be found in the Mössbauer spectra. The Mössbauer hyperfine lines of TM68 (figures 1c and d) and TM80 (figure 1f) are complex and are not well-resolved even at temperatures well below their respective $T_N$. (For TM68, $T_N$ = 400 K and for TM80, $T_N$ = 240 K). Such spectra have been seen in many mixed oxide solid solutions (Shirane *et al* 1962; Nagarajan and Srivastava 1977). Various mechanisms, including that of superparamagnetism, have been suggested

for these line shapes but all of them arise out of disturbance in long range order resulting in magnetic inhomogeneity. In this paper we will not discuss the possible mechanisms but make use of the presence of magnetic inhomogeneity in TM68 and TM80. On the other hand, in materials with good long range order one gets well-resolved hyperfine spectra very close to $T_N$, as close as $T/T_N \sim 0{\cdot}98$ (Häggström *et al* 1978; Preston *et al* 1962). This being not the case for TM68 and TM80, we believe that the SP-SD behaviour of the bulk material arises out of local disorder in the distribution of Fe ions as a result of the introduction of Ti ions in the system. It is reasonable to expect that multidomains with domain walls would be formed only when magnetic order exists at least over such dimensions as are required energetically, about 200-1000 A for ferrite systems. Otherwise, only SD state would be possible. It appears that beyond TM20 the local disorder might not allow domain wall formation and hence only SP-SD mixtures could result. Considering that disorder is a statistical phenomenon, to that extent some MD region may be found in samples with $x > 0.2$, but as a whole only SP-SD behaviour will be reflected as they seem to dominate the magnetic state in these materials. This view is also consistent with the fact that upto about TM20, the MD state is clearly indicated, as statistically, though some SP-SD would be formed, MD could dominate the magnetic state. In principle it may be possible to estimate the amount of Ti required to weaken the exchange coupling to such an extent that almost no MD regions are formed. The experimental results suggest that this might be happening in the region of TM30 for this system (Radhakrishnamurty and Nanadikar 1979; Radhakrishnamurty *et al* 1981). Also, as Ti concentration increases, it is to be expected that the maximum size of the SD cluster will decrease. Considering that there has to be a minimum cluster size to sustain magnetism and to contribute to the bulk susceptibility, the range of cluster sizes should decrease as Ti is increased. This view is confirmed by the $\chi$–$T$ curves.

It may be argued that if bulk measurements indicate SP behaviour, Mössbauer spectra should have shown superparamagnetically relaxed spectra with typical central enhancement in intensity at some appropriate $T \cdot T_0$ get this kind of Mössbauer line shape, the relaxation time should be of the order of $10^{-8}$ sec which is obtained only if the cluster size is about 100 A (Roggwiller and Kündig 1973). The cluster sizes in TM68 and TM80 are not small enough to give the relaxation pattern in Mössbauer spectra whereas they are small enough to show SP behaviour in the above bulk measurements, where the time scale is of the order of $10^{-2}$ sec.

It has been observed (Roggwiller and Kündig 1973) that under favourable conditions of relaxation time and temperature even a small externally applied magnetic field to the absorber slows down the magnetic fluctuation to produce a better resolved Mössbauer spectrum. We tried to see if any component of this nature could be distinguished in Mössbauer spectra by applying a magnetic field of about 5 kOe to TM68 using a permanent magnet and recording spectrum at RT. We could not see any visible change in the Mössbauer line shapes (not shown in figure). Since TM75 showed maximum SP behaviour at RT as per the $\chi$–$T$ curve, we studied TM75 also under the same external magnetic field at RT. This result is shown in figure 4 and it shows a broadening which effectively amounts to an increase in internal field of about 20 kOe. However this need not mean that there is a change in relaxation time of Mössbauer data. The $T_N$ of this sample is just around RT and this broadening may be due to the magnetisation induced by the external magnetic field. Near the $T_N$ the induced field can be large even for a small external field. Similar effect

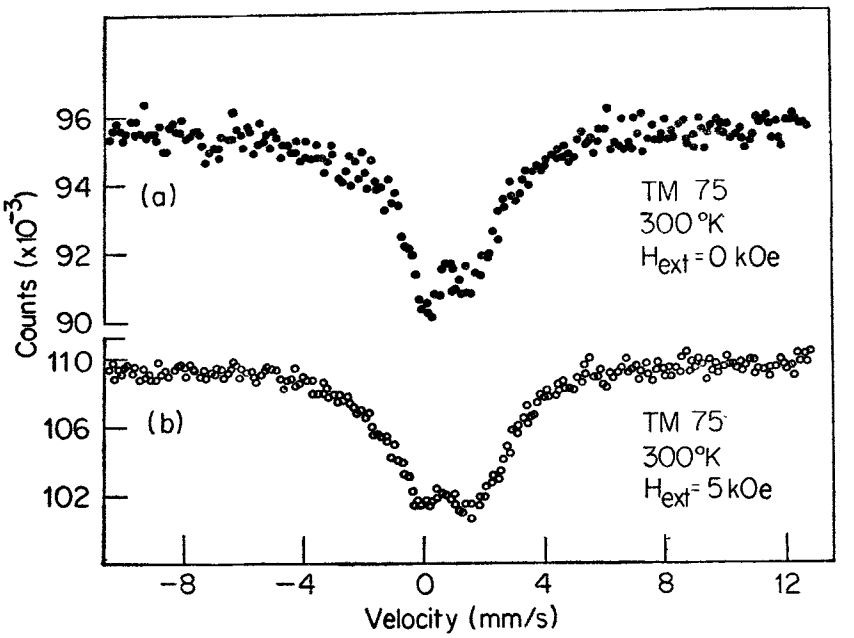


**Figure 4.** Mossbauer spectra for TM75 ($Fe_{2.25}Ti_{0.75}O_4$) with and without external magnetic field.

has been observed in $Fe_{2.65}Pd_{97.35}$ system (Craig *et al* 1965). Therefore we believe that even here the SP behaviour of the sample is not directly seen in the Mössbauer data. However, this does not affect our earlier arguments based on disorder.

It would be of interest to study similar systems with the combination of the three techniques to see if the above findings are true in general.

## 5. Conclusions

(i) Ti ions in magnetite causes magnetic disorder even though the material is a single phase crystallographically.

(ii) The extent of magnetic disorder in TM30 and above inhibits the formation of multidomains and the material behaves as a mixture of superparamagnetic and single domain clusters.

(iii) Mössbauer spectra of well-formed multidomain material is expected to show narrow well resolved lines even close to its $T_N$.

(iv) Magnetic materials showing complex and unresolved Mössbauer spectra might in some cases imply bulk superparamagnetic behaviour and this could be checked by hysteresis and susceptibility measurements at different temperatures.

## References

Banerjee S K and O'Reilly W 1966 *IEEE Trans. Magn. and Magn.* **2** 463
Banerjee S K, O'Reilly W and Johnson C E 1967a *J. Appl. Phys.* **38** 1289

Banerjee S K, O'Reilly W, Gibb T C and Greenwood N N 1967b *J. Phys. Chem. Solids* **28** 1323
Bean C P 1955 *J. Appl. Phys.* **26** 1381
Bickford Jr L R 1950 *Phys. Rev.* **78** 449
Cohen R L, McMullin P G and Wertheim G K 1963 *Rev. Sci. Instrum.* **34** 671
Craig P P, Perisho R C, Segnan R and Steyert W A 1965 *Phys. Rev.* **138** A1460
Haggstrom L, Annersten H, Ericsson T, Wappling R, Karner W and Bjarman S 1978 *Hyperfine Interact.* **5** 201
Nagarajan R and Memon K J 1977 *TIFR Tech. Rept.* **TFR/RN4**
Nagarajan R and Srivastava J K 1977 *Phys. Status. Solidi.* **81** 107
Nagata T 1961 *Rock magnetism* (Tokyo:Muruzen) pp 350
Preston R S, Hanna S S and Heberle J 1962 *Phys. Rev.* **128** 2207
Radhakrishnamurty C and Deutsch E R 1974 *J. Geophys.* **40** 453
Radhakrishnamurty C and Likhite S D 1970 *Earth Planet. Sci. Lett.* **7** 389
Radhakrishnamurty C, Likhite S D, Deutsch E R and Murthy G S 1978 *Proc. Indian Acad. Sci. (Earth. Planet Sci.)* **A87** 235
Radhakrishnamurty C, Likhite S D, Deutsch E R and Murthy G S 1981a *Phys. Earth Planet. Inter* **26** 37
Radhakrishnamurty C, Likhite S D and Nagarajan R 1980 *J. Magn. Magn. & Mater.* **15-18** 195
Radhakrishnamurty C, Likhite S D and Sastry N P 1971 *Philos. Mag.* **23** 503
Radhakrishnamurty C and Nanadikar N G 1979 *Pramana* **13** 413
Roggwiller P and Kundig W 1973 *Solid State Commun.* **12** 901
Sawatky G A, Coey J M D and Morrish A H 1969 *J. Appl. Phys.* **40** 1402
Shirane G, Cox D E, Takei W J and Ruby S L 1962 *J. Phys. Soc. Jpn.* **17** 1958
Syono Y and Ishikawa Y 1963 *J. Phys. Soc. Jpn.* **18** 1230
Uyeda S 1958 *Jpn. J. Geophys.* **2** 1