

## On determination of the Curie point from thermomagnetic curves

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[1] In many rock magnetic studies, information on magnetic mineralogy is of crucial importance. Besides standard analytical methods, such as X-ray spectroscopy, more sensitive thermomagnetic analyses are often used. Temperature dependence of magnetic parameters can serve as basis for determination of magnetic second-order phase transition temperatures. Although limited by several drawbacks, the most serious being thermally induced transformations of the original minerals, this method provides useful information not only about the presence of magnetic minerals, but also additional knowledge on, e.g., the prevailing grain size distribution or degree of substitution. In thermomagnetic analysis, temperature dependence of two parameters, induced magnetization and magnetic susceptibility, is mostly used. However, let us say because of historical reasons, the same approach for the Curie point determination has been often used in analyzing the two parameters. In our contribution, we discuss the physical principles of the two parameters, showing that the methods developed and used for induced magnetization cannot be used also for temperature dependence of magnetic susceptibility because there is no physical justification to do so. Otherwise, the error in determining the Curie point can be some few degrees but can reach also several tens of degrees. Such an error has serious consequences for further interpretation of the data, e.g., in terms of degree of Ti substitution in Ti magnetite.

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### 1. Introduction

[2] Magnetic susceptibility is definitely one of the most commonly measured parameters in various rock magnetic studies, mainly due to high sensitivity and present availability of instruments, as well as to the ease with which it is measured. However, its proper interpretation is not that easy and straightforward, and it is quite often interpreted in the same way as magnetization. For example, it is usually translated as concentration of magnetic particles. This holds true for cases of linear dependence of induced magnetization on the applied field, where magnetic susceptibility is defined as simple ratio of induced magnetization and the intensity of the applied field. This is valid for paramagnets, diamagnets and ferrimagnets in the field range where the ferromagnetic contribution is saturated. However, in the case of ferrimagnets or antiferromagnets, studied in rock magnetic applications, induced magnetization is not a linear function of the applied magnetic field, and magnetic susceptibility depends also on the magnetization processes. In simple words, it expresses the character and intensity of a sample response to external magnetic field, and is not controlled solely by concentration of magnetic particles (although this effect is for given composition the most

significant). In recent years, due to availability of suitable instruments, such as the AGICO Kappabridge [Hrouda, 1994, 2003; Hrouda *et al.*, 1997], as well as methods of evaluation [Hrouda, 2003; Bohnel *et al.*, 2002] temperature dependence of magnetic susceptibility is used in order to determine the Curie (Néel) temperatures.

[3] Interpretation of Curie temperatures ( $T_C$ ) covers a quite wide range of problems. First of all, it serves as a tool for identification of magnetic minerals. Other studies focus on various structural aspects. For instance, Harrison and Putnis [1999] evaluated cation ordering in magnesioferrite on the basis of Curie temperatures. Dependence of  $T_C$  on composition is often used for estimation of Ti content in titanomagnetites [e.g., Genshaft and Zhdanov, 2005] or degree of oxidation of titanomagnetites [e.g., Wang *et al.*, 2006; Krasa *et al.*, 2005]. Most recently, Lattard *et al.* [2006] examine in detail the relationship between Ti substitution and  $T_C$ , determined using temperature dependence of magnetic susceptibility.

[4] Because of the increasing significance of this parameter, several methods were developed for the Curie point determination from thermomagnetic curves. In the case of temperature dependence of induced magnetization, several methods were discussed by Moskowitz [1981]. It seems that there is general consensus to use the two-tangent method, developed by Grommé *et al.* [1969]. This method, although developed originally for temperature dependence of magnetization, has been applied by several authors also on curves of temperature dependence of magnetic susceptibility.

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ity [e.g., *Harrison and Putnis*, 1999; *Kontny et al.*, 2004; *de Wall and Nano*, 2004; *Deng et al.*, 2006]. Other authors used approaches different from that developed by *Grommé et al.* [1969] for magnetization curves. For instance, *Wehland et al.* [2005] used Hopkinson peak as the Curie point. *Hrouda et al.* [2005] tested paramagnetic behavior above the Curie point using the Curie-Weiss paramagnetic law. *Lattard et al.* [2006] combine the two possibilities, in dependence of the shape of the susceptibility curve.

[5] Apparently, different authors use different approaches. In this contribution, we would like to highlight some problems associated with the use of the two-tangent method of *Grommé et al.* [1969] to susceptibility curves. We understand, that this method has been used mainly due to the fact that instrumentation, enabling measurements of temperature dependence of magnetic susceptibility, became available only recently, and that curves of susceptibility and magnetization often look quite similar to each other. However, we would like to emphasize that the application of this approach to magnetic susceptibility is not justified by physics and yields erroneous results. Although this problem was briefly discussed by *Petrovský and Kapička* [2005], in this paper we would like to bring up a more detailed discussion, and using some experimental examples we intend to show that values of  $T_C$ , determined from temperature dependence of magnetic susceptibility using the two-tangent method, are overestimated and fall within temperature range, where the substance in concern behaves paramagnetically.

## 2. Short Excursion Into Theory

[6] The theory of magnetically aligned structures (ferromagnetism, ferrimagnetism, antiferromagnetism) is already well established and known for a long time, and was described in numerous handbooks. Let us name at least the handbooks of *Chikazumi and Charap* [1964], *Craik* [1995], or a more recent one by *Morrish* [2001]. A handbook by *Dunlop and Özdemir* [1997] is written mainly for rock magnetists and provides very good insight into the physical principles of magnetism. Among the classical literature, let us refer to the Nobel lecture of *Néel* [1970], and older, very good handbooks of *Krupička* [1969, 1973], focusing on magnetism of ferrites and iron oxides.

### 2.1. Diamagnetism and Paramagnetism

[7] Let us start briefly with diamagnetism and paramagnetism. Macroscopically, both the phenomena are induced and relatively weak. Diamagnetism alone occurs in materials consisting of atoms with no net magnetic moment. The application of a magnetic field induces a moment in the atom that, by Lenz's law, opposes the applied field. This effect is weak and temperature-independent.

[8] Paramagnetism occurs in substances consisting of atoms that have permanent magnetic moment. In the presence of an applied field, such a moment will experience a torque tending to align it with the field. Maximum net magnetization (saturation magnetization  $M_s$ ) is defined as complete alignment of all atomic magnetic moments parallel to the applied field, and equal to the product of their moment and their density.  $M_s$  corresponds to a temperature of absolute zero, when the atomic magnetic moments in

assembly would align themselves with the magnetic field. Atoms possess a magnetic moment  $m$  that is an integer number of Bohr magnetons  $\mu_B$ , which is the moment of an electron (in SI units  $0.9274 \times 10^{-23}$  Am<sup>2</sup>). At temperatures higher than absolute zero, thermal agitation will prevent them from completely aligning with that field. Induced magnetization  $M$  can be expressed as  $M = M_s B_J(\xi)$ , with the Brillouin function

$$B_J(\xi) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} \xi - \frac{1}{2J} \coth \frac{\xi}{2J},$$

where  $J$ , integer, is the angular momentum quantum number and  $\xi = \mu_0 m H / kT$ . Here,  $\mu_0$  is permeability of vacuum,  $m$  stands for magnetic moment of the atom,  $k$  is Boltzmann's constant and  $T$  absolute temperature.

[9] Magnetic susceptibility  $\chi$ , defined as first derivative of induced magnetization  $M$  with respect to the applied field  $H$ , can be for small fields (i.e., low-field susceptibility) expressed as

$$\chi = \frac{\mu_0 m M_s}{3kT}. \quad (1)$$

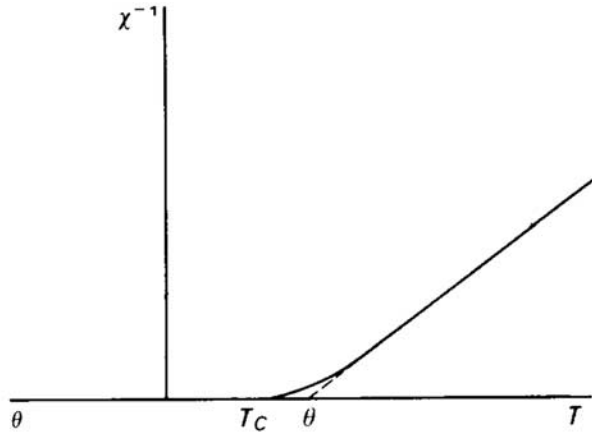
[10] Note that we use  $\chi$  for susceptibility, which is volume-specific, unlike  $\kappa$ , used in most rock magnetic literature. This notation is in agreement with Anglo-Saxon physics literature, and in contrast to Russian literature, where  $\kappa$  is used for volume-specific and  $\chi$  for mass-specific susceptibility.

[11] According to equation (1), paramagnetic magnetic susceptibility exhibits hyperbolic decay with temperature, while the inverse susceptibility  $1/\chi$  shows linear increase with increasing temperature, passing through absolute zero temperature.

### 2.2. Ferromagnetism

[12] Ferromagnetism is the phenomenon of spontaneous net magnetization; the magnetization exists in the absence of applied magnetic field. This phenomenon involves the alignment of an appreciable fraction of the atomic/molecular magnetic moments in some favorable direction in the crystal. The best known examples of ferromagnets are the transition metals Fe, Co, and Ni, but other elements and alloys involving transition or rare earth elements also show ferromagnetism. The fact that this phenomenon, like paramagnetism, is restricted to transition and rare earth elements indicates, that it is related to the unfilled 3d and 4f shells in these substances. On the basis of the mutual orientation of the neighboring atomic magnetic moments and their relative magnitude, three types of materials with aligned magnetic structure are distinguished: ferromagnets, ferrimagnets and antiferromagnets. The phenomenon of ferromagnetism appears only below a certain temperature, which is known as the Curie point (called Curie temperature  $T_C$  in the case of ferromagnets and ferrimagnets, and Néel temperature  $T_N$  in antiferromagnets). This temperature depends on the substance and, in general, includes the whole of the usual temperature region.

[13] In the case of ferromagnetic substances above the Curie temperature, magnetic moments are oriented randomly, resulting in a zero net magnetization. In this region the



**Figure 1.** Temperature dependence of inverse susceptibility of ferromagnets above the Curie temperature.

substance is paramagnetic, and its susceptibility is given by Curie-Weiss law

$$\chi = \frac{C}{T - T_C}, \quad (2)$$

where  $C$  is the Curie constant, given as  $C = Ng^2S(S+1)\mu_B^2/3k$  ( $N$  is number of atoms,  $g$  is factor of spectral split,  $g = 2$  for spin magnetic moment only,  $S$  stands for spin magnetic moment). The Curie-Weiss law can be derived using a molecular field, the origin of which is in the exchange interaction. However, the linearity of inverse susceptibility above  $T_C$  is not ideal for temperatures slightly above the transition temperature (Figure 1). This is due to the fact that strong fluctuations of the magnetic moments close to the phase transition temperature (Curie temperature) cannot be described by the Weiss mean field theory, which was used for deriving the Curie-Weiss law. Nevertheless, experimental results suggest that this deviation is practically negligible [e.g., *Lichtenstein et al.*, 2001].

[14] Since there are no known ferromagnetic natural minerals of terrestrial origin, we refer the reader interested in the theory of ferromagnets to the references mentioned at the beginning of this section. It is true that hematite is sometimes considered as ferromagnetic, because it shows weak ferromagnetic moment, but this is not a result of parallel magnetic moments of neighboring atoms, but of canted moments of two sublattices, instead. In terms of magnetic alignment of atomic magnetic moments, hematite is antiferromagnetic.

### 2.3. Ferrimagnetism and Antiferromagnetism

[15] In the case of ferrimagnets and antiferromagnets, the situation is more complicated due to the existence of two magnetic sublattices and corresponding exchange interactions within the two sublattices as well as between them. For the following, we used the approach described in the handbooks of *Krupička* [1969, 1973].

[16] Let us assume a simple case with two sublattices A and B, with the corresponding magnetizations  $M_a$  and  $M_b$ , respectively, and each sublattice contains ions of one type only. According to the molecular field approximation, three

different types of interactions are present, which can be denoted as A-A, A-B and B-B. Considering generalized molecular (exchange) fields, acting on ions A and B, expressed as  $\mathbf{h}_a = v_{aa}\mathbf{M}_a + v_{ab}\mathbf{M}_b$ ,  $\mathbf{h}_b = v_{ab}\mathbf{M}_a + v_{bb}\mathbf{M}_b$  (the coefficients  $v_{aa}$ ,  $v_{ab}$  and  $v_{bb}$  can be positive or negative, reflecting the nature of the exchange interactions), and putting  $|v_{ab}| = v$ ,  $v_{aa} = \alpha v$ ,  $v_{bb} = \beta v$  (in order to distinguish between the ferromagnetic interactions, with positive  $v_{ab}$ , and ferrimagnetic (antiferromagnetic) case, with negative  $v_{ab}$ ), one can arrive at the resulting magnetization is then given as

$$\begin{aligned} \mathbf{M} &= \mathbf{M}_a + \mathbf{M}_b \\ |\mathbf{M}_a| &= M_{a0} B_{Sa} \left( \frac{g_a S_a \mu_B |\mathbf{H} + \mathbf{h}_a|}{kT} \right), \\ |\mathbf{M}_b| &= M_{b0} B_{Sb} \left( \frac{g_b S_b \mu_B |\mathbf{H} + \mathbf{h}_b|}{kT} \right). \end{aligned} \quad (3)$$

[17] Like in ferromagnets, also in ferrimagnets spontaneous net magnetization vanishes at the Curie temperature. At higher temperatures, due to higher entropy and lower free energy, disordered assembly of atomic magnetic moments is preferred, and ferrimagnets become paramagnetic. Exchange interactions between individual atoms are present also in the paramagnetic temperature region, but are not sufficient to keep spontaneous alignment of magnetic moments. However, they affect the magnitude of induced magnetization and its temperature dependence. In other words, the induced magnetization does not vanish completely at  $T_C$ . Since for  $T > T_C$  magnetization within the sublattices is not spontaneous, but is caused by the inducing effect of the applied magnetic field  $H$ , the corresponding sublattice magnetizations  $M_a$  and  $M_b$  will be much smaller than for  $T < T_C$ . Accordingly, the molecular (exchange) fields  $\mathbf{h}_a$  and  $\mathbf{h}_b$  will be small as well, and arguments of the Brillouin functions in equation (3) will be  $\ll 1$ . Corresponding simplification of the cotangents in the Brillouin function by power series and neglecting members of higher orders, one will arrive at system of two linear equation (in scalar form, components in the direction of the applied field  $H$ )

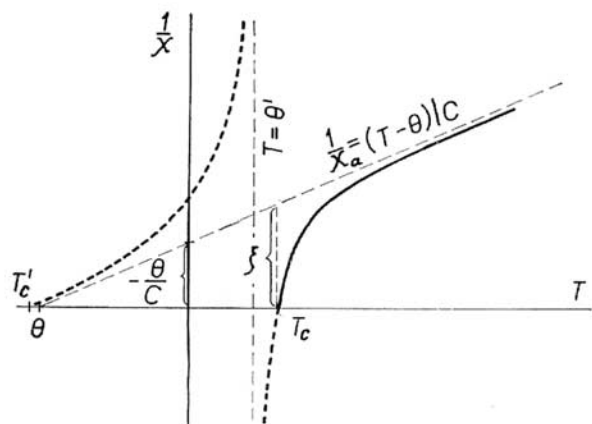
$$\left( \frac{T}{C_a} - v\alpha \right) M_a - \eta v M_b = H, \quad -\eta v M_a + \left( \frac{T}{C_b} - v\beta \right) M_b = H. \quad (4)$$

[18] Finally, applying  $M = M_a + M_b$  and some more mathematics, we get inverse magnetic susceptibility (for  $T > T_C$ )

$$\frac{1}{\chi} = \frac{T^2 - v(C_a\alpha + C_b\beta)T + C_a C_b v^2 (\alpha\beta - 1)}{(C_a + C_b) \left\{ T + \left[ \frac{C_a C_b}{(C_a + C_b)} \right] v(2\eta - \alpha - \beta) \right\}}, \quad (5)$$

which corresponds to hyperbolic dependence of  $1/\chi$  on temperature  $T$ . This function can be expressed in more simple form as follows:

$$\frac{1}{\chi} = \frac{T - \Theta}{C} - \frac{\zeta}{T - \Theta'}, \quad (6)$$



**Figure 2.** Temperature dependence of magnetic susceptibility for ferrimagnets, with symbols according to equation (6). After *Krupička* [1969] (copyright Academia Prague).

where meaning of the symbols used in equation (6) is obvious from schematic depiction in Figure 2. Note that the parameter  $\theta$ , called paramagnetic Curie temperature, may be negative on the absolute temperature axis, and thus has no actual physical meaning. However, it can serve for distinguishing between paramagnets (ideally  $\theta = 0$ ), ferromagnets and ferrimagnets ( $\theta > 0$ ) and antiferromagnets ( $\theta < 0$ ).

[19] This particular behavior is independent of the character of interactions between the sublattices (positive, fer-

romagnetic with  $v_{ab} > 0$  and  $\eta = +1$ ; or negative, antiferromagnetic with  $v_{ab} < 0$  and  $\eta = -1$ ) and is direct consequence of the existence of nonequivalent sublattices and different corresponding molecular (exchange) fields. If expressions of equation (4) are modified in order to get  $h_a$  and  $h_b$  of equal magnitude, the expression (6) will be reduced to simple Curie-Weiss linear equation for  $1/\chi$ , typical for ferromagnets and antiferromagnets. Nonlinear, hyperbolic shape of temperature dependence of inverse susceptibility above  $T_C$  is a typical feature for ferrimagnets.

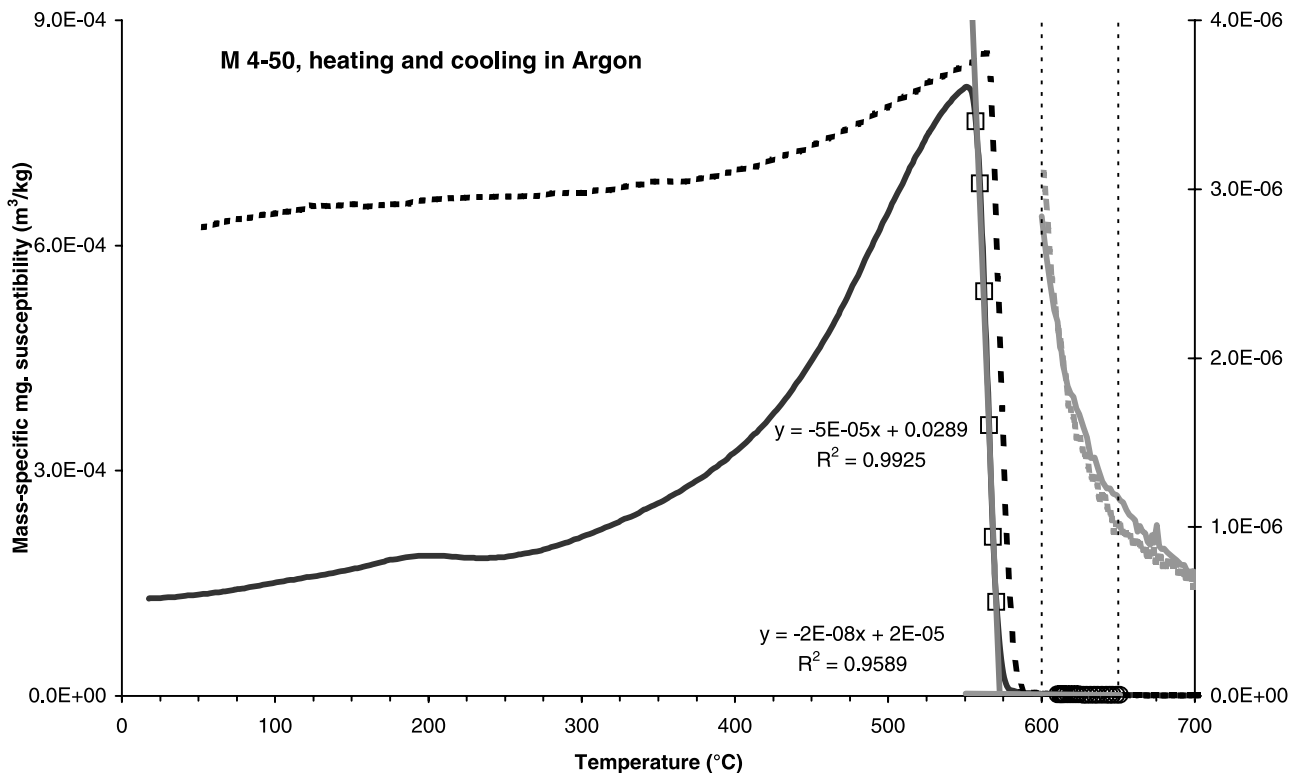
[20] Curie temperature  $T_C$  can be derived as solution of equation (6) for  $1/\chi = 0$ :

$$T_C = \frac{1}{2}v \left\{ C_a\alpha + C_b\beta + \sqrt{(C_a\alpha - C_b\beta)^2 + 4C_aC_b} \right\}. \quad (7)$$

[21] For temperatures well above  $T_C$ , further decrease of  $M_a$  and  $M_b$  will reduce the corresponding exchange fields  $h_a$  and  $h_b$  so that these will be not sufficient to keep antiparallel orientation of spin moments. This will result in disordered, paramagnetic configuration in the applied low field, and inverse susceptibility will be now controlled by linear Curie-Weiss law.

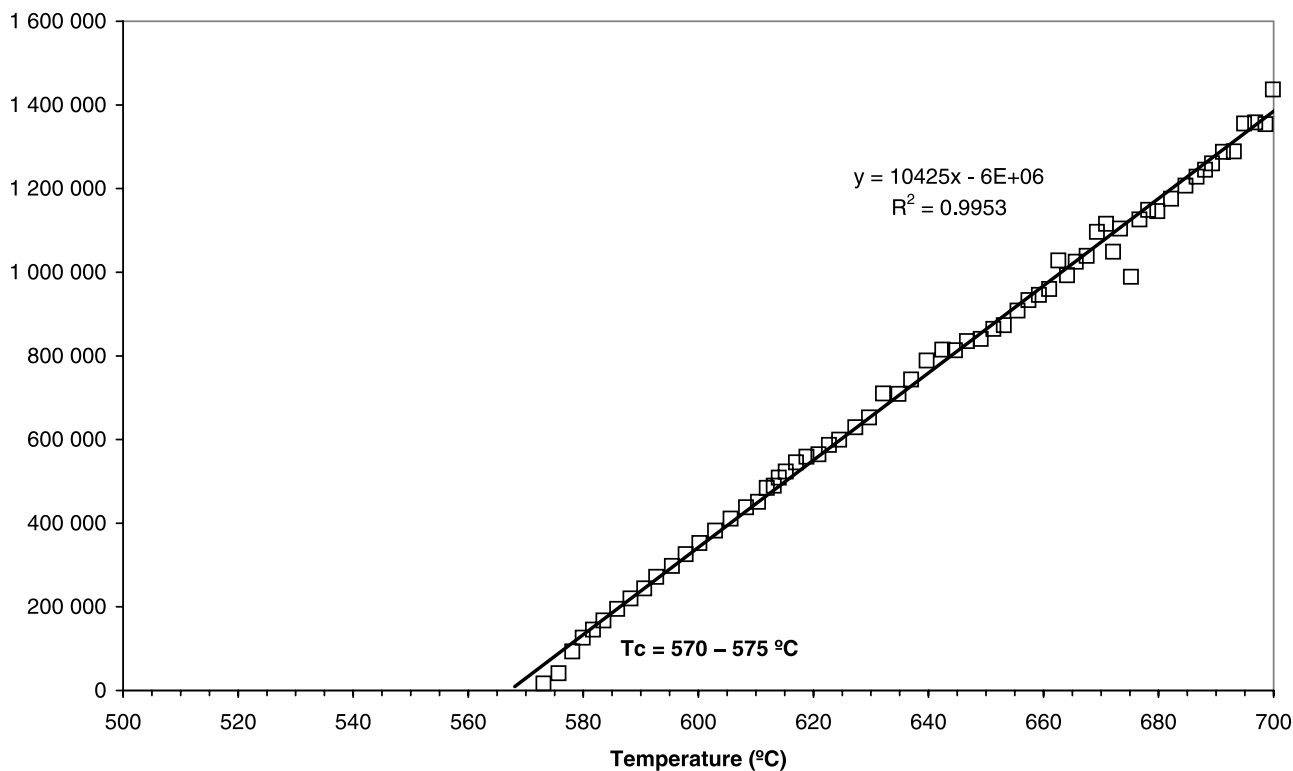
### 3. Experimental Examples

[22] In this section, we intend to show some experimental data, demonstrating possible errors resulting from the application of the two-tangent method of *Grommé et al.* [1969] to temperature dependence of magnetic susceptibility,



**Figure 3.** Temperature dependence of magnetic susceptibility, measured in Argon, for pure magnetite sample [*Petrovský et al.*, 2000]. Solid line, heating; dashed line, cooling. Right-hand axis is related to the rescaled section above 600°C.





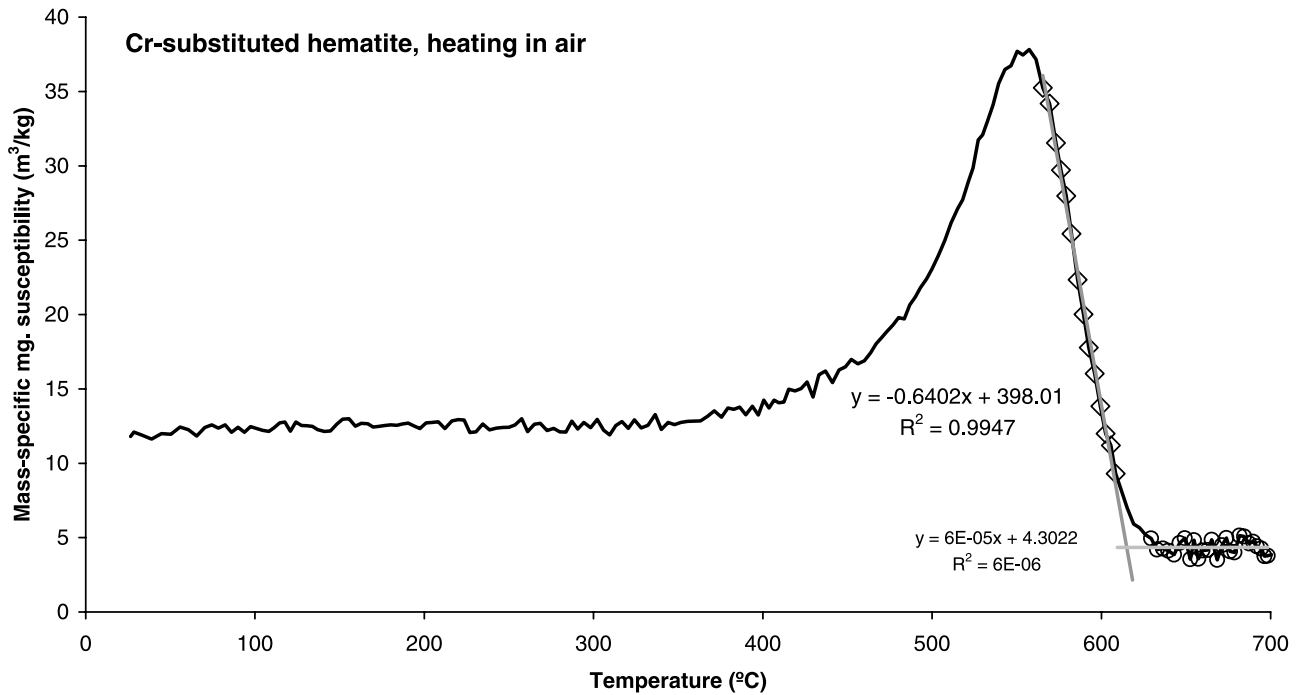
**Figure 4.** Temperature dependence of inverse susceptibility in the high-temperature region during heating of the sample shown in Figure 3. Curie-Weiss linear law is obeyed with more than 99% reliability, departure from linearity can be observed only within some 5°C above the intersection of data with the temperature axis (between 570°C and 575°C).

measured using KLY3-S kappabridge (Agico, Brno, Czech Republic, with a thermocouple placed less than 1 mm above the sample, intermediate heating rate was used, and the accuracy of temperature measurement is  $\pm 3\%$ ).

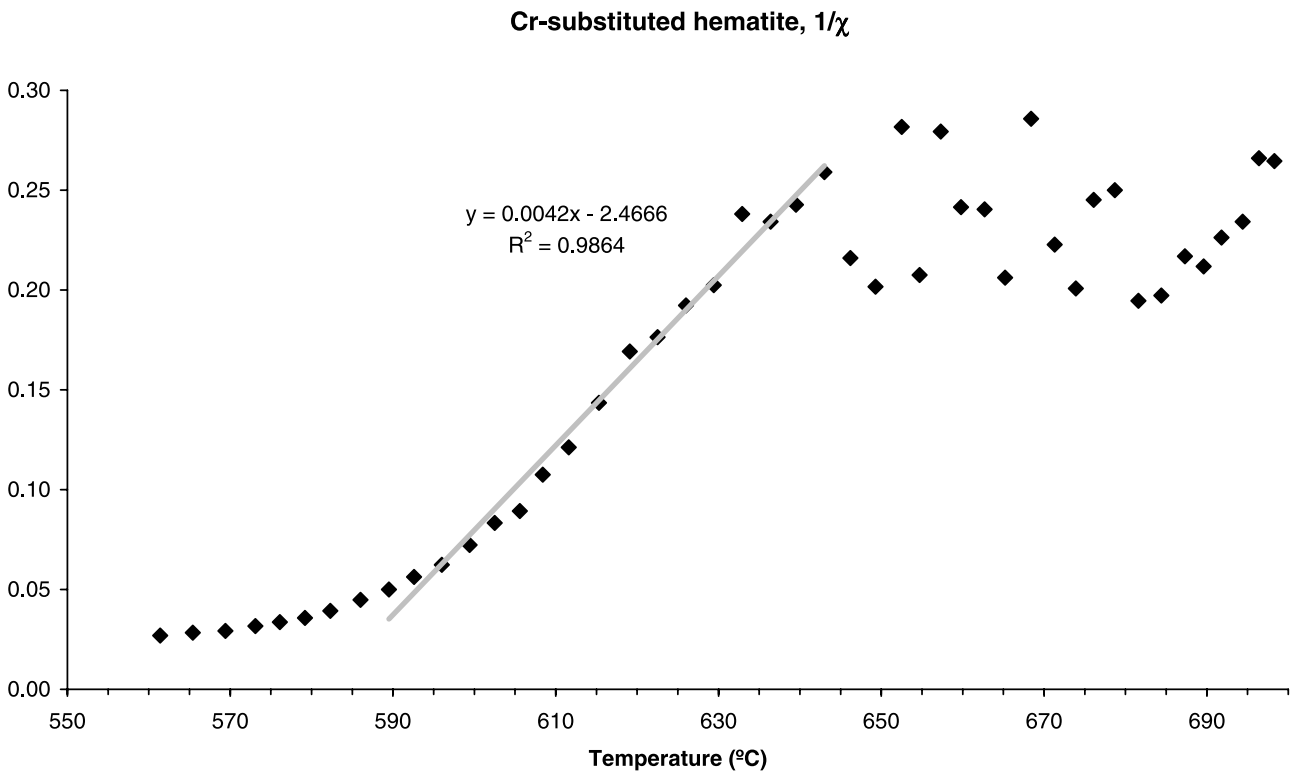
[23] In the case of well defined, synthetic minerals, such as pure magnetite measured in Argon, a sharp Hopkinson peak, followed by a steep decay can be observed on temperature dependence of magnetic susceptibility. Figure 3 depicts such a curve, measured on sample M4-50, studied and described previously by *Petrovský et al.* [2000]. It is obvious from the rescaled high-temperature section, that hematite is not present. If the two-tangent method of *Grommé et al.* [1969] is used, we arrived at a temperature of 573°C. Inverse susceptibility (Figure 4) intersects the temperature axis between 570 and 575°C, while the linear fit to inverse susceptibility data intersects the temperature axis at 567°C. The hyperbolic deviation from linearity can be observed only over some 5°C, otherwise the inverse susceptibility obeys the linear Curie-Weiss paramagnetic law with more than 99% reliability. In this specific case, the deviation from linearity is very small, but it can be also of some tens of degrees [e.g., *Néel*, 1970]. In case of synthetic hematite [*Petrovský et al.*, 2000], the two tangent method yields a transition temperature of 677°C, while inverse susceptibility shows linearity (with  $R^2$  of 0.94) at temperatures between 660°C and 668°C. At higher temperatures, inverse susceptibility is too noisy and cannot be interpreted. In these specific cases, when a sharp Hopkinson peak is obvious, followed by steep decay in susceptibility, difference between the two results is small. However, also in such

case, the two-tangent method yields values that are in a temperature range, which, according to the test of inverse susceptibility, is already dominated by paramagnetic behavior above the Curie temperature.

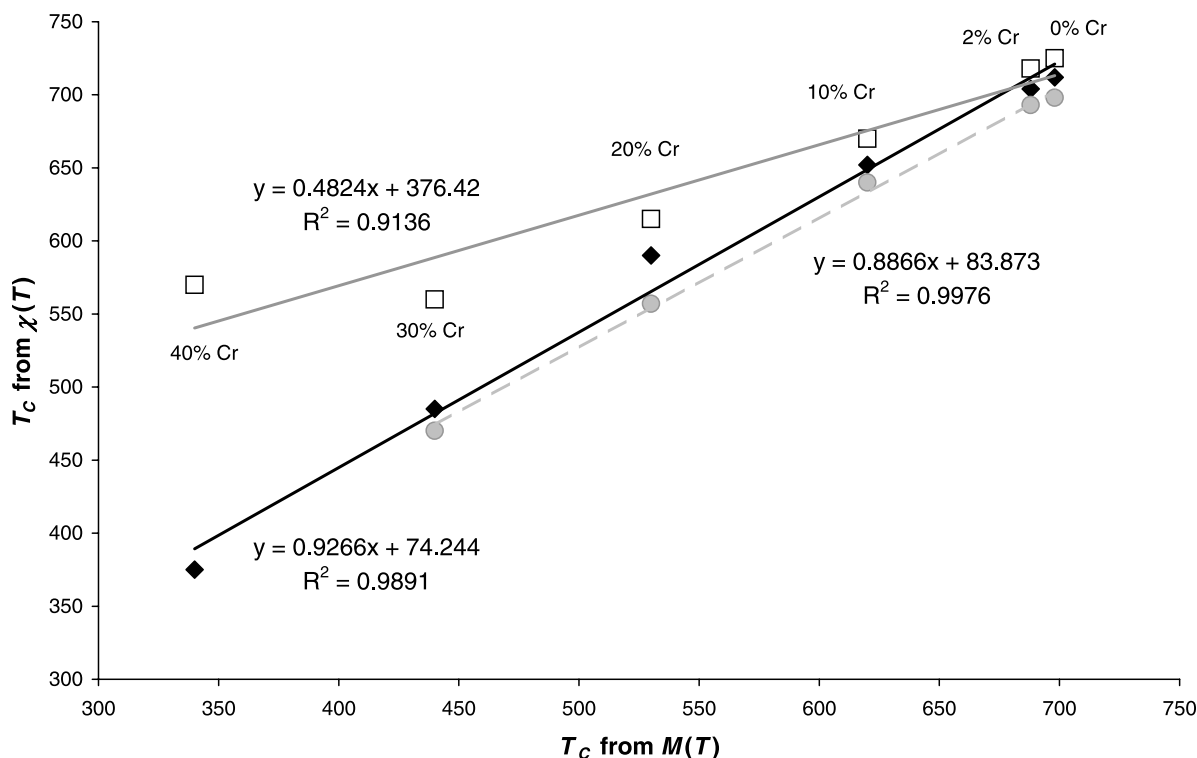
[24] Somewhat different is the situation in samples which do not show a sharp Hopkinson peak. For the purpose of this study, we used Cr-substituted synthetic hematite, with Curie point depending upon the degree of substitution [*Grygar et al.*, 2003]. (*Grygar et al.* [2003] use the term Néel temperature and refer to this material as to antiferromagnetic. However, the intersection of linear fit to inverse susceptibility with the temperature axis is not negative, as it should be for antiferromagnets, but positive, suggesting that the magnetically ordered phase is ferrimagnet. This issue requires more detailed study. For the purpose of this paper, we use more general term Curie point.) In this case, susceptibility decays gradually after a wide maximum. Figure 5 shows an example of temperature dependence of magnetic susceptibility upon heating of Cr-substituted hematite, with 20% substitution. The two-tangent method, despite very noisy data in the uppermost temperature range, yields Curie point of 615°C. However, inverse susceptibility (Figure 6) shows linear behavior (with almost 99% reliability) over temperature range from 590°C to 640°C. Therefore we have to admit that susceptibility in this temperature range is dominated by paramagnetic behavior of a phase, which already passed its transition temperature. If the transect of the linear fit with the temperature axis is considered, than the Curie point would be 581°C. This means that this temperature, determined using two-tangent



**Figure 5.** Temperature dependence of magnetic susceptibility during heating of Cr-substituted hematite, 20% of substitution [Grygar *et al.*, 2003]. The two-tangent method yields intersection at 615°C.



**Figure 6.** Temperature dependence of inverse susceptibility in the high-temperature region during heating of the sample shown in Figure 5. Curie-Weiss linear law is obeyed above 590°C with almost 99% reliability; departure from linearity can be observed below this temperature. Extrapolation of the linear fit yields the intersection with the temperature axis at 581°C.



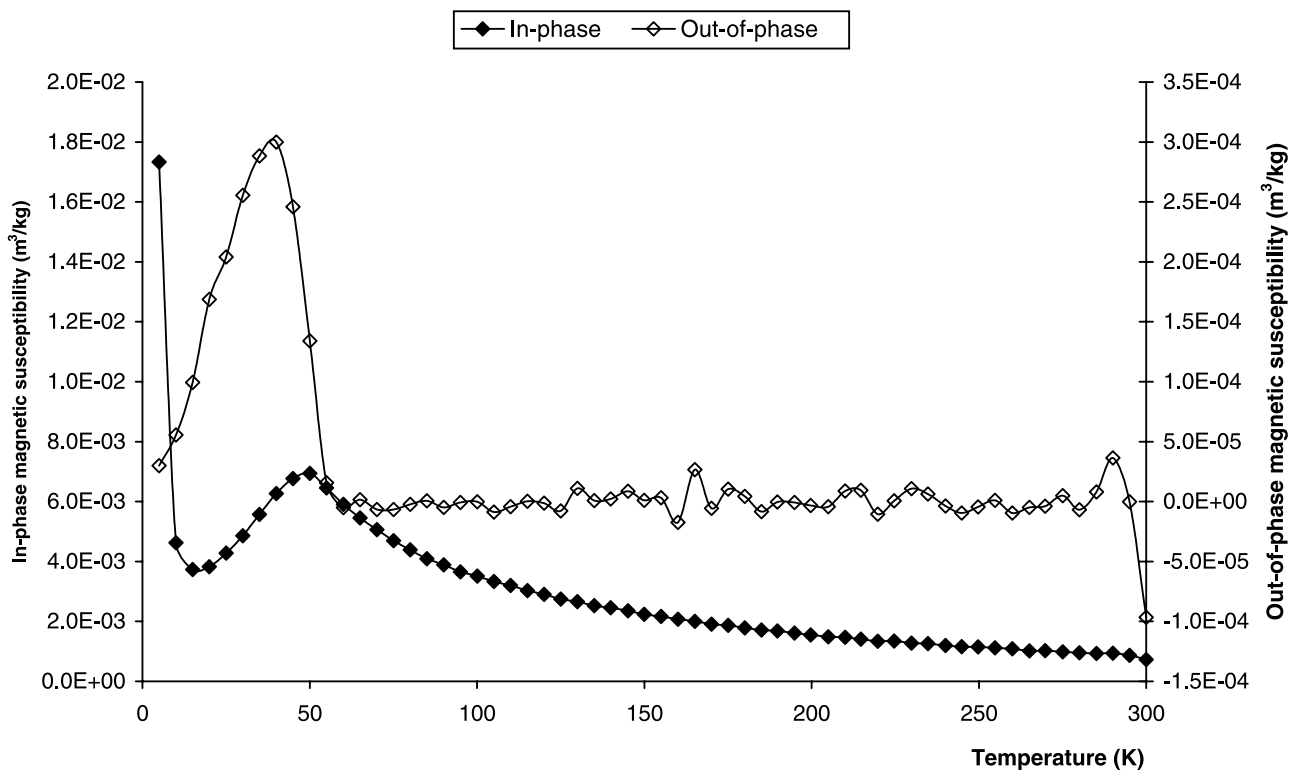
**Figure 7.** Approximation of Curie points of Cr-substituted hematite [Grygar *et al.*, 2003], determined from temperature dependence of magnetic susceptibility ( $y$  axis) using the two-tangent method (open squares, gray fit line), using the paramagnetic test of inverse susceptibility (diamonds, black fit line), and as temperature of the susceptibility peak (gray circles, dashed gray fit line, peak for the sample with 40% Cr substitution is not pronounced), with reference values determined using the two-tangent method from temperature dependence of induced magnetization ( $x$  axis).

method of Grommé *et al.* [1969], is overestimated by at least 25°C to 34°C. Such an error cannot be neglected. However, we think that 590°C is the best approximation of the Curie point, because this is the onset of temperature interval where the Curie-Weiss law is obeyed.

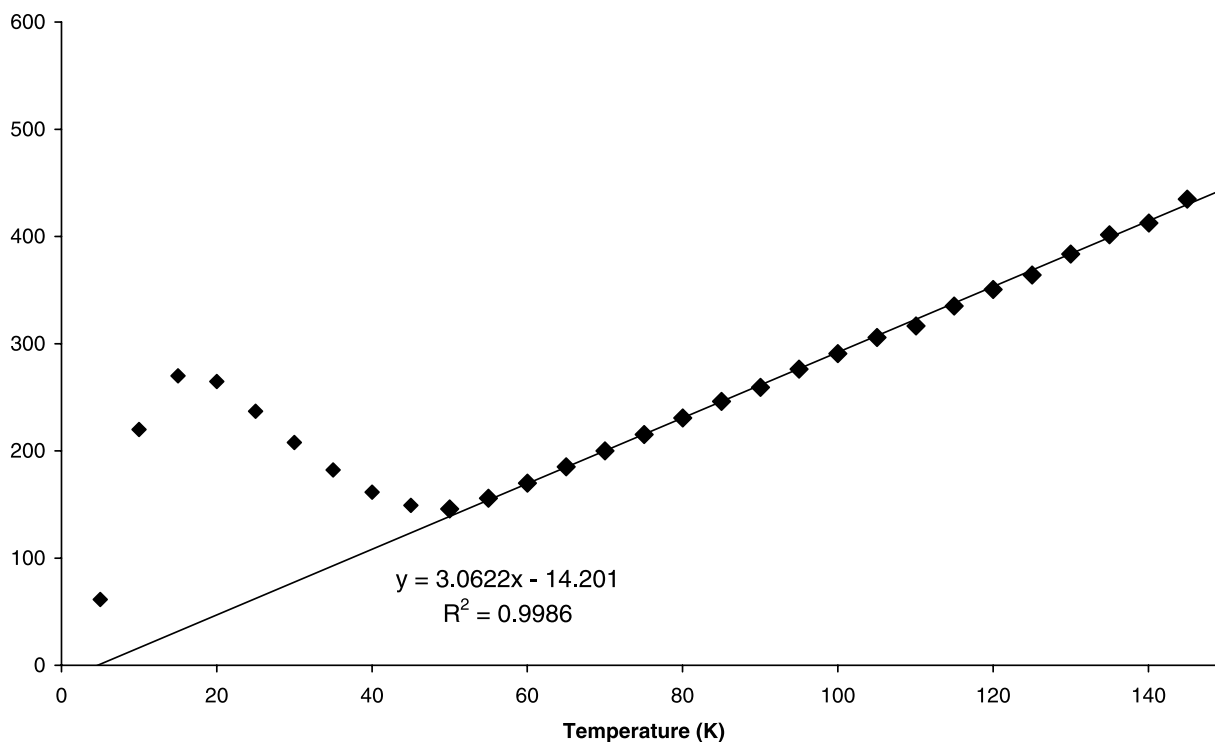
[25] In order to support our interpretation, we have compared the Curie points for a set of Cr-substituted hematite samples, determined using the two-tangent method from temperature dependence of magnetization [Grygar *et al.*, 2003], measured using Curie balance at Fort Foofdijk laboratory in Utrecht [Mullender *et al.*, 1993], with those obtained from temperature dependence of magnetic susceptibility using both the two-tangent method and paramagnetic test of inverse susceptibility. This comparison is shown in Figure 7, with the Curie points determined using the two-tangent method from magnetization curves ( $x$  axis) considered as “the correct values.” Obviously, the two-tangent method applied to susceptibility curves (empty squares, gray fit line) yields erroneous values, overestimating the correct values by 2% to more than 50%. Contrary to that, the transition temperatures estimated from paramagnetic behavior of inverse susceptibility (solid diamonds, black fit line) are much closer to the correct values, the maximum error being 12% at the lower limit of the considered temperature range. In this case of inverse susceptibility, the error is mostly due to two facts: deviation from linearity at temperatures close to the transition temperature, and wide

maximum on the susceptibility curve, followed by gradual decay over a large temperature range.

[26] Last, but not least, we would like to draw the reader’s attention to another method capable to determine the magnetic transition temperature, based on the measurements of the temperature dependence of AC magnetic susceptibility. In this case, the out-of-phase component of the complex magnetic susceptibility is used. Since this parameter reflects the area of the minor hysteresis loop, produced by the applied alternating magnetic field, it vanishes at the magnetic transition temperature. Unfortunately, to the best of our knowledge, there is no commercially available instrument in rock magnetic laboratories, enabling measurements of the out-of-phase susceptibility at high temperatures. However, at low temperatures, for instance, Quantum Design MPMS can be used. One such example is shown in Figure 8, depicting temperature dependence of in-phase and out-of-phase susceptibility of amorphous  $\text{Fe}_2\text{O}_3$ , prepared by thermal decomposition of Prussian Blue [Zbořil *et al.*, 2004]. It is obvious that the two-tangent method cannot be applied here at all, because the curve does not show suitable linear sections on its descending section, which is hyperbolic after the maximum at 50 K. The minor hysteresis loop reduces to a straight line at 55 K, as evident from the decay of out-of-phase susceptibility to zero. This temperature agrees well with 50 K, at which the inverse value of the in-phase susceptibility starts to obey the Curie-Weiss linear paramagnetic law (with  $R^2 = 0.9986$ , Figure 9). At higher



**Figure 8.** Temperature dependence of in-phase and out-of-phase magnetic susceptibility of amorphous  $Fe_2O_3$  [Zbořil *et al.*, 2004]. Decrease of the latter parameter to zero at 55 K reflects that the onset of paramagnetic behavior (absence of the minor hysteresis loop area) corresponds well with the onset of hyperbolic decay on the in-phase susceptibility.



**Figure 9.** Inverse in-phase susceptibility of the sample shown in Figure 8. Linear fit (applied to data spanning temperature range from 55 K to 150 K) intersects the temperature axis close to absolute zero. This indicates that the transition temperature is actually blocking temperature of SP particles.



temperatures (above 150 K), the values slightly deviate from linearity, however, reliability of the linear fit over the temperature range from 50 K to room temperature is 98.3%. The fact that the linear fit of inverse susceptibility intersects the temperature axis close to absolute zero indicates, that the transition at 50 K represents rather blocking temperature of SP particles. Like in case of pure paramagnets, inverse susceptibility of the substance above this point is proportional to temperature.

#### 4. Conclusions

[27] In this paper, we wanted to highlight the nature of magnetically ordered systems, in particular from the point of view of approximate experimental determination of the Curie point from thermomagnetic curves. In the case of temperature dependence of induced magnetization, the approximation by two-tangent method of *Grommé et al.* [1969] is fully justified by physics, and it approximates fairly well the temperature at which spontaneous net magnetization vanishes, when approaching  $T_C$  ( $T_N$ ) from temperatures just below it.

[28] However, the situation is substantially different in case of temperature dependence of magnetic susceptibility. According to physics, susceptibility for  $T \rightarrow T_C$  and  $T < T_C$  increases to infinity, and we have to use analytical formulas developed for susceptibility behavior above the Curie point. Here, due to the geometry of the susceptibility curve, the two-tangent method will always yield temperature above the inflection point, which is higher than the temperature at which the substance starts to obey the paramagnetic Curie-Weiss law. The resulting error in  $T_C$  (or  $T_N$ ) can be on the order of several degrees to several tens of degrees. Therefore, in the case of temperature dependence of magnetic susceptibility, application of the two-tangent method is not justified.

[29] In case of antiferromagnets, linear fit to inverse susceptibility intersects the absolute temperature axis at negative value. In case of ferrimagnets, inverse susceptibility is described by hyperbolic function, departing from the Curie-Weiss linear law in temperatures higher than, but close to  $T_C$ . The question is, how big is this temperature interval with pronounced hyperbolic departure from linear line and how large will be the resulting error in estimating  $T_C$  using the Curie-Weiss law.

[30] In the case of synthetic magnetite and hematite, with sharp Hopkinson peak, the difference between transition temperatures determined using the two-tangent method and Curie-Weiss paramagnetic law is in the order of some few degrees. In the case of samples with wide susceptibility maximum and gradual decrease, reflecting e.g., wide distribution of grain sizes, or in the case of substituted hematite, application of the two-tangent method to susceptibility curves overestimates the transition temperature by several tens of degrees. In such cases, inverse magnetic susceptibility should be used, and linear section, obeying the Curie-Weiss law, can serve as verification of dominant paramagnetic behavior.

[31] One has to keep in mind that thermomagnetic measurements are associated with several secondary phenomena, such as thermally induced changes in sample composition, superposition of contributions in mineral mixtures, etc.

These effects definitely obstruct the analysis of thermomagnetic curves (although the superposition in mixtures is more easy to be resolved in the magnetization curves), and in many cases it is virtually impossible to determine the Curie point(s) of such samples. However, instead of determining exact value of the Curie point, in many cases we can at least assess the onset of temperature range, at which paramagnetic behavior of substance, which passed its magnetic transition temperature, dominates.

[32] To conclude, if linear behavior of inverse susceptibility is found with high enough reliability over sufficiently large temperature interval, then magnetic susceptibility in this temperature range is controlled by paramagnetic behavior of the phase, which already passed through its Curie point. If sharp Hopkinson peak is observed, than the temperature of the peak can be used as the Curie point. If wide maximum is observed, instead, then the transition from magnetically ordered to paramagnetic state is realized smoothly over large temperature range. In such a case, inflection point on the decreasing branch of susceptibility curve indicates temperature, at which paramagnetic behavior starts to dominate. If linear fit is evaluated, than reliability of such assessment can be judged from the goodness of the fit.

[33] Hence, although it is practically impossible to determine the Curie point precisely, using physics we can approximate this temperature from the behavior above it. If the two-tangent method, developed for temperature dependence of magnetization (and fully justified for this parameter), is applied to susceptibility curves, the Curie point will be always overestimated, and the error may be even of several tens of degrees.

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