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LOW-FREQUENCY SUSCEPTIBILITY OF SINGLE-DOMAIN NICKEL PARTICLES FROM 2 K UP TO THE CURIE POINT

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The magnetic susceptibility of small single-domain nickel particles chemisorbed on a silica carrier has been studied as a function of temperature in the range $1.7 < T < 700$ K. The mean particle size was obtained from the blocking temperature in good agreement with results deduced from magnetization measurements. A slightly sintered specimen shows the typical behaviour of bulk nickel. The remarkable thermostability of the small particles seems to be of considerable interest.

IN RECENT YEARS interest has been grown in the magnetic properties of small magnetic particles from the theoretical as well as from the experimental side [1–3]. Specimens containing very small particles generally display a broad particle size distribution, which hampers interpretation of the experimental results. Geus and co-workers developed methods to produce specimens containing nickel particles of rather narrow size distribution in the nanometer range. Contact of small metal particles brings about rapid sintering; to prevent contact the nickel particles have been applied onto a finely divided, non-magnetic support *viz.* silica [5, 6]. The method of preparation has been described elsewhere [7]. From the shape of the magnetization curves at different temperatures the distribution of particle radii r could be determined in the range $2 < r < 6$ nm in good agreement with electron microscopic observations [6].

In this note we report results from measurements of the low-frequency susceptibility of the same specimens in a temperature range from 1.7 up to 700 K. The aim of this work was twofold: (i) to confirm the results of [6] by an independent magnetic method, which allows to determine the particle size, and (ii) to investigate simultaneously the critical behaviour as well as magnetostatic coupling of the particles.

The measurements have been performed with a balanced mutual induction bridge in connection with a phase sensitive amplifier. The a.c. magnetic field was smaller than 0.01 A cm^{-1} at frequencies between 1 and 100 kHz. The signal obtained is related to the complex initial susceptibility $\tilde{\chi} = \chi' - i\chi''$. The temperature stability was better than ± 0.1 K, its absolute calibration ± 0.5 K at the lowest and ± 3 K at the highest temperature covered by our experiment.

Typical examples of χ–T-curves are shown in Fig. 1. Curves 1 and 2 are for two different single-domain specimens, curve 3 for a sintered and possibly multidomain material. The single-domain behaviour is characterized by a rather sharp maximum in χ' at the blocking temperatures T_b. At T_b the relaxation time of thermal activation becomes equal to the reciprocal frequency of the measuring field [4]. The sintered material (curve 3) shows the typical behaviour of bulk nickel with a broad Hopkinson-like maximum about 100 K below T_c (630 K).

One of the single-domain specimens (curve 2) exhibits a splitting of the blocking temperature which is in agreement with the findings of Hermans [6]. He observed for this specimen a bimodal size distribution with two well separated peaks. The inset of Fig. 1 shows the neighbourhood of the splitted peak of curve 2 in enlarged scale for two different frequencies. The shift in temperature with frequency is of the expected magnitude (cf. Table 1). The particle size distribution of specimens 1 and 2, as calculated from the (static) magnetized-vs-field strength plot are represented in Fig. 2. The bimodal particle size distribution of specimen 2 is clearly evident. Though it is difficult to determine particle size distributions of particles of the nanometer range correctly from electron micrographs, the micrographs in [6] exhibit the presence of larger nickel particles in specimen 2.

From the value of the blocking temperature T_b the mean particle radius $\bar{r}$ has been calculated using a relation derived by Gittleman *et al.* [2].

Table 1. Parameters of the specimens

Specimen No.	Internal classification	Nickel content	T_b [K]		$\bar{r}$ [nm] from T_b	$\bar{r}$ [nm] from Fig. 2
			14 KHz	50 KHz		
1	U 20	10	26	–	2.4	2.0
2	I 42 (25)	47	38, 59	43, 63	2.7, 3.1	1.8, 3.5
3	I 42 (25) sintered	47	–	–	–	–

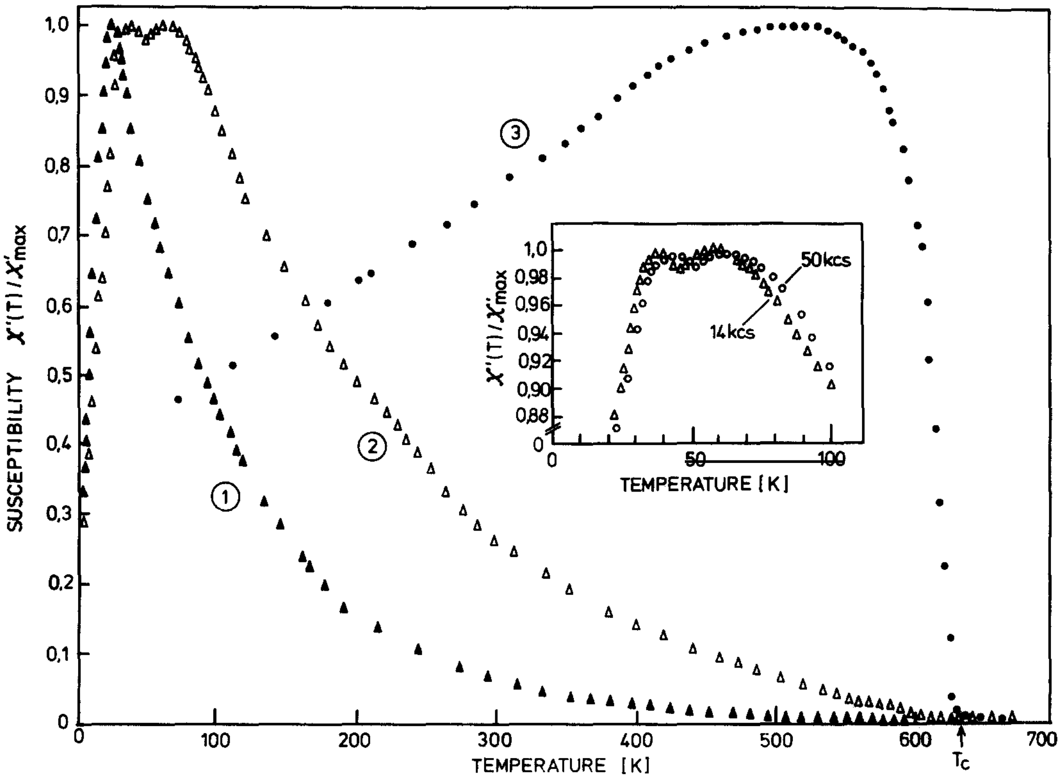

Fig. 1. Temperature dependence of the real part χ' of the initial susceptibilities normalized at their respective maximal values χ'_{max} at 14 KHz for Ni–SiO$_2$ specimens. ① 10% Ni, single-domain particles, $\bar{r} = 2.4$ nm; ② 47% Ni, single-domain particles, $\bar{r} = 2.7$ and 3.1 nm; ③ 47% Ni, sintered in air. Inset: neighbourhood of the maximum of curve 2 at two different frequencies.

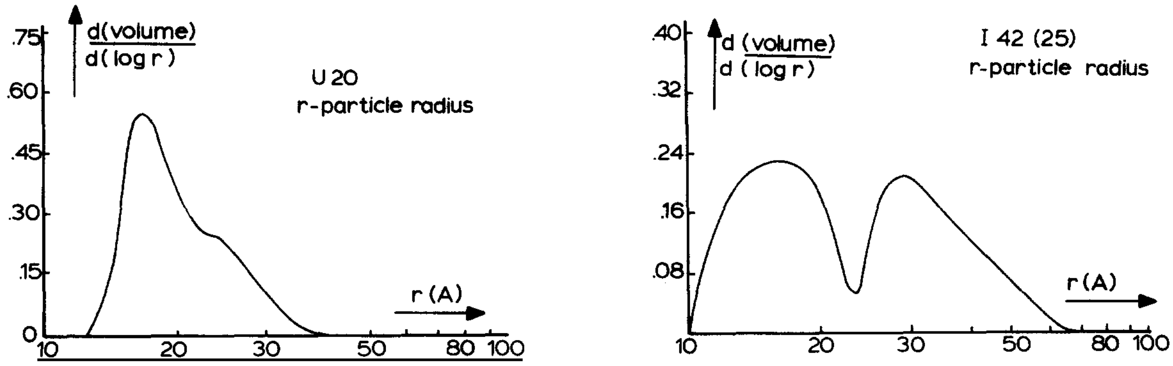

Fig. 2. Size distribution of nickel particles in specimens No. 1(a) and No. 2(b), determined from static magnetization measurements [6].

$$T_b = 1.8K\bar{V}/k_B|\ln \omega\tau_0|. \quad (1)$$

Here K is a uniaxial anisotropy constant evaluated in [2] to be $4.2 \times 10^4 \, \mathrm{J\,m^{-3}}$ near T_b for nickel particles of a similar size as used in this work, $\bar{V}$ is the mean particle volume, k_B is Boltzmann's constant, ω is the measuring frequency times 2π, τ_0 is a time constant of about 10^{-10} s [8], and 1.8 is a numerical factor derived in [2] for a Poisson distribution of particle volumes. The results of the calculations are summarized in the table.

One purpose of our experiment was to observe the critical behaviour and the effects of magnetostatic coupling between the particles. Magnetostatic coupling can be expected especially with specimen 2, which has a larger packing ratio. In Fig. 1 a slight enhancement of χ' over the simple $\chi \propto 1/T$ behaviour appears to be present at about 200 K. This may be interpreted as the effect of magnetostatic coupling, according to [9] with a coupling temperature of the order of 150 K for our specimens. A forthcoming publication will deal with this feature, which we have not studied in detail as yet.

We have looked at the critical peak in χ' near T_c, which should be present in the single-domain specimens (curves 1 and 2) due to the divergence of the spin susceptibility. According to Binder [13] the temperature T^* of the susceptibility peak depends on particle size

$$T^* = T_c(1 - \bar{n}^{1/\nu}). \quad (2)$$

T_c is the Curie temperature of the bulk material, ν the critical exponent of the correlation length, and $\bar{n}$ the mean particle diameter divided by the lattice spacing a. With $T_c = 630\,\mathrm{K}$, $\nu = 0.67$ [10] and $\bar{n} = 2\bar{r}/a \approx (6\,\mathrm{nm})/(0.35\,\mathrm{nm}) = 17$ we obtain $T^* = 617\,\mathrm{K}$ for specimen No. 1 and $T^* = 621\,\mathrm{K}$ for specimen No. 2.

The height of the critical peak in χ' at T^* can be estimated as follows. Due to the small size of the individual nickel particles, the correlation length ξ of the critical fluctuations is also limited. Its largest possible value is $\xi^* \approx \bar{r}$. By the same argument the divergent susceptibility χ' cannot grow larger than a certain value χ^*.

We estimate χ^* by setting $\xi^* = \xi_0(\tau^*)^{-\nu}$ and $\chi^* = \chi_0(\tau^*)^{-\gamma}$, so that

$$\chi^* = \chi_0(\xi^*/\xi_0)^{\gamma/\nu}. \quad (3)$$

Here $\tau = |T - T_c|/T_c$, $\xi_0 = 0.24\,\mathrm{nm}$ from [11] and $\chi_0 = 4.3 \times 10^{-4}$ (in SI units) from [12] are the critical amplitudes of ξ and χ'; $\nu = 0.67$ from [10] and $\gamma = 1.41$ from [12] are their critical exponents respectively. With these numbers, and with $\xi^* \approx \bar{r} \approx 3\,\mathrm{nm}$ we obtain the peak value of the susceptibility $\chi^*(T^*) = 8.7 \times 10^{-2}$.

This value has to be compared with $\chi_{\max}$ at T_b. It can be approximated by the susceptibility of noninteracting superparamagnetic particles of volume $\bar{V}$ and with spontaneous magnetization M_s

$$\chi_{\max}(T_b) = \mu_0\bar{V}M_s^2\,p/3k_BT_b, \quad (4)$$

where p is the volume fraction occupied by the nickel particles in the specimen and $\mu_0 = 4\pi \times 10^{-7}\,\mathrm{V\,sec\,A^{-1}\,m^{-1}}$. With $\bar{r} \approx 3\,\mathrm{nm}$, $p = 0.47$, $M_s = 5.09 \times 10^5\,\mathrm{A\,m^{-1}}$ and $T_b \approx 50\,\mathrm{K}$ we obtain $\chi_{\max}(T_b) = 8.36$. A comparison of this value with $\chi^*(T^*)$, which is smaller by two orders of magnitude, demonstrates that we were not able to observed the critical peak within the limits of sensitivity of our apparatus.

The authors suggest that the results presented above provide further support for the choice of the investigated material for studying superparamagnetism in more detail. In particular the thermostability over a wide temperature range of the chemisorbed nickel particles, deposited onto a silica carrier are of considerable current interest.

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