

## **QUANTITATIVE PHASE ANALYSIS FROM PERMEABILITY VERSUS TEMPERATURE CURVES**

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The expressions for quantitative phase analysis from permeability versus temperature curves are discussed, and the results are illustrated by the determination of magnetic  $\text{Co}_2\text{Y}$  remnants ( $2\text{CoO} \cdot 2\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ ) in  $\text{Co}_2\text{Z}$  ( $2\text{CoO} \cdot 3\text{BaO} \cdot 12\text{Fe}_2\text{O}_3$ ) samples. The method is well suited for the determination of small inclusions of a magnetic phase in a given magnetic material, in a range where X-ray methods become useless as a rule.

Qualitative phase analysis, in polycrystalline materials containing several magnetic phases can usually readily be performed by recording the variation with temperature of some magnetic parameter, such as the magnetization (thermomagnetic analysis, TMA) or the permeability (permeability vs. temperature curves) [1, 2]. In these cases, the information is obtained from the Curie temperature, an intrinsic parameter for each given phase, which does not depend on the presence of other phases in the material.

In quantitative analysis, several factors tend to make the use of magnetic methods difficult. The magnetization of a material depends on external factors such as the intensity of the externally applied magnetic field, and also on extrinsic parameters such as the porosity or the apparent density of the material and, in the case of the permeability, on the mean grain size. For these reasons, the quantitative phase analysis of magnetic samples is always carried out by X-ray diffraction methods, which are intrinsic in nature; however, in certain cases, the crystalline structures of the different magnetic phases are very similar, and special methods are needed to carry out the X-ray procedures, which become more involved and inaccurate [3]. In such cases, analysis from the magnetic curves may be very helpful, and it will be shown that it may provide a fast way to determine the amount of a given phase in an inhomogeneous material.

In the following, the expressions for quantitative phase analysis from permeability vs. temperature curves are discussed, and the results are applied to the

determination of magnetic  $\text{Co}_2\text{Y}$  ( $2\text{CoO} \cdot 2\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ ) remnants in  $\text{Co}_2\text{Z}$  ( $2\text{CoO} \cdot 3\text{BaO} \cdot 12\text{Fe}_2\text{O}_3$ ) samples. In this type of material, a mixture of phases is usually to be expected in the equilibrium state [4].

### Theory

The magnetization of a magnetic material exposed to an external magnetic field  $H$  may be written as

$$M = \frac{1}{V} \left| \sum \bar{u}_a \right| \quad (1)$$

where  $\bar{u}_a$  is the atomic magnetic dipole moment and  $V$  is a volume that is very small from a macroscopic point of view, but large enough to contain a statistically large number of atoms [5]. The direction of  $M$  is that of the applied field  $H$ .

Let us suppose a polycrystalline isotropic material which has grains of two different magnetic phases 1 and 2 in the volume unit, together with some empty spaces (pores), under the action of a magnetic field of low intensity  $H \rightarrow 0$  (Rayleigh region of the hysteresis loop). The total volume will be that occupied by the two phases, plus that occupied by the pores:  $V = V_1 + V_2 + V_p$  (Fig. 1).

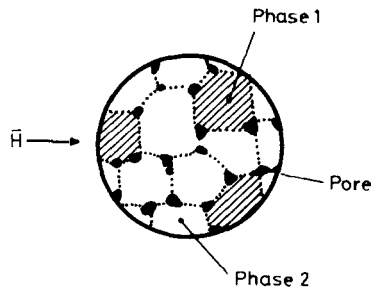


Fig. 1 Microscopic model of the magnetic material

According to this model, the magnetization is given by

$$M = \frac{\left| \sum \bar{u}_a \right|_1 + \left| \sum \bar{u}_a \right|_2}{V} \quad (2)$$

where  $\left| \sum \bar{u}_a \right|_1$  corresponds to phase 1, and the other term to phase 2. Both summations are taken over all possible grain orientations in relation to the direction

of the external applied field. Expression (2) may be written as:

$$M = \frac{1}{V}(M_1V_1 + M_2V_2) \quad (3)$$

where  $M_i$  is the magnetization of phase  $i$  in a material without pores. Dividing by the intensity of the applied magnetic field  $H$ , we obtain the initial magnetic susceptibility  $X(H \rightarrow 0)$ :

$$X = X_1 \frac{V_1}{V} + X_2 \frac{V_2}{V} \quad (4)$$

where  $X_i$  is the pore-free initial susceptibility of phase  $i$ .

If  $\rho_{c_i}$  is the crystallographic density of phase  $i$ , taken from X-ray diffraction data, then  $v_i = m_i/\rho_{c_i}$ , and likewise for phase 2. For the total volume,  $V = m/\rho$ , where  $m = m_1 + m_2$  and  $\rho$  is the apparent density of the sample. Substitution in (4) leads to

$$X = X_1 \frac{m_1\rho}{m\rho_{c_1}} + X_2 \frac{m_2\rho}{m\rho_{c_2}} \quad (5)$$

Let us consider a variation of the initial susceptibility with temperature according to Fig. 2, where  $T_{c_1}$  and  $T_{c_2}$  are the Curie temperatures of phases 1 and 2, respectively.

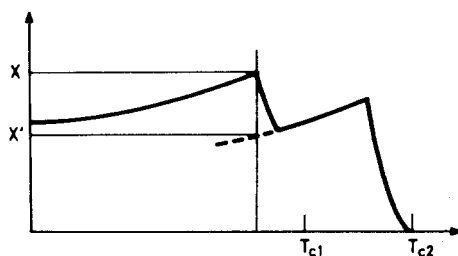


Fig. 2 Susceptibility vs. temperature curve

Equation (5) holds for  $T < T_{c_1}$ , while for  $T > T_{c_1}$  we have  $X_1 = 0$ , and

$$X' = X_2 \frac{m_2\rho}{m\rho_{c_2}} \quad (6)$$

Subtracting (6) from (5), we have

$$X - X' = X_1 \frac{m_1\rho}{m\rho_{c_1}} \quad (7)$$

The value of  $X_i$  at the Curie temperature for the "standard" sample of pure phase I may be obtained experimentally but, since the magnetic susceptibility is known to depend on the mean grain size in polycrystalline materials, the influence due to the differences in grain size between the standard and the unknown sample should be taken into account. As a first approximation, let us consider these differences to be negligibly small. This latter assumption is not a very stringent one, since a similar grain size must be expected in polycrystalline sintered samples of related materials when they are submitted to similar synthesis procedures.

The porosity of a single-phased material is usually defined as  $p = V_p/V$ , and it may easily be shown that

$$p = i - \frac{\rho}{\rho_c} \quad (8)$$

The connection between the susceptibility  $X$  in a porous material and that of the pore-free single-phased material may then be obtained from the expressions

$$X = \frac{\left| \sum \bar{u}_a \right|}{V_i + V_p}; \quad X' = \frac{\left| \sum \bar{u}_a \right|}{V_i}$$

where now  $V = V_i + V_p$ . It follows that  $X' = X/(1-p)$ , or

$$X' = \frac{\rho_c}{\rho} X \quad (9)$$

The substitution of (9) in (7), denoting the unknown mass fraction  $m_1/m$  as  $f_1$ , leads to

$$f_1 = \frac{(X - X')}{X_1} \cdot \frac{\rho_1}{\rho} \quad (10)$$

where  $\rho_1$  is the apparent density of the standard material, and  $\rho$  is that of the analyzed sample.

Expression (10) can easily be generalized to the case when there are more than two phases in the material. If there are  $N$  phases with  $T_{c_1} < T_{c_2} < \dots < T_{c_N}$ , then a similar summatory term must be added in (2) for each different phase, which leads to the addition of the terms  $M_3V_3, M_4V_4, \dots, M_NV_N$  between the brackets of (3). Following this reasoning, from (5) and (9) we arrive at

$$X = \sum_{i=1}^N X_i f_i \frac{\rho}{\rho_i} \quad (11)$$

where  $f_i = m_i/m$  and  $\sum f_i = 1$ .

Let us consider the sample at a temperature near  $T_{ck}$ . For  $T_{c(k-1)} < T < T_{ck}$ ,  $X_i = 0$  when  $i < k$ , and

$$X = \sum_{i=k}^N X_i f_i \frac{\rho}{\rho_i} \quad (12)$$

Now, for  $T > T_k$ ,  $X_k = 0$  too, and

$$X' = \sum_{i=k+1}^N X_i f_i \frac{\rho}{\rho_i} \quad (13)$$

Subtraction of (13) from (12) leads, after rearrangement of the terms, to an equation similar to (10):

$$f_k = \frac{(X - X')}{X_k} \cdot \frac{\rho_k}{\rho} \quad (14)$$

where  $X - X'$  is now the difference in susceptibility in the  $X$  vs.  $T$  plot at the temperature  $T_{ck}$ .  $X_k$  and  $\rho_k$  are the susceptibility and apparent density, respectively, of the standard pure sample of phase  $k$ .

In principle, if the difference  $X - X'$  is not too small, it may be measured with a high degree of accuracy, as can the mass  $m$  and the density of the sample. The relative error in  $f$  is then mainly that involved in the determination of  $X_i$  for the standard:

$$df/f - dX_i/X_i \quad (15)$$

## Experimental

Figure 3 shows the curve of initial relative permeability ( $u = i + X$ ) vs. temperature for a polycrystalline  $\text{Co}_2\text{Z}$  sample with 0.2 BaO in excess over the stoichiometric composition; this sample was obtained in our laboratory through the use of conventional ceramic techniques. The sample was sintered for 1 hour at

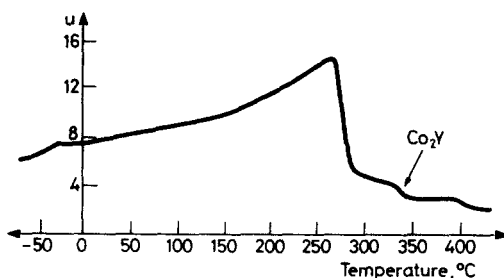


Fig. 3 Permeability vs. temperature curve for  $\text{Co}_2\text{Z}$  sample, with remnants of  $\text{Co}_2\text{Y}$

1250°. The equipment and the method used to draw the curve have been described elsewhere [2].

The steep variation of the permeability around 250° is caused by a change in the direction of easy magnetization, from the basal plane of the hexagonal cell to an axial direction, along the  $c$  axis [6]. The small variation around 400° indicates the Curie temperature of  $\text{Co}_2\text{Z}$ , while the abrupt variation of  $\mu$  between 330 and 350° is caused by  $\text{Co}_2\text{Y}$  remnants ( $T_c = 340^\circ$ ). By similar arguments to those referred to for the grain size in the previous section, let us consider  $p_i \approx p$ . For  $\text{Co}_2\text{Y}$  and  $\text{Co}_2\text{Z}$ , the crystallographic densities are 5.29 and 5.33 g/cm<sup>3</sup>, respectively; (10) may then be substituted as a function of the porosity using (8), leading, in this approximation, to

$$f_1 = \frac{X - X'}{X_1} \quad (16)$$

From Fig. 3, it is found that  $X - X' = 1$ . The value of  $X_Y$  ( $X_i$  in (1) at a temperature just below  $T_c$  ( $X_Y = 20$ ) was taken from the literature [3], with an assumed error, due to the unknown differences in porosity and grain size, of 20%. This value is the maximum allowed variation of the permeability reported for different types of commercial ferrites [7, 8], and is well above the range of variation usually obtained in laboratory work under more controlled conditions. The substitution of these values in (16) and (15) leads to

$$f_i = 5 \pm 1\%$$

### Discussion and conclusions

From the results obtained in the previous section, it is clear that the method is well suited for the determination of small inclusions of a magnetic phase in a given magnetic material, in a range where X-ray methods usually become useless. In the case analyzed, an inaccuracy of 20% in the permeability of the standard leads to an error of only 1% in the determination of the amount of inclusions. For larger amounts, an impairment of the accuracy is expected, since, from (15), it is seen that the absolute error of the mass fraction  $df$  is proportional to  $f$ .

Disadvantages of the method are that (a) it must be applied exclusively to sintered samples conformed in closed shapes; i.e. it can not be applied to powdered samples, since the initial permeability must be measured in closed cores; (b) in order to improve the accuracy, it is necessary to collect data and make corrections for differences in grain size, but this can be done only at the cost of a great deal of additional experimental work [9].

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**Zusammenfassung** — Zwecks quantitativer Phasenuntersuchungen wird die Auswertung von Permeabilitäts-Temperatur Diagrammen näher beschrieben und die Ergebnisse mit der Bestimmung von magnetischen  $\text{Co}_2\text{Y}$  Resten ( $2\text{CoO}\cdot 2\text{BaO}\cdot 6\text{Fe}_2\text{O}_3$ ) in  $\text{Co}_2\text{Z}$  ( $2\text{CoO}\cdot 3\text{BaO}\cdot 12\text{Fe}_2\text{O}_3$ ) Proben illustriert. Diese Methode ist zur Bestimmung von geringen, mittels röntgenographischen Verfahren nicht feststellbaren magnetischen Phaseneinschlüssen in einem bestimmten magnetischen Material sehr geeignet.

**Резюме** — Обсуждены выражения для количественного фазового анализа, установленные из кривых температурной зависимости проницаемости и которые представлены на примере определения магнитных сплавов  $\text{Co}_2\text{Y}$  ( $2\text{CoO}\cdot 2\text{BaO}\cdot 6\text{Fe}_2\text{O}_3$ ) в образцах  $\text{Co}_2\text{Z}$  ( $2\text{CoO}\cdot 3\text{BaO}\cdot 12\text{Fe}_2\text{O}_3$ ). Метод пригоден для определения небольших включений магнитной фазы в данном магнитном материале в области, где, как правило, рентгеноструктурные методы являются бесполезными.