A sensitive method for the determination of the Curie temperature in ferrimagnets

The magnetic transition temperature (Curie point for ferromagnets and ferrimagnets, Néel point for antiferromagnets), from a long-range ordered to a disordered paramagnetic phase is a very important property. A certain number of techniques for its experimental measurement have been proposed. They are generally based on the changes of a physical property during the passage through the transition temperature.

The occurrence of spontaneous demagnetization has often been used for the determination of the Curie point. The magnetization decreases and vanishes, in principle, at the Curie temperature, T_c. However, the paramagnetic contribution is generally difficult to separate from the low magnetization values near T_c. This leads to some uncertainty in the reported temperature. An example of this "paramagnetic tail" can be found in [1].

Resistivity [2] and dilatation [3] measurements have also been used to measure the transition temperature. Generally, the change in the physical property during the transition is small and it can only be detected by means of a rather sensitive device.

The magnetic contribution to the specific heat can also be used to detect the transition temperature. This contribution increases as the temperature approaches the transition and vanishes when the Curie point is reached. However, specific heat measurements are generally difficult and slow to perform. A technique that is simple and fast is Differential Scanning Calorimetry (DSC), but so far, there are but a few reported results on ferro- and ferrimagnetic materials.

In this paper, a very sensitive method for the measurement of the Curie point in ferrimagnetic materials is presented. It is based on the continuous measurement of the initial magnetic permeability as a function of the temperature. This method is compared with Differential Scanning Calorimetry results obtained for Ni–Zn ferrites.

Ferrite samples of the composition $Ni_{0.36}Zn_{0.64}Fe_2O_4$ were prepared by the normal ceramic method from the stoichiometric mixture of the corresponding oxides. A relatively low sintering temperature (1145° C) was used in order to prevent zinc volatilization [4]. The sintering time was varied from 14 to 144 h to obtain a wide range of chemical homogeneity. During sintering, an oxidant atmosphere (O_2 100%, 1 atm) was maintained to avoid any reduction [5] of the ferric ions. The samples were toroidally shaped to simplify the measurement of the magnetic permeability.

The magnetic permiability was measured at low fields (i.e. in the reversible magnetization range) at temperatures from room temperature up to the transition temperature in an apparatus especially adapted [6] for these materials. In this work, the sample was used as the core of a small transformer. If the frequency and the amplitude of the primary coil are kept constant, it can be shown that the voltage in the secondary coil is proportional to the initial magnetic permeability. In the case of ferrites, magnetic isolators, a relatively high frequency can be used (1 kHz) without significant conductivity losses. The secondary signal was amplified, rectified and sent to the Y-axis of a plotter. A thermocouple in contact with the sample provided the X-signal and a continuous recording was obtained by heating or cooling the sample holder.

A DSC 1B "Perkin Elmer" Differential Scanning Calorimeter was used for the DSC measurements. A preliminary study [7] showed that the best conditions to detect the transition temerature were a heating rate of 20° min^{-1} and a small chip (50 mg) of ferrite.

Each sample was used to produce a pair of curves: first the initial magnetic permiability curve, and then (using a small chip from the sample of about 50 mg) the DSC enthalpy curve. Samples having the longest sintering time (144 h, Sample 1) and the shortest (14 h, Sample 2) were chosen. The initial permeability and the enthalpy, both as a function of the temperature, are shown for Sample 1 in Fig. 1. Good agreement is found for the transition temperature indicated by the two curves, i.e. the drop of the permeability from 4000 to 1 and the peak of the enthalpy curve. This temperature, 416 K, agrees with the one reported in [8] for this composition. The results for Sample 2 are presented in Fig. 2. The per-

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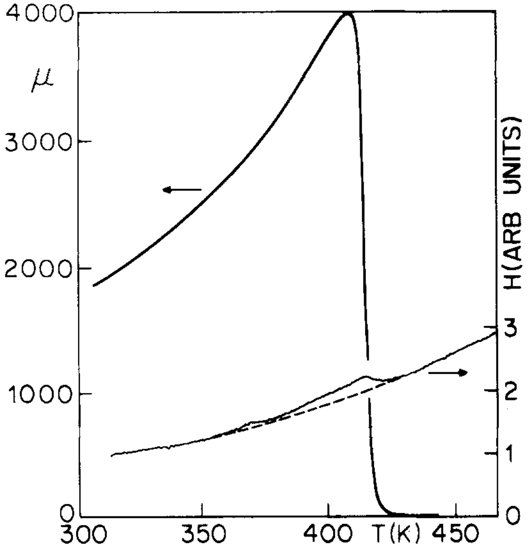

Figure 1 The initial magnetic permeability and the enthalpy both as a function of temperature for Sample 1. The almost vertical drop of the permeability curve is characteristic of an homogeneous sample.

meability curve exhibits a drop extending from 395 to 445 K, while the enthalpy shows a less defined peak.

The determination of the Curie temperature from the permeability curve is obviously easier as far as this property passes from its maximum to 1, while the transition temperature represents only a small deviation in the DSC curve. This is probably due to the fact that the magnetic transition is a 2nd order thermodynamic transition [9] and the enthalpy involved is generally lower than that for a 1st order transition. The DSC method, however, presents some advantages, because it is a rapid technique that needs only small quantities of sample with no limitations on shape. This method seems a good pre-characterization technique.

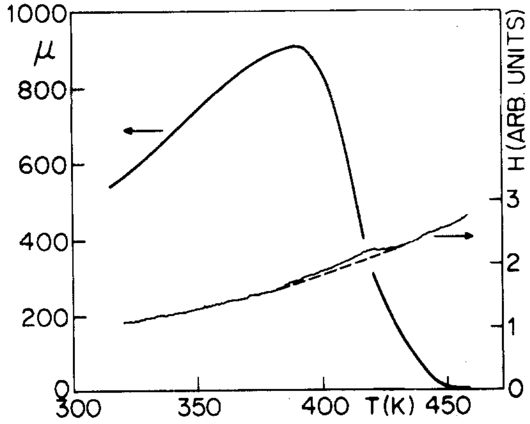

Figure 2 The permeability and the enthalpy curves for Sample 2. The chemical homogeneity is lower than for Sample 1 as shown by the permeability drop and the small enthalpy peak at the transition temperature.

The permeability method can lead to an evaluation of the chemical homogeneity of the sample, based for example, on the steepness of the drop at the Curie temperature. If this drop deviates from a vertical, this means (provided there are no thermal inhomogeneities in the sample) that the Curie point (and hence the composition) is not exactly the same for the whole sample. This is the case with Sample 2, where the chemical inhomogeneity can be attributed to the short sintering time.

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