Magnetic properties and dipole interaction in systems of superparamagnetic particles

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Singularities due to dipole interparticle interaction have been observed for the first time in the magnetic properties of superparamagnets.

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Although the possibility of a phase transition (due to the magnetostatic interaction) in a system of superparamagnetic particles is discussed in[1], no experimental confirmation of this possibility existed until recently.

In the present paper we consider the interaction in a system of single-domain cobalt particles (more accurately, a solid solution based on Co) in a copper matrix. These particles are produced in the course of the decay of supersaturated Cu-Co solid solutions. Three alloys of this system were used, with the compositions listed in the Table I.

When the samples are quenched in water and tempered at 873 K, spherical particles are segregated, with a diameter that increases with the soaking time. The temper-

TABLE I.

№	Alloy composition at.%	I_s, G	$M \cdot 10^{16}$ erg/G	$n \cdot 10^{-16}$ cm^{-3}	$d \cdot 10^{19}$ cm^3	d, Å
1	Cu + 4.04% Co	58	6.0	9.78	5.0	100
2	Cu + 1.47% Co	17	11.8	1.42	9.8	125
3	Cu + 1.11% Co	12	16.4	0.73	13.7	140

ing times were chosen such to obtain a particle diameter that ranges from ~50 to ~150 Å. Segregation of ferromagnetic particles with dimension < 150 Å in the Cu-Co alloy samples makes them superparamagnetic at room temperature.[2]

We chose the induction method of measuring weak-field magnetic susceptibility as the principal method for the experimental investigation of our problem.

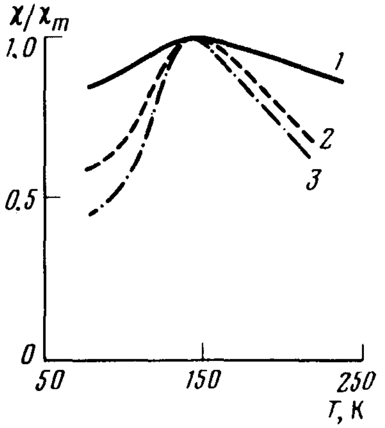

FIG. 1. Temperature dependence of the magnetic susceptibility χ/χ_m of the alloy Cu+4.04% Co. χ_m is the value of the susceptibility at the maximum. Curves 3, 2, and 1 correspond to measuring-field frequencies 50, 5×10^2, and 5×10^3 Hz, respectively. Heating for 2.5 hours at 873 K.

Figure 1 shows the temperature dependences of the magnetic susceptibility $\chi(T)$ measured in fields of different frequency. The presence on the $\chi(T)$ curves of maxima whose positions do not depend on the measuring-field frequency gives grounds for assuming that the observed change of the susceptibility is due to dipole interaction between the magnetic moments of the macroscopic particles. (There are no localized magnetic moments at the Co atoms in Cu-Co alloys in the investigated temperature interval.[3]) If the temperatures of the maxima-(T_L) were dependent on the frequency, this would be evidence that they are due to blocking of the magnetic moment of the particles in the anisotropy field. According to a concept first proposed by Néel, the relaxation time of the magnetic moment of a ferromagnetic particle is $\tau=\tau_0\exp(KV/kT)$, where K is the effective anisotropy constant, V is the volume of the particle, k is Boltzmann's constant, T is the temperature, and τ_0 is a constant. The temperature at which the measurement time coincides with τ is called the blocking temperature T_B. At $\tau_0=10^9$ sec, with the temperature increased by two orders of magnitude, it is easy to obtain $T_{B(2)}=1.4T_{B(1)}$, where $T_{B(2)}$ is the blocking temperature for the increased frequency. If we were to assume that the blocking effect had appeared in our experiment, then we would obtain at $T_{B(1)}\sim200$ K a shift of the maximum of $\chi(T)$ by an amount ~80 K, which exceeds significantly the measurement error. A third obvious possibility, that the maxima correspond to the Curie temperature of the Co particles, was rejected on the basis of the results of high-temperature measurements in fields of intensity $H=10$ kOe (the Curie temperature exceeded T_L noticeably). Although the results shown in Fig. 1 allow us to assume that a bound state is produced in the system of the magnetic moments of single-domain particles when the temperature is lowered (phase transition from the superparamagnetic state to a state of the "spin-glass" type), we still need additional proof that the singularities of $\chi(T)$ are determined by parameters of the aggregate of particles, and not by the characteristics of the individual particles. In this case the maxima of $\chi(T)$ are smeared compared with spin glasses,[4] but this can be explained if it is recognized that a sufficiently broadened particle size distribution is established in the coalescence process.

Increasing the tempering time raises the temperature of the maxima on the $\chi(T)$ curves. Figure 2 shows plots of T_L against the tempering time for samples of the three alloy compositions. Within the limits of the experimental error, the points fall on straight lines. According to[5], the aging times used by us (Fig. 2) correspond to the

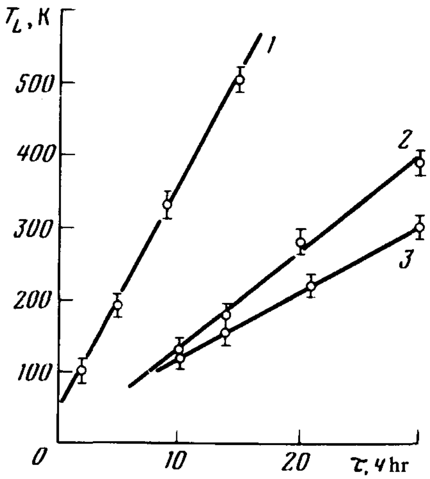

FIG. 2. Plot of T_L against the time of tempering at 873 K for the different alloys; 1—Cu−4.04% Co, 2—Cu−1.47% Co, 3—Cu−1.11% Co.

stage of stationary coalescence of the particles.

We measured the parameters of the particle systems (by methods of magnetic and x-ray structure analysis) for the structured states of the three alloys, corresponding to the same value $T_L \sim 110$ K. The results are listed in Table I, where I_s is the saturation magnetization, M is the average magnetic moment of the particles, n is the particle density, V is the average volume, and d is the particle diameter. The time of tempering at 873 K was 70 minutes, 10 hours, and 14 hours, respectively for alloys 1, 2, and 3.

In fact, the value of T_L is determined not by the characteristics of the individual particles alone (identical values of T_L correspond to different particle volumes). According to the results listed in Table I, T_L depends on the particle density, i.e., on the average distance between the individual particles. This is precisely the dependence expected by assuming a phase transition in the system of the magnetic moments of the particles. Using an approximate expression for the dipole-interaction energy, we can estimate the value of T_L from the formula $T_L = M^2/kl^3$, where l is the average distance between particles. Using the data in Table I to estimate T_L, we obtain $T_L \sim 250$, 141, 140° for alloys 1, 2, and 3, respectively. Consequently, we obtain satisfactory order-of-magnitude agreement with the experimental value of T_L obtained by measuring $\chi(T)$.

Maxima were observed also in the measured temperature dependences of the

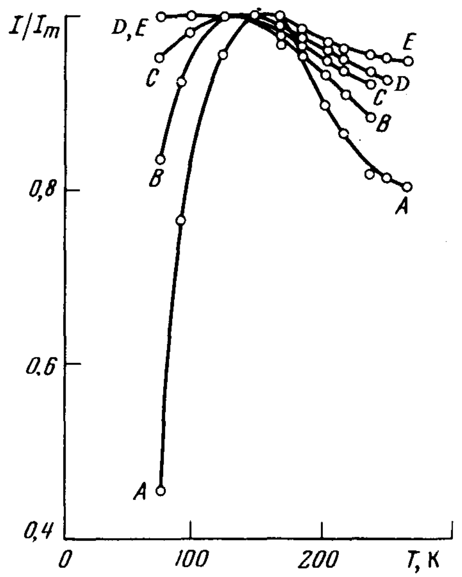

FIG. 3. Temperature dependences of the magnetization I/I_m (I_m is the maximum value) of the alloy Cu+4.04% Co. Heating for 2.5 hours at 873 K. Curves *A*, *B*, *C*, *D*, and *E* were obtained in fields of 10, 25, 50, 100, and 200 Oe, respectively.

magnetization. Figure 3 shows data corresponding to fields of different intensity. Increasing the intensity of the measurement field leads to a gradual broadening and vanishing of the maxima. Thus, the change in the shapes of the maxima is the same as for spin glasses,[6] but in this case weaker fields are needed to smooth out the singularities. This is understandable, since the magnetic moments of the interacting particles reach in our case values $\sim 10^5 \mu_B$ (as against $\lesssim 10 \mu_B$ for spin glasses, where μ_B is the Bohr magneton), so that the magnetic fields have a stronger orienting action on the magnetic moments of the particles than in spin glasses.

The foregoing results and arguments suggest that we have observed a new phenomenon—formation of a bound state in a system of superparamagnetic particles. The low-temperature state is apparently the analog of spin glasses and can be called macroscopic glass. That is to say, the magnetic moments are fixed ("freeze") in arbitrary orientations, this being due to the dependence of the energy of the pair interaction of the dipoles on the angles and to the disordered diposition of the particle themselves in the sample volume.

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