EFFECT OF PRESSURE ON THE CURIE TEMPERATURE OF TITANOMAGNETITES $[(1 - x) \cdot Fe_3O_4 - x \cdot TiFe_2O_4]$

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The effect of pressure up to 60 kbar on the Curie temperature T_c of titanomagnetites was measured T_c increases linearly over this range For magnetite the magnetic Gruneisen parameter γ_m = d ln T_c/d ln V equals about −4 ± 10% γ_m increases in magnitude for increasing titanium content with a maximum of γ_m = −5 1 ± 10% for $x \approx 0$ 7 This result is consistent with relative strong and positive exchange interaction J_{BB} in the B-sublattice one can deduce from other investigations It is suggested that a large J_{BB} makes self-reversal of magnetization unlikely, which is based on a change of the predominant magnetization from one sublattice to the other

1 Introduction

The strength of exchange interactions which are responsible for the ordering of magnetic ions in ferrites depends critically upon the interatomic distances In spinels the different exchange interactions may be described by J_{AA} between A-site (tetrahedral-site) ions, by J_{BB} between B-site (octahedral-site) ions, and by J_{AB} between A- and B-site ions These exchange interactions are related to the Curie temperature T_c [1] Thus the variation of T_c with hydrostatic pressure provides a measure for the dependence of the exchange interactions upon interatomic distances and under certain assumptions a measure for the exchange interactions itself.

Strength and sign of the exchange interactions are important for the behaviour of a possible self-reversal of magnetization originating from a change of the sublattice magnetizations [1, 2] Self-reversal of magnetization in titanomagnetites due to this mechanism and the consequences for rock magnetism have been discussed by several authors [e g.3–6].

In the present work the shift of the Curie temperatures of titanomagnetites $(1 - x) \cdot Fe_3O_4$ $- x \cdot TiFe_2O_4$ with pressure has been measured and some conclusions about the exchange interactions have been drawn. Previous investigations of the

pressure dependence of the Curie temperature of natural magnetite were done by Schult [7] and Samara et al [8]

2 Experimental procedure and results

The Curie temperatures of the synthetic titanomagnetites were measured in a "belt" high pressure apparatus up to 60 kbar The pressure calibration was done with the following transitions and pressure values Bi_{I-II} (25 5 kbar), Tl_{II-III} (36 7 kbar), Ba_{I-II} (55 kbar), and Bi_{III-V} (77 kbar) [9]

The titanomagnetites investigated were sintered at 1300°C under controlled oxygen pressure (CO_2-H_2 mixture) (except that with $x = 0$ 5) A detailed description will be given elsewhere [10] Beside synthetic magnetite two samples of natural magnetite were investigated a single crystal (powdered before measurement) from Pfitscherjoch, Austria and a polycrystalline sample from Kirunavaara, Sweden

The sample assembly in the "belt" consisted of a coil wound on a threaded thin wall of a boron nitride cylinder with the sample of compact powder inside The low-field self-inductance of the coil, which is related to the initial susceptibility of the sample, was measured as a function of temperature at different
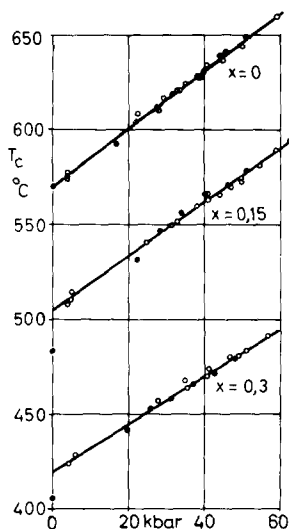
Fig 1 Pressure dependence of the Curie temperatures of synthetic titanomagnetites $(1-x) \cdot Fe_3O_4 - x \cdot TiFe_2O_4$ Closed circles denote Curie points determined in the first pressure increasing cycle, open circles in the first pressure decreasing cycle and further increasing and decreasing cycles

constant pressures, using the Hopkinson peak for the determination of the Curie temperature The experimental technique has been described in detail elsewhere [7]
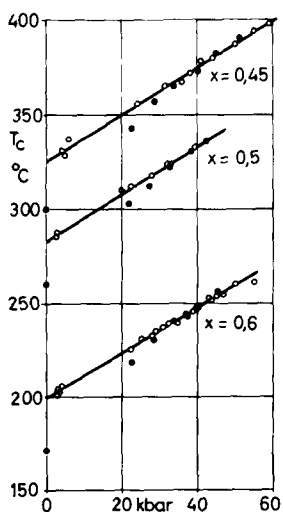
At the Curie temperature the initial susceptibility

and by this the self-inductance of the coil drops sharply with increasing temperature The shift of the Curie temperature with pressure was estimated by finding the relative shift of the self-inductance curves under various pressures [7] The results for the various compositions of the titanomagnetites are shown in figs 1–3 These are the experimental data not corrected for the effect of pressure on the emf of the chromal-alumel thermocouple used

Except for magnetite the change of the Curie temperature was not reversible upon lowering the pressure after the first rising cycle (the closed circles in figs 1–3 represent data obtained by the first pressure rise) The Curie temperatures were increased irreversibly (at zero pressure) in the order of 20° However, after the first rising and lowering cycle the shift was reversible in a second and third cycle No explanation could be found for the irreversible increase of the Curie temperatures A detailed X-ray study of the samples may solve this problem In the following discussion only the reversible shift of the Curie temperatures with pressure will be considered

The Curie temperatures seem to increase linearly with pressure in all cases The slopes dT_c/dp taken from figs 1–3 were all corrected for the effect of pressure on the emf of the chromel-alumel thermocouple used according to the results of Hanneman et al [11] The final slopes dT_c/dp for the various com-
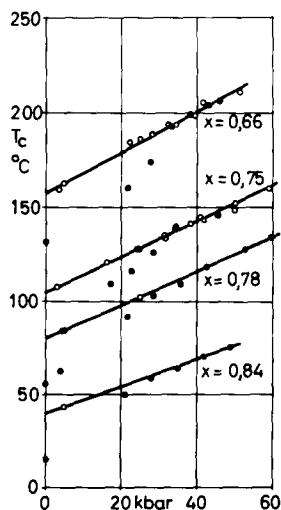

Fig 2. See fig 1

Fig 3 See fig. 1

positions of synthetic titanomagnetites are shown in fig. 4 Table 1 compares values of dT_c/dp for natural and synthetic Fe_3O_4

3 Discussion

It is uniformly suggested that the Curie temperature is a linear function of the exchange interactions J_{ij}

$$T_c = \sum_{ij} A_{ij} J_{ij} \qquad (1)$$

The A_{ij} are constants The exchange interactions vary with volume (i e with interatomic distances) The variation can be described by the so-called "magnetic Gruneisen parameter" [12]

$$\gamma_m = \frac{d \ln T_c}{d \ln V} = \frac{dT_c}{dp} \frac{dp\ V}{T_c\ dV} = d \ln \sum_{ij} A_{ij} J_{ij}/d \ln V \qquad (2)$$

dV/Vdp is the isothermal volume compressibility near the Curie temperature These values are not available. We have adopted therefore the uniform value $5\ 5 \pm 0\ 3 \times 10^{-4}$/kbar, the compressibility of magnetite at room temperature (cit. in [8]). It can be assumed that the compressibility is not drastically

Table 1
Pressure dependence of the Curie temperature of natural and synthetic magnetite

Sample	dT_c/dp (°C/kbar)	Ref
Natural from Kirunavaara, Sweden	2 3 ± 10%	[7]
Natural	2 05 ± 5%	[8]
Natural from Pfitscherjoch, Austria	1 9 ± 10%	Present work
Natural from Kirunavaara, Sweden	1 85 ± 5%	Present work
Synthetic	1 85 ± 5%	Present work

different from this value for the titanomagnetites at their Curie temperatures The values of γ_m determined by eq (2) are shown in fig 5

A quantitative interrelationship between T_c and the various exchange interactions in Fe_3O_4 was given by Kouvel [13].

$$kT_c \approx 4\sqrt{2} J_{AB}\ \sigma_A\ \sigma_B - \tfrac{4}{3} J_{AA}\ \sigma_A^2 - 2J_{BB}\ \sigma_B^2 , \qquad (3)$$

where

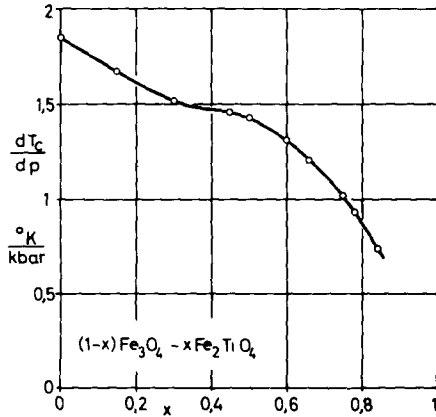$$\sigma_A^2 = S_A(S_A + 1) , \qquad \sigma_B^2 = S_B(S_B + 1) \qquad (4)$$

Fig 4 Shift of the Curie temperature dT_c/dp as a function of the composition of the titanomagnetites dT_c/dp was determined from the slopes of the curves in figs 1–3 and corrected for the effect of pressure on the emf of the chromel-alumel thermocouple used according to Hanneman et al. [11].
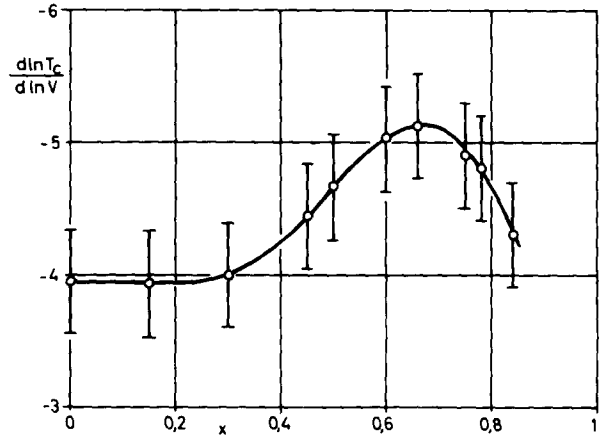

Fig 5. Magnetic Gruneisen parameter $\gamma m = d \ln T_c/d \ln V$ as a function of the composition of the titanomagnetites $(1-x) \cdot Fe_3O_4 - x \cdot TiFe_2O_4$

k Is the Boltzmann constant S_A and S_B are the average spins of electrons associated with the iron moments on A- and B-sites, respectively S_A amounts to $\frac{5}{2}$ because the A-sites are occupied by Fe^{3+} ions The average value for S_B can be written (Fe^{2+} and Fe^{3+} ions) $S_B = \frac{1}{2}(\frac{4}{2} + \frac{5}{2}) = 2\ 25$ We assume now that J_{AA} is negligibly small with respect to J_{AB} and J_{BB} This has been proved by theoretical and experimental results for ferrites by Blasse [2] and particularly for magnetite by Glasser et al [14] Eq (3) reduces to

$$kT_c \approx 4\sqrt{2}J_{AB}\ \sigma_A\ \sigma_B - 2J_{BB}\ \sigma_B^2 \qquad (5)$$

The exchange interactions are assumed to depend only on volume but not necessarily in the same way Deriving eq (5) in the same way as eq (2) yields after some substitutions

$$\gamma_m = \frac{d \ln T_c}{d \ln V} = \frac{d \ln J_{AB}}{(1 - 1/a)\ d \ln V} - \frac{d \ln J_{BB}}{(a - 1)d \ln V}, \qquad (6)$$

with

$$a = \frac{4\sqrt{2}\ \sigma_A\ \sigma_B\ J_{AB}}{2\sigma_B^2\ J_{BB}} \qquad (7)$$

J_{AB} is an indirect exchange interaction between cations via an oxygen ion whereas it is evident from theoretical and experimental investigations that J_{BB} is a direct cation-cation interaction [2, 15] Bloch [12] has shown that in simple ferrites, oxides and garnets the indirect exchange interactions vary as the $-\frac{10}{3}$ power of the volume (i e $\gamma_m = -3\ 33$ in simple compounds with any other than the indirect exchange interactions negligible) The direct exchange interactions are much stronger dependent on the interatomic distances [15] We assume therefore that the relatively large γ_m found for titanomagnetites (see fig 5) is related to the strong (positive) direct exchange interactions J_{BB}

Schwob [16] assumed that the direct exchange interactions are inversely proportional to the square of the cubic crystalline-field splitting of the ion energy levels By the aid of paramagnetic resonance spectra measurements Walsh [17, 18] determined for iron ion that the cubic crystalline-field splitting is proportional to the −21 power of the interatomic distances This implies that the direct exchange

interaction J_{BB} should vary as the −14 power of the volume We set therefore in eq (6) for d ln J_{AB}/ d ln V = −14 Grasser et al [14] on both experimental and theoretical grounds have shown that in magnetite $J_{BB} \approx -0\ 1\ J_{AB}$ (with J_{AB} negative) Under the assumption that σ_A and σ_B are independent of pressure equation (6) yields $\gamma_m = -3\ 7$ which is in agreement with the measured value of about −4 within the experimental errors

The larger γ_m (in magnitude) for $x > 0\ 4$ (fig 5) implies that also the ratio $|J_{BB}/J_{AB}|$ (J_{BB} positive) is larger for these titanomagnetites than for magnetite Under certain conditions a calculation of the J_{BB}/J_{AB} ratio is possible with the aid of Néel's [1] theory from the change of the shape of the spontaneous magnetization versus temperature curves ($M_S(T)$-curves) in a solid solution series [2]

In the notation of Néel [1] the exchange interactions J_{AB}, J_{BB} and J_{AA} are linearly related to the molecular field coefficients n, $n\beta$ and $n\alpha$ respectively If e g in $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$ the iron ions in octahedral sites (put in brackets) are replaced by diamagnetic ions the ratio of the spontaneous sublattice magnetizations at $0°K$ M_A/M_B increases (starting with $M_A/M_B < 1$) Now it is again assumed that J_{AA} is very weak (i e $\alpha \approx 0$) Then it follows directly from Néel's [1] theory that the $M_S(T)$-curve is of the P-type for M_A/M_B values between 1 and $(1 - \beta)$ and of the N-type for M_A/M_B between 1 and $(1 + \beta)$. For $M_A/M_B = 1$ the $M_S(T)$ curve is of the L-type and for all other M_A/M_B values of the Q-type (see fig 6) From the sequence of the different $M_S(T)$ curves as a function of M_A/M_B the sign of β can be determined and from the concentration range in which the curves change their shape the magnitude of β (see fig 6)

The situation for the titanomagnetites is shown in fig 7. The M_A/M_B ratio as a function of x was deduced from the cation distribution given by O'Reilly et al [19] The $M_S(T)$ curves are of the Q-type for $x < 0\ 6$ and of the P-type for $x > 0\ 6$ according to Akimoto et al [20] With the conversion from the exchange interaction ratio $J_{BB} = -0\ 1\ J_{AB}$ for magnetite to the molecular field coefficient one gets $\beta = +0\ 05$ For $x = 0\ 6$ where the Q-type changes to the P-type follows $M_A/M_B = 1 - \beta$ (see figs 6 and 7) From the cation distribution [19] for $x = 0\ 6$

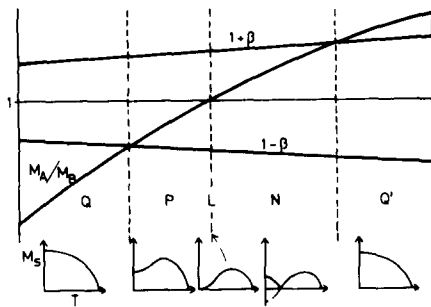$$Fe_{0\ 4}^{2+}\ Fe_{0\ 6}^{3+}\ (Fe_{1\ 2}^{2+}\ Fe_{0\ 2}^{3+}\ Ti_{0\ 6}^{4+})\ O_4 \qquad (8)$$
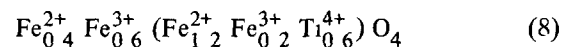
Fig 6 Change of types of $M_S(T)$ curves – given at the bottom of the figure – as a function of M_A/M_B The abscissa denotes a variation in chemical composition (e g substitution of paramagnetic ions by diamagnetic ions in the B-sublattice) For increasing M_A/M_B the sequence of the $M_S(T)$ curve types is Q→P→L→N→Q' for β positive (as shown in the figure) and Q→N→L→P→Q' for β negative If β is large the composition ranges of P- and N-type curves are also large and vice versa

one finds $M_A/M_B = 0\ 79$ and $\beta = +0\ 21$ and finally $J_{BB} = -0\ 42\ J_{AB}$ (J_{BB} positive) With the approximation that the relation for the Curie temperature given in equation (5) is also valid for the titanomagnetites eq (6) yields $\gamma_m = -4\ 6$ again in agreement with the measured value of about -5 (for $x = 0\ 6$) within the experimental errors

Generally it can be said that the behaviour of the exchange interactions in titanomagnetites deduced from the high pressure measurements is consistent with the results one gets from other investigations We therefore assume that γ_m varies as a function of x qualitatively in the way as shown in fig 7 (β should vary in a similar way as γ_m shown in fig 5)
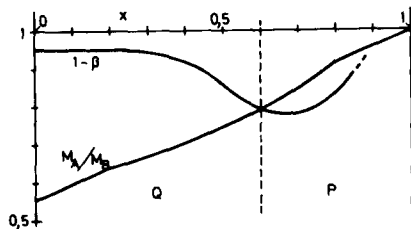
The relative large and positive β (strong J_{BB}

Fig 7 Behaviour of M_A/M_B, $1 + \beta$ and $1 - \beta$ and types of $M_S(T)$ curves as a function of x for titanomagnetites
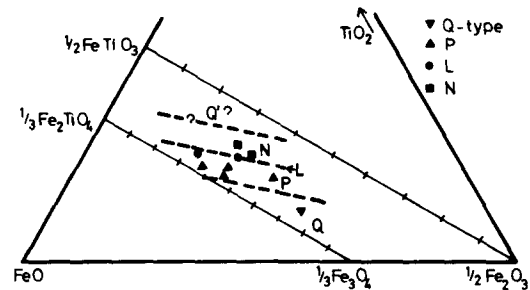$(1 - x) \cdot Fe_3O_4 - x \cdot TiFe_2O_4$

Fig 8 Chemical composition of natural (cation deficient) titanomagnetites in basalts after Schult [6] Probable borders between ranges with different types of $M_S(T)$ curves are indicated with broken lines

interaction) has some consequences for self-reversal models discussed on the background that titanomagnetites can produce single phase cation deficient spinels by slow oxidation at low temperatures Starting from a given cation distribution and an octahedral site predominant magnetization several authors showed theoretically and experimentally (e g refs [3–6]) that with slow oxidation vacancies can be formed on B-sites producing an A-site predominant magnetization after long enough oxidation (only possible for $x > 0\ 5$) As the exchange interaction in the B-sublattice is positive the sequence of the $M_S(T)$ curve types for increasing degree of oxidation (that is increasing M_A/M_B ratio) is Q→P→L→N→Q' (fig 6) (Q' denotes a $M_S(T)$ curve with A-sublattice predominant at any temperature below the Curie temperature, a complete "irreversible" self-reversal of magnetization takes place when the composition is shifted over the border N/Q') The relative large β – particularly for $x > 0\ 5$ – implies that the concentration range in which the $M_S(T)$ curves change their shape is also large (see fig 6) This is in agreement with investigations on natural titanomagnetites as shown in fig. 8 [6]

It must be kept in mind, however, that the slope of the M_A/M_B curve in fig 6 (as a function of the degree of oxidation) determines the extension of the chemical composition of the different types of $M_S(T)$ curves as shown in fig 8 as well The slope depends on the cation distribution which is not exactly known and we do not intend to discuss this problem here After all it can be assumed that the composition range

with the Q'-type $M_S(T)$ curve — if there is any — is relatively far away from the Fe_3O_4-Fe_2TiO_4 join in fig 8, probably near or above the Fe_2O_3-$FeTiO_3$ join

The titanomagnetites in the hypothetical Q'-range should be highly cation deficient. Until now it has not been definitely shown that they exist, neither for synthetic nor for natural titanomagnetites Compositions of iron-titanium minerals in the range in question sometimes reported seem more to be average compositions of mixed phases and not those of a single spinel phase

If the highly cation deficient titanomagnetites in the Q'-region exist it would be more likely that also the somewhat less cation deficient titanomagnetites in the N-region exist The N-type titanomagnetites have been found rarely but only with compensation temperatures below room temperatures [6] This means that these titanomagnetites are located in the N-range closer to the P-range than to the Q'-range The higher cation deficient titanomagnetites in the N-range near the Q'-range should have a compensation temperature above room temperature, but these titanomagnetites have not been found until now, despite an enormous number of existing measurements of $M_S(T)$ curves and remanence versus temperature curves above room temperature On the other hand the composition range of these N-type titanomagnetites should be fairly large because of the strong J_{BB} interaction We regard therefore the self-reversal mechanism discussed here to have no importance in rock magnetism

Acknowledgements

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