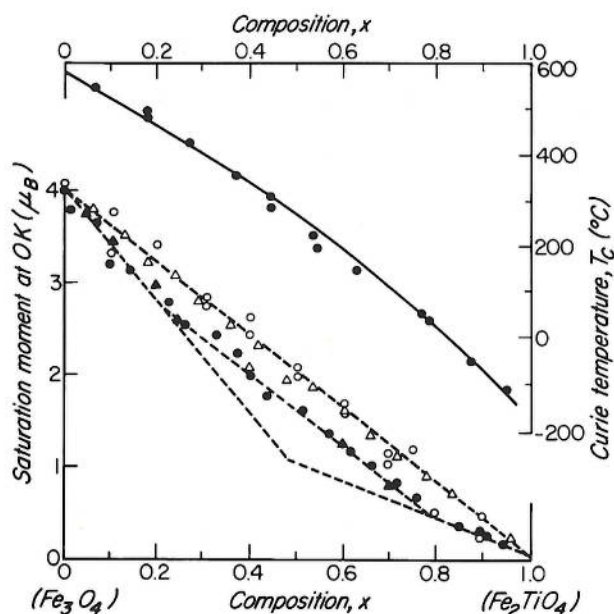


almost linearly with increasing  $x$  (Fig. 3.11). A Curie point of  $\approx 150\text{--}200^\circ\text{C}$  is characteristic of stoichiometric  $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$  or TM60, which is the primary titanomagnetite in rapidly cooled basaltic lavas. An independent way of determining composition is from the X-ray unit cell edge, which increases steadily from  $8.396\text{ \AA}$  in  $\text{Fe}_3\text{O}_4$  to about  $8.54\text{ \AA}$  in ulvöspinel ( $\text{Fe}_2\text{TiO}_4$ ) (O'Reilly, 1984, Fig. 2.4). If  $x$  values deduced from  $T_C$  and from X-ray data disagree, the titanomagnetite is probably oxidized or contains impurities such as Al and Mg.

The distribution of cations on A and B sublattices is uncertain for intermediate titanomagnetites. The predicted variations of magnetic moment with composition for several different models are shown in Fig. 3.11 and compared with experimental observations. Part of the problem in testing cation distribution models stems from the difficulty of preparing stoichiometric single-phase spinels. The observations all support a regular decrease in magnetic moment from  $4\mu_B$  for  $\text{Fe}_3\text{O}_4$  to 0 for  $\text{Fe}_2\text{TiO}_4$ . At room temperature, TM60 has an  $M_s$  value of  $\approx 125\text{ kA/m}$ , about one-quarter that of magnetite. Natural intermediate titanomagnetites may contain up to 10% Mg and Al, further lowering their  $M_s$  and  $T_C$  values. Thermomagnetic or  $M_s(T)$  curves for pure and Al-substituted TM60 are illustrated in Fig. 3.12(a).

Electrical conductivity falls rapidly with  $\text{Ti}^{4+}$  substitution and the Verwey transition is suppressed for  $x > 0.1$ . However, the isotropic point does not disappear. To preserve charge balance, when  $\text{Ti}^{4+}$  is substituted for  $\text{Fe}^{3+}$ , another  $\text{Fe}^{3+}$  must be converted to  $\text{Fe}^{2+}$ :  $2\text{Fe}^{3+} \rightarrow \text{Ti}^{4+} + \text{Fe}^{2+}$ . The additional anisotropy of the  $\text{Fe}^{2+}$  ions causes  $K_1$  to increase to a peak value of  $-2.50 \times 10^4\text{ J/m}^3$



**Figure 3.11** Saturation moment at 0 K and Curie temperature of titanomagnetite as a function of titanium content  $x$ . Saturation moment data: solid circles, Akimoto (1962); solid triangles, O'Reilly and Banerjee (1965); open circles, Stephenson (1969); open triangles, Bleil (1971). The dashed lines are theoretical predictions based on the Akimoto and Néel-Chevallier models of sublattice cation distributions. [After O'Reilly (1976), with the permission of the author and the publisher, Institute of Physics Publishing, Bristol, UK.]