(Mittelwert aus 10 Meßreihen). Dieser Wert liegt erheblich über dem von FORSTER angegebenen (0,42 eV).

Mehrere Autoren [7-9] weisen auf einen Zusammenhang zwischen der Aktivierungsenergie ΔE des elektrischen Stromes in aromatischen Verbindungen und der Anzahl der π-Elektronen im Molekül hin. In Abb. 2 sind Literaturwerte für das ΔE verschiedener linearer Polyacene aufgetragen (von Naphthalin bis Pentacen als Mittelwerte der Angaben mehrerer Beobachter [9]). Der hier gefundene Wert für Benzol paßt zwanglos in diese Reihe.

Herrn Professor Dr. H. U. HARTEN danken wir recht herzlich für wertvolle Diskussionen und stete Förderung der Arbeit.

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Magnetic Hysteresis above Curie Temperature *

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Measurements of non equilibrium critical magnetic properties of 99.998% nickel between 348 and 360 °C lead to the following conclusion: If temperature increases from below the Curie point ($T_c = 356.6$ °C) the magnetic structure of the material changes from the ferromagnetic state to a system of single domain or superparamagnetic particles, which are relatively stable in the paramagnetic region just above Curie temperature. Remanence, coercivity and after effect show typical behaviour of small ferromagnetic particles. The critical exponents in the ferromagnetic region are 0.439 and 0.462 for remanence and coercivity respectively.

Magnetic hysteresis properties disappear gradually but not abruptly while passing the Curie temperature T_c from below. It is therefore an open question whether remanence and coercivity go to zero at exactly the same temperature which is found by extrapolation [1, 2] of spontaneous magnetization or reciprocal initial susceptibility to the temperature axis. From an experimental point of view the problem is not as simple as one may suppose because of the strong magnetic viscosity near T_c [3].

We have investigated the hysteresis curves of soft [$H_c(20 °C) = 0.70$ Oe] polycrystalline 99.998% nickel (Cu < 1, Fe 2, Mg 2, Si < 3 ppm.) between 348 and 360 °C by means of a self recording magnetometer device. Cylindrical rods of 0.5 cm diameter, and 10.0 cm in length, were magnetized in a field with 0.1% overall homogeneity and 0.001% stability with time. The field measurement was accurate within 0.5%. Magnetization was measured by a second-harmonic magnetometer with a relative accuracy of 1%, while the absolute values were better than 6%. The temperature could be kept constant within $\pm 0.1°$ over the volume of the specimen and within $\pm 0.01°$ during the recording time of one hysteresis cycle. Temperatures were measured by a resistance bridge with relative accuracy of $0.01°$; absolute calibration $\pm 0.5°$.

The magnetic properties were recorded as follows: In order to observe isothermal conditions during remanence measurements the field strength was lowered from its saturation value to zero so slowly that the magnetocaloric effect did not exceed $0.03°$. The initial remanence I_r and its time dependence could be observed from 0.1 sec after switching off the external field; the initial coercitivity H_c was recorded 30 sec afterwards.

Figs. 1 and 2 show the initial values of I_r and H_c respectively. The points were taken partly with increasing, partly with decreasing temperature, and they can be reproduced at thet same specimen within the above cited accuracy. Below 355.5 °C both figures present the well known ferromagnetic behaviour. Above 355.5 °C I_r decreases continuously while H_c goes through a maximum at T_c.
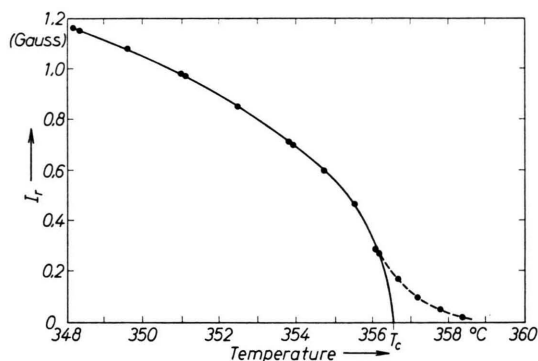

Fig. 1. Temperature dependence of remanence I_r. The solid curve is calculated according to Eqs. (1), (2). The dashed curve represents the critical contribution above T_c.

For further discussion the temperature dependence in the feromagnetic region, that is below 355.5 °C, is approximated by a relation

$$H_c, I_r \propto (T_c - T)^{p, q}. \qquad (1)$$

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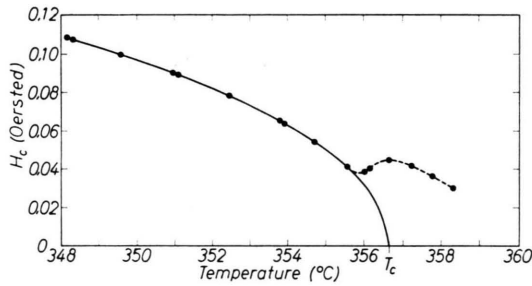[3] R. KOHLHAAS and R. K. PANDEY, Z. Angew. Phys. 21, 365 [1966].

Fig. 2. Temperature dependence of coercivity H_c. The solid curve is calculated according to Eqs. (1), (2). Above T_c the dashed curve represents the critical contribution.

Best fit to the measured values is obtained for:

H_c: $T_c = 356.62 \pm 0.23\,°C$; $p = 0.462 \pm 0.039$,

I_r: $T_c = 356.58 \pm 0.26\,°C$; $q = 0.439 \pm 0.044$.

The I_r- and H_c-contributions given by Eqs. (1), (2) are represented in Figs. 1 and 2 respectively by the solid curves and will be called "ferromagnetic fraction". The difference between measured values (dashed lines above 355.5 °C) and the solid curve is shown in Fig. 3. We will characterize these contributions to the total measured effects as "critical remanence" I_{rc} and
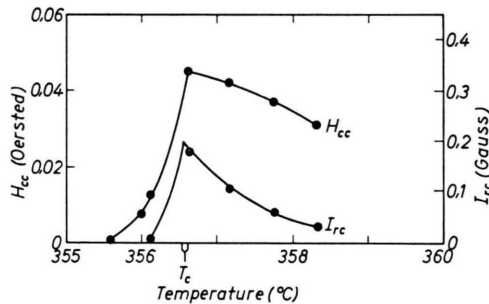

Fig. 3. Critical contributions to remanence (I_{rc}) and coercivity (H_{cc}) given by the difference between measured values and the solid lines in Figs. 1 and 2 respectively.

"critical coercitivity" H_{cc}. Both critical quantities reach well marked peak values at $T = T_c$.

The time constant τ of after effect in I_r depends on the temperature in a manner quite similar to I_r itself. In the ferromagnetic region, τ decreases with increasing temperature from 1200 sec at 354 °C to 800 sec at 356 °C. Inside the critical region, τ increases again up to 1200 sec at 356.6 °C and then decreases gradually at higher temperatures. Te cited τ-values are accurate only within 10%. At present we are concerned with more detailed measurements of critical magnetic viscosity.

The results can be summarized as follows:

1. Ferromagnetic hysteresis properties are present above the Curie point T_c determined by formula (1).

2. The temperature dependence of I_r, H_c and τ leads to the conclusion that magnetization processes above T_c must be quite different from those in the ferromagnetic region. Otherwise the minimum values in $H_c(T)$ and $\tau(T)$ at 356 °C cannot be explained.

3. The temperature dependence of the "critical magnetization" (Fig. 3) is similar to the size dependence of small ferromagnetic particles. If one replaces increasing temperature by decreasing particle size d the H_{cc} curve of Fig. 3 is strongly suggestive[4] of $H_c(d)$. Measurements of the internal demagnetizing factor near T_c lead to the same conclusion[5], i. e. a magnetic structure of single domain or superparamagnetic particles.

4. So far no theoretical estimations are available for the critical exponents p and q in Eq. (1). One could possibly compare them with the exponent β for spontaneous magnetization I_s in thermal equilibrium: $I_s \propto (T_c - T)^\beta$. Theoretical values for β can be found between 0.312 (approximation for 3-dimensional Ising model) and 0.5 (molecular field theory)[6]. A few experimental values have been published so far for nickel, i. e. $\beta = 0.36 \pm 0.04$[7] and $\beta = 0.51 \pm 0.04$[8]. As our exponents p and q lie inside the limits given for β it may be concluded that non equilibrium critical exponents do not differ considerably from equilibrium values.

A detailed study as well as experimental results on single crystals will be published elsewhere[9].

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