Refined technique for susceptibility resolution into ferromagnetic and paramagnetic components based on susceptibility temperature-variation measurement

František Hrouda,[1,2] Vít Jelínek[1] and Karel Zapletal[1]

[1] *AGICO, Inc. Brno, Ječná' 29a CZ-612 H6 Brno, Czech Republic. E-mail agico@vtx.cz*
[2] *Institute of Petrology and Structural Geology, Charles University, albertov 6, CZ-12843, Prague, Czech Republic*

SUMMARY

The measurement of the temperature variation of magnetic susceptibility can be used for the separation of ferromagnetic and paramagnetic susceptibility components. The method suggested by Hrouda (1994) assumes a hyperbolic dependence of paramagnetic susceptibility and constant ferromagnetic susceptibility in the temperature interval used for the separation. Our new method works with a paramagnetic hyperbola again, but assumes that the ferromagnetic susceptibility temperature variation is represented by a linear relationship in the resolution interval, as indicated by the investigation of monomineralic ferromagnetic fractions.

Key words: magnetic susceptibility, temperature variation.

INTRODUCTION

A knowledge of the contributions of ferromagnetic (*sensu lato*) and paramagnetic minerals to rock susceptibility is very important in magnetic anisotropy investigations, because the minerals show different behaviour in different geological situations (e.g. Hrouda 1982; Tarling & Hrouda 1993). One of the methods for the resolution of the rock susceptibility into its ferromagnetic and paramagnetic components is based on the investigation of the temperature variation of susceptibility. The curve representing the temperature variation of susceptibility (henceforth called the thermomagnetic curve) of paramagnetic minerals is represented by a hyperbola, while the thermomagnetic curve of ferromagnetic minerals is a complex curve, fortunately in its initial part being represented by a straight line of zero or very shallow slope. The resolution technique developed by Hrouda (1994) is based on the above susceptibility behaviour; through fitting a hyperbola to the initial part of a thermomagnetic curve, using the least-squares method, one can separate the susceptibility into its paramagnetic and ferromagnetic components and determine errors in this separation.

However, our investigations of pure mineral fractions of ferromagnetic minerals have shown many examples of relatively steep slopes of the straight line representing the initial part of the ferromagnetic thermomagnetic curve. The question arises how significant is this effect for the accuracy of the susceptibility separation into its components. This paper attempts to solve this problem through mathematical modelling and introduces a new technique for the component resolution considering the

non-zero slope of the initial ferromagnetic thermomagnetic curve.

INITIAL SLOPES OF THE THERMOMAGNETIC CURVES OF SOME MINERALS

In order to obtain information about the temperature changes of susceptibility in the initial part of the thermomagnetic curves of the most important ferromagnetic minerals, necessary for the successful modelling of the problem, the thermomagnetic curves of the monomineralic fractions recently investigated in our laboratory using the CS-2 Apparatus and KLY-2 Kappabridge were re-evaluated. The results are presented in Figs 1 and 2 and Table 1. Fig. 1 shows examples of the heating thermomagnetic curves of magnetite, haematite and pyrrhotite. It is obvious from Fig. 1 that the thermomagnetic curves of all three minerals show in their initial parts clearly non-zero slopes. Fig. 2 shows the slopes (the b parameter in eq. 2; see below) of the straight lines fitted to the thermomagnetic curves of haematite, magnetite and pyrrhotite in three temperature intervals (20 °C to 100 °C, to 150 °C, and to 200 °C). (The temperature interval to be used for the component resolution will henceforth be called the resolution interval.) Table 1 shows the variation of the b parameter with grain size in the case of magnetite.

It can be seen in Fig. 2 that the constant b approaches zero only rarely. It is in general low in haematite and magnetite and relatively high in pyrrhotite. It is surprising that the constant b is even negative in two specimens, which indicates
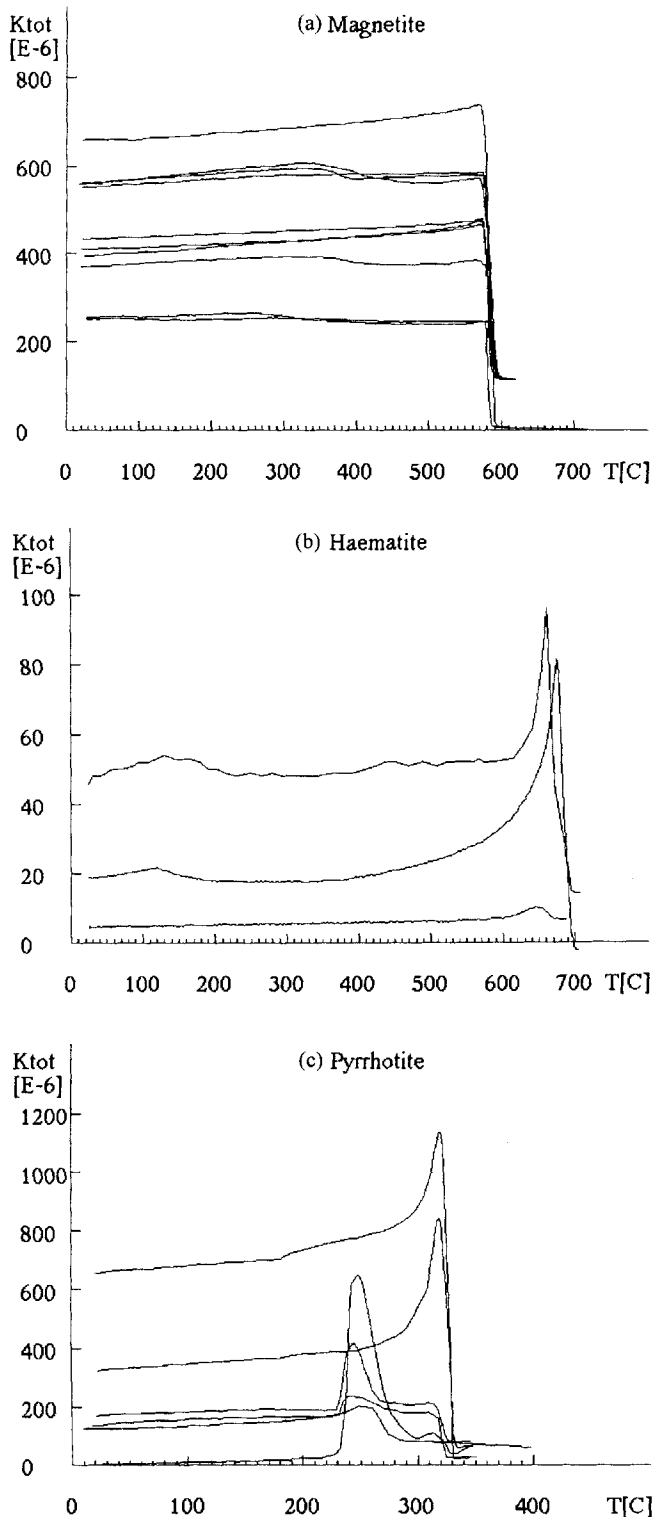
Figure 1. Heating thermomagnetic curves of monomineralic magnetite (a), haematite (b) and pyrrhotite (c). The susceptibility data are in terms of total susceptibility (sensu Jelínek 1977, see eq. 4) dimensionless units (in SI) of the order 10^{-6}.

that in some rare cases the thermomagnetic curve can be more complex than a weakly sloping straight line, even at relatively low temperatures (see Fig. 1b). Nevertheless, in many specimens the *b* values calculated for all three temperature intervals
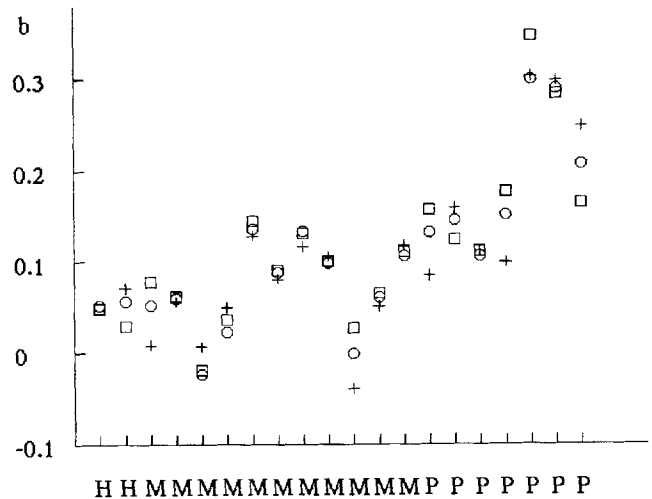

Figure 2. The values of the slope (*b*) of the straight lines representing the thermomagnetic curves of monomineralic fractions in three resolution intervals. Crosses, circles, and squares correspond to the resolution intervals of 20–100 °C, 20–150 °C and 20–200 °C, respectively. H: haematite; M: magnetite; P: pyrrhotite.

Table 1. Variation of the *b* constant according to the grain size in magnetite.

Specimen	b	Grain Size (mm)	Characteristics
M36M	0.10	1	single crystal
M76	0.03	0.002-0.3, mostly 01	polycrystalline ore
M96	0.07	0.001-1.0, mostly 0.6	polycrystalline ore
M962	0.11	0.001-1.0, mostly 0.6	polycrystalline ore
M14	0.08	0.02-2.0, mostly 0.7	polycrystalline ore
M16	0.06	0.02-0.7, mostly 0.3	polycrystalline ore
M360400	0.14	<0.04	powder
M36904	0.09	0.09-0.04	powder
K362009	0.13	0.09-0.2	powder

are close to each other, which indicates the validity of the straight-line representation; most magnetites are among these specimens. From Table 1 it is obvious that the *b* constant in magnetite tends to increase with increasing grain size, but this correlation is relatively poor. In those specimens in which the *b* values differ from interval to interval, the thermomagnetic curve is not represented by a well-defined straight line; this is the case for most pyrrhotites.

MODELLING THE PROBLEM

The susceptibility of a rock containing both ferromagnetic and paramagnetic minerals was modelled mathematically using a very simple model in the temperature interval between room temperature (20 °C) and 200 °C. The model rock susceptibility considered was 5×10^{-4} (SI), which is a value typical for weakly magnetic rocks in which both the ferromagnetic and paramagnetic fractions contribute significantly to the rock susceptibility. The paramagnetic to ferromagnetic susceptibility ratio was considered as ranging from 0.5 to 2.

The paramagnetic susceptibility considered was as follows:

$$k_p = C/T, \tag{1}$$

where C is the constant of the hyperbolic Curie law and T

is the absolute temperature (in Kelvin). The ferromagnetic susceptibility considered in the resolution interval was as follows:

$$k_f = bT + a, \tag{2}$$

where T is the absolute temperature and a and b are the constants in the straight line considered. The constant b was considered to vary from 0 to 0.2 (which corresponds to the natural data) and the constant a was calculated from the ferromagnetic susceptibility at room temperature and from the constant b.

The rock susceptibility varies then as follows:

$$k_r = C/T + bT + a. \tag{3}$$

Thermomagnetic curves were constructed using eq. (3). These curves were evaluated using the original CUREVAL (version 1.0) program (Hrouda 1994). The contributions of the paramagnetic and ferromagnetic susceptibilities to the room-temperature rock susceptibility were calculated assuming that the ferromagnetic susceptibility was constant in the interval considered. The results are presented in Fig. 3, which shows the calculated to modelled ratios (R) for both components against the constant b and for various paramagnetic to ferromagnetic susceptibility ratios. The upper suite of straight lines represents the calculated to modelled ratios for the ferromagnetic component, while the lower suite represents the ratios for the paramagnetic component. The individual straight lines represent the modelled paramagnetic to ferromagnetic susceptibility ratios (ranging from 0.5 in the innermost lines of the suites to 2 in the outermost lines). It can be seen in Fig. 3 that the Hrouda (1994) method gives acceptable results if the slope of the ferromagnetic straight line is very low. In the other cases, the method underestimates the paramagnetic component and overestimates the ferromagnetic component. Consequently, the Hrouda (1994) method is applicable only to rocks whose ferromagnetic susceptibility is virtually constant in the resolution interval, while in rocks whose ferromagnetic
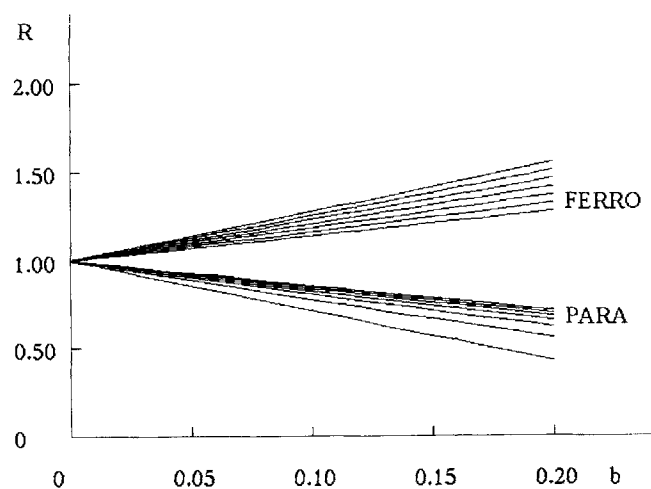
susceptibility is represented by clearly sloping straight lines the errors in the component resolution can be significant.

REFINEMENT OF THE METHOD

Our new method considers the sloped-straight-line representation of the ferromagnetic thermomagnetic curve in the resolution interval. It was developed using the general formula of the least-squares method as presented by Rektorys *et al.* (1988). It fits the thermomagnetic curve in the resolution interval to the composite curve consisting of the hyperbola (representing paramagnetics) and straight line (representing ferromagnetics) and calculates the constant C of the hyperbola (see eq. 1) and the constants a, b of the straight line (eq. 2) and their errors.

This method was incorporated into the CUREVAL program (version 2.0). (This program is supplied with the CS-2 and KLY-2 measuring instruments as well as with their successors, CS-3 and KLY-3S.) We have tested its accuracy on the above models. The results are presented in Fig. 4, which shows that the resolved components are very close to the modelled ones (the calculated deviations are due to the rounding of the input data used in the construction of the theoretical thermomagnetic curves in order to model the measurement accuracy).

The new method was also tested on artificial specimens prepared as mixtures of paramagnetic biotite and a ferromagnetic mineral (magnetite, haematite, pyrrhotite). The biotite was extracted from the crushed granodiorite of the Nasavrky massif by Dr. Š. Táborská. It is very pure magnetically, with its thermomagnetic curve following the paramagnetic hyperbola (Fig. 5) well; its paramagnetic susceptibility at room temperature is at least 12 times higher than the susceptibility of ferromagnetic impurities. The results of the investigation of biotite/magnetite mixtures (the thermomagnetic curve of the magnetite used for this experiment is shown in Fig. 6) are summarized in Table 2, showing the paramagnetic and ferromagnetic susceptibilities measured separately and those determined through measurement of mixtures and calculated using the old and new methods. The susceptibilities in Table 2 are given in terms of the total susceptibility (as introduced by Jelínek 1977), which is more convenient for our purpose than

Figure 3. Diagram showing the variation of the ratio of the calculated (k_p, using the Hrouda 1994, method) to the modelled (k_{pm}) paramagnetic susceptibility ($R = k_p/k_{pm}$; lower suite of lines) and that of the ratio of the calculated (k_f) to modelled (k_{fm}) ferromagnetic susceptibility ($R = k_f/k_{fm}$; upper suite of lines) according to the slope of the ferromagnetic susceptibility.
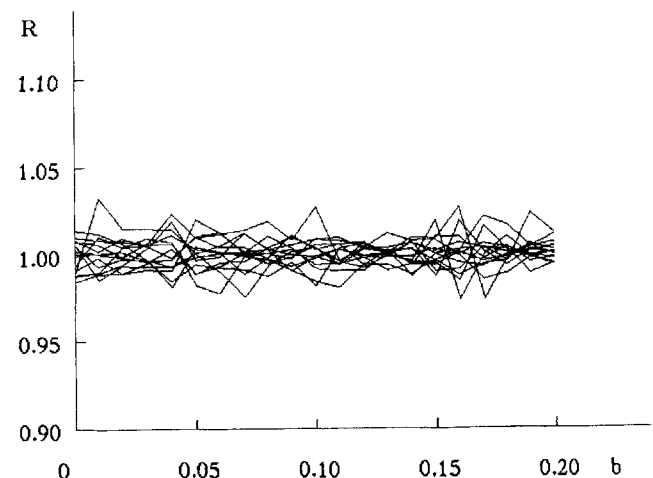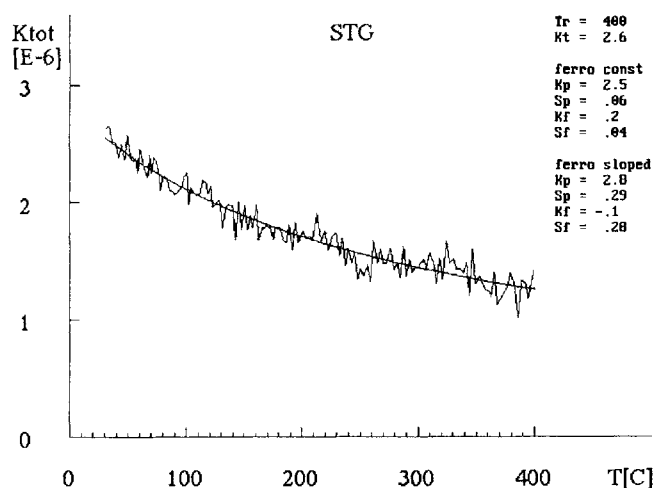

Figure 4. Diagram showing the variation of the ratio of the calculated (using our new method) to modelled paramagnetic susceptibility and that of the ratio of the calculated to modelled ferromagnetic susceptibility according to the slope of the ferromagnetic susceptibility.

Figure 5. Heating thermomagnetic curve of biotite used for mixing experiments (extracted from the Nasavrky Massif granodiorite), with the fitted paramagnetic hyperbola. The susceptibility data are in terms of total susceptibility (as in Fig. 1). The susceptibility is resolved into the paramagnetic component (Kp; Sp is the resolution error) and ferromagnetic component (Kf; Sf is the error) using the old method (ferro const) and new method (ferro sloped) (Tr is the upper limit of the resolution interval, Kt is the total susceptibility of the specimen).
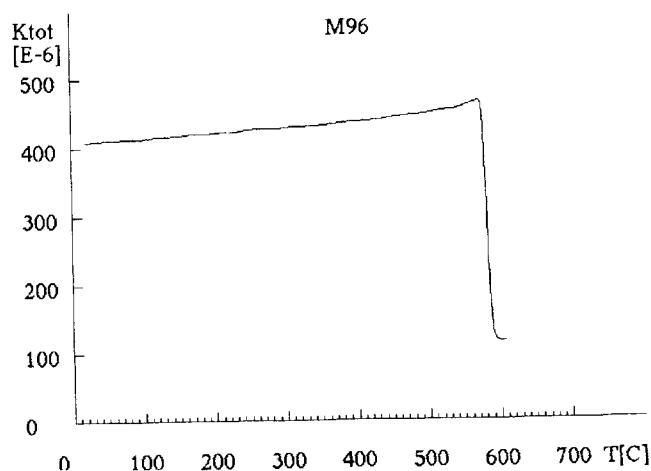
Figure 6. Heating thermomagnetic curve of magnetite used for mixing experiments.

Table 2. Magnetic susceptibilities of mineral mixtures as resolved using the old and new methods.

Specimen	Fraction	Actual	Old	New
magnetite 1	para	53.6	50.0	55.8
	ferro	48.2	53.2	47.7
magnetite 2	para	81.3	80.3	81.9
	ferro	22.6	26.0	24.4
magnetite 3	para	63.8	60.0	65.7
	ferro	44.5	49.3	44.4
magnetite 4	para	38.7	32.6	42.3
	ferro	74.4	81.2	72.0
magnetite 5	para	46.9	41.9	49.9
	ferro	63.8	69.9	62.2

bulk susceptibility because it provides information about the magnetic signal directly measured by the instrument without any necessity of laborious determination of the volume of the powder specimen measured. The total susceptibility *sensu* Jelínek (1977) is defined as follows:

$$k_T = (V/V_0)k_B, \qquad (4)$$

where k_T is the total susceptibility, k_B is the bulk susceptibility, V is the actual volume of the specimen and V_0 is the nominal volume of the specimen (in the case of the KLY-2 and/or KLY-3/KLY3S Kappabridges with a standard pick up unit $V_0 = 10 \, cm^3$). It should be noted that the total susceptibility *sensu* Jelínek (1977) is dimensionless, while the total susceptibility *sensu* Collinson (1983) has the dimension m^3 (it is defined as $k_T = Vk_B$).

It is obvious from Table 2 that the paramagnetic susceptibilities determined by the old method are clearly lower than the actual ones, and the ferromagnetic susceptibilities determined by the old method are in turn clearly higher than the actual ones. Both the paramagnetic and ferromagnetic susceptibilities determined by the new method are very near to the actual ones. (In fact, the former are slightly higher, while the latter are slightly lower.) It can be concluded that the results obtained from the new method are more realistic than those given by the old method, even though they are not precisely the same as actual susceptibilities. The small differences probably result from a more complicated resolution procedure from susceptibility temperature variation than simple measurement of room-temperature susceptibility.

In the investigation of biotite/pyrrhotite mixtures and biotite/haematite mixtures, both the old and new methods gave results very different from those measured directly. One can conclude that both methods fail for the case of pyrrhotite and haematite as representatives of the ferromagnetics. The reason is probably that the pyrrhotite heating thermomagnetic curve is in most cases clearly non-linear and intensely curved, and the haematite curve can be even more complex (see Figs 1b and c). Approximation of those curves by straight lines (sloping or non-sloping) is no doubt insufficient.

DISCUSSION AND CONCLUSIONS

Even though the use of the susceptibility temperature variation in susceptibility resolution into ferromagnetic and paramagnetic components is theoretically clear, there, are two factors that can limit its practical application. The first is possible phase or mineral changes of ferromagnetic minerals due to heating. Consequently, there is the problem of how wide the most convenient resolution interval should be. It should be wide enough to provide a sufficient number of measurements for reliable fits of the hyperbola and the straight line, and narrow enough to avoid phase or mineral changes due to heating. Our experience of the investigation of several hundred thermomagnetic curves shows that a reasonable compromise is the interval between room temperature and 200 °C for magnetite.

The second factor is the non-existence of the functional relationship of susceptibility versus temperature for ferromagnetic minerals (in contrast to paramagnetic minerals, whose thermomagnetic curve is certainly a hyperbola). For this reason, one can work only with empirical data that does not necessarily represent the natural variability. Two models of

the susceptibility versus temperature relationship in the resolution interval for ferromagnetic minerals have been suggested previously. In the first model the ferromagnetic thermomagnetic curve is represented by a straight line of zero slope (Hrouda 1994; the old method is based on this model), while in the second model it is represented by a straight line of non-zero slope (the new method of this paper is based on this model). The results obtained by these two methods are in some cases relatively different. At first glance, one might think that the new method is more general and, therefore, the differences are due to the lower accuracy of the old method. This is no doubt true if the ferromagnetic thermomagnetic curve in the resolution interval is really represented by a straight line of non-zero slope. Unfortunately, the new method has given in some cases negative ferromagnetic susceptibilities, which is certainly incorrect. There are no simple criteria for favouring one of the above methods in a particular case. The fitting errors in both cases are usually so small (probably because of many measured data) that their use for the above purpose fails. For this reason, we recommend the following solution, even though we realize that it is still far from perfect. In the program CUREVAL (ver. 2.0) both methods are used. The user can decide relatively easily which method gives better results. Using a narrow resolution interval, one can separate the ferromagnetic curve and display it on the screen. Then, one can find whether the curve in the resolution interval passes approximately parallel to the abscissa or is represented by a straight line of non-zero slope.

It can be concluded that the susceptibility temperature variation can be used in principle for the susceptibility resolution into ferromagnetic and paramagnetic components, but the application must be made with care, because of the possible problems mentioned above concerning the susceptibility versus temperature relationship for the ferromagnetic minerals in the resolution interval.

ACKNOWLEDGMENT

REFERENCES

Collinson, D.W., 1983. *Methods in Rock Magnetism and Palaeomagnetism,* Chapman & Hall, London.

Hrouda, F., 1982. Magnetic anisotropy of rocks and its application in geology and geophysics, *Geophys. Surv.,* **5,** 37–82.

Hrouda, F., 1994. A technique for the measurement of thermal changes of magnetic susceptibility of weakly magnetic rocks by the CS-2 Apparatus and KLY-2 Kappabridge, *Geophys. J. Int.,* **118,** 604–612.

Jelínek, V., 1977. *The Statistical Theory of Measuring Anisotropy of Magnetic Susceptibility of Rocks and its Application,* Geofyzika Brno.

Rektorys, K. (ed.) *et al.,* 1988. *Survey of Applicable Mathematics* (in Czech), NTL Publ. House, Praha; English version, Iliffe Books, London, 1969.

Tarling, D.H. & Hrouda, F., 1993. *The Magnetic Aniostropy of Rocks,* Chapman & Hall, London.