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Magnetic and transport properties of granular cobalt films

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Simultaneous magnetization and magnetoresistance measurements have yielded the magnetic phase diagram of the granular Co-SiO_2 system. The superparamagnetic-to-ferromagnetic transition temperature changes gradually with composition from ~80 K at 20 vol % Co to ~280 K at 43 vol % Co. The results confirm the theory of spin-dependent tunneling in granular magnetic metals and yield the value of $JP = (1.0 \pm 0.3)$ meV. Here P is the spin polarization of the tunneling electrons and J their exchange-coupling constant. This quantity has not been measured previously for cobalt. A quantitative comparison shows that the molecular-field theory does not provide an adequate description of the magnetization of granular cobalt.

I. INTRODUCTION

Granular metals were intensively studied mainly because of their interesting transport properties.[1-3] The conductivity varies as a function of composition from metallic to almost insulating. It was proposed theoretically[2] that in the high-resistance region the electron transport is governed by a unique combination of thermally activated charging of the metal grains and electron tunneling between the isolated metal grains. Experimental results on the many granular systems investigated confirm this theory.

The magnetic properties of granular magnetic metals were studied only on one system, i.e., Ni-SiO_2. One of the most interesting discoveries was the existence of a superparamagnetic phase and a superparamagnetic-to-ferromagnetic phase transition at a temperature T_M which depends on metal concentration.[4-6] The first evidence for such a transition was borne out by measurements[4] of the magnetoresistance of granular Ni, where the observed negative magnetoresistance was found to be peaked at T_M. The negative magnetoresistance was interpreted as due to electron-spin-dependent tunneling between neighboring magnetic grains. The effect of the magnetic field is to align neighboring grains so that the exchange energy needed for the tunneling is lowered, thus increasing the tunneling efficiency.[5] These ideas were later incorporated[7] into the transport theory[2] to account for the observed magnetoresistance. According to this theory the magnetoresistance is expected to be proportional to the spin-spin correlation function of neighboring grains. A comparison to experiment, using molecular-field approximation for the spin-correlation function, has shown that the theory[7] predicts the essential features, i.e., a negative magnetoresistance which is peaked at T_M.

In this paper we present results of extensive studies of the magnetic properties of another granular magnetic system, the Co-SiO_2 system. We report here the first simultaneous study of magnetization and magnetoresistance on a granular magnetic metal. Systematic measurements as a function of composition and temperature reveal the existence of a superparamagnetic-to-ferromagnetic phase transition. The similarity between the present observations and those reported[4-6] for Ni-SiO_2 suggest that such a transition is a general property of granular magnetic metals. The combined measurement of magnetization and magnetoresistance enabled us to provide new independent evidence that the peak in the magnetoresistance is indeed associated with the ferromagnetic-to-superparamagnetic phase transition.

When trying to account for our magnetization data we found that the magnetization of granular Co-SiO_2 is not properly described by the molecular-field theory. Satisfactory agreement between magnetoresistance theory and experiment could be obtained only using experimental magnetization values to derive the spin-spin correlation function. From this fit we obtain the value of the product JP, where P is the spin polarization of the tunneling electrons and J their exchange-coupling constant.

II. THEORETICAL BACKGROUND

Granular films consist of fine metal grains (~50-Å diameter) dispersed in an amorphous insulator (SiO_2, Al_2O_3). Their electrical conductivity (at not too high volume fractions of metal) is due to tunneling of electrons between the grains.[2,3] The temperature dependence of the tunneling conductivity is determined by the electrostatic charging energy E_c^0 required to generate a fully dissociated pair of positively and negatively charged grains. According to the conductivity model of Sheng *et al.*,[2,3] the granular metal is represented by a conductance network in which the metal grains are interconnected by conductances σ_s of the form

$$\sigma_s \propto e^{-2\kappa s - E_c^0/2kT}, \quad (1)$$

where s is the tunnel barrier thickness, $\kappa = (2m\phi/\hbar^2)^{1/2}$, m is the effective electron mass, ϕ is the barrier height, $\hbar$ is Planck's constant, k is Boltzmann's constant, and T is the absolute temperature. It is assumed that the grains are spherical in shape with a distribution in diameter d and charging energy $E_c^0 (\propto 1/d)$ such that the product sE_c^0 is constant for a film of a given composition (labeled by the metal volume fraction x). The constancy of the ratio s/d is a consequence of the preparation procedure of the samples, since the grains are formed by condensation of neighboring metal, so that larger grains are surrounded by a thicker dielectric. The parameter C, henceforth called the tunneling-activation energy, is defined by

$$sE_c^0\kappa = C. \quad (2)$$

C and κ depend only on x.

It is also assumed that only the tunneling between neighboring grains of nearly equal size is relevant. At each temperature T there is a tunnel barrier thickness s_m,

$$s_m = (C/kT)^{1/2}/2\kappa, \quad (3)$$

for which σ_s has a maximum σ_m given by $\sigma_m \propto \exp[-2(C/kT)^{1/2}]$. It is further assumed that the temperature dependence of the network conductivity $\sigma(T)$ is given by σ_m, that is,

$$\sigma(T) \propto e^{-2(C/kT)^{1/2}}. \quad (4)$$

From Eqs. (2) and (3) it follows that the dominant contribution to the conductivity at high temperatures is due to tunneling between small grains (large E_c^0) separated by thin tunnel barriers (small s), while at low temperatures the tunneling between large grains (small E_c^0) separated by thick tunnel barriers (large s) is dominant. It should be noted that the above model represents a gross simplification of the actual conductivity network. In particular, the model does not take into account either the tunneling between grains of unequal size or the contribution to the conductivity due to conductances other than σ_m. Notwithstanding these objections, the model predicts remarkably well the observed temperature dependence of the conductivity of granular metals, and hence it is expected to contain the essential physics of the problem. This theory applies in the limit of low electric fields.

Elementary electrostatic theory applied to a simplified picture of a spherical metal grain of diameter d surrounded by a dielectric of thickness s and imbedded into a metal leads to an expression for the charging energy[3]:

$$E_c^0 = 4s(e^2/\epsilon d)/(d+2s), \quad (5)$$

where e is the electron charge and ϵ the dielectric constant of the insulator. If the granular metal in the dielectric regime ($x \lesssim 0.5$) is approximated by a simple cubic lattice of metal spheres with lattice constant $s+d$, a relation is obtained between x, s, and d, namely,

$$x = \pi/6(1+s/d)^3, \quad (6)$$

and from Eqs. (2), (5), and (6),

$$C(x) = \eta[(\pi/6x)^{1/3} - 1]^2/[(\pi/6x)^{1/3} - \tfrac{1}{2}], \quad (7)$$

with $\eta = 2\kappa e^2/\epsilon$. Equation (7) gives the essential dependence of C on the volume fraction, since κ is a slowly varying function of x.

As the volume fraction x is increased, metallic paths start appearing and becoming longer until eventually at a critical volume fraction x_c, a metallic network from contact to contact is established and the conductivity increases by several orders of magnitude. In this paper, only the range of volume fractions belonging to tunneling conductivity is of interest.

The magnetic structure of granular magnetic metals in the dielectric regime can be described as follows. Above the Curie temperature T_C of the pure metal the material is paramagnetic. As the temperature is lowered below T_C the individual grains become ferromagnetic. (This transition may happen at a somewhat lower temperature for very small grains.) One may expect that at these temperatures the ensemble of grains is superparamagnetic. At a lower temperature T_M, the superparamagnetic ensemble may exhibit a superparamagnetic-to-ferromagnetic transition, where long-range order of the grain magnetic moments takes place. Since in this work measurements are performed well below T_C we restrict ourselves to the consideration of the superparamagnetic and ferromagnetic phases. The grains themselves are assumed to be ferromagnetic with the saturation magnetization of the pure metal, that is, with a magnetic moment μ given by

$$\mu = n\Omega\beta\mu_B, \quad (8)$$

where n is the atomic density of the metal, Ω is the volume of the grain, and $\beta = 1.715$ is the magnetic moment per atom[8] in units of the Bohr magneton μ_B.

The conductivity theory has been generalized to granular metals in which the metal grains are ferromagnetic.[7] In that case a small additional energy E_M is required to generate a pair of charged grains. E_M is an exchange energy which arises when the magnetic moments of the grains are not parallel and electron spin is conserved in the

tunneling process. Thus, for ferromagnetic metal grains we have

$$\sigma(H,T) \propto e^{-2Ks}[(1+P)e^{-(E_c^0+E_M)/2kT} + (1-P)e^{-(E_c^0-E_M)/2kT}]/2 . \quad (9)$$

The coefficients $(1+P)/2$ and $(1-P)/2$ are the probabilities that an electron tunneling from grain 1 to grain 2 has its spin parallel and antiparallel, respectively, to that of grain 1; E_M is the difference between the exchange energies of an electron situated in grain 2 and grain 1, and H is the applied magnetic field. Equation (9) expresses the fact that if the moments of grain 2 and grain 1 are not parallel, an additional energy E_M is required to transfer an electron if its spin is parallel to that of grain 1, while less energy (by an amount $-E_M$) is required if its spin is antiparallel to that of grain 1. Assuming[7] that $E_M/kT \lesssim 1$, one may retain only linear terms in the magnetic energy, and Eq. (9) reduces to

$$\sigma(H,T) = \sigma(T)(1 - PE_M/2kT) . \quad (10)$$

The magnetoresistance $\Delta\rho/\rho$ can now be written as

$$\frac{\Delta\rho}{\rho} = \frac{\rho(H,T)-\rho(0,T)}{\rho(0,T)} = \left(\frac{P}{2kT}\right)[E_M(H) - E_M(0)] . \quad (11)$$

The magnetic exchange energy can be expressed in terms of the spin-correlation function of two neighboring grains $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle$ as

$$E_M = (J/2)(1 - \langle \vec{S}_1 \cdot \vec{S}_2 \rangle / S^2) , \quad (12)$$

where spins $\vec{S}_1$ and $\vec{S}_2$ have the same magnitude, equal to S, and J is the corresponding exchange-coupling constant.

For our purposes it appears to be sufficient[9] to approximate the correlation function by

$$\langle \vec{S}_1 \cdot \vec{S}_2 \rangle / S^2 \simeq m^2(H,T) , \quad (13)$$

where $m(H,T)$ is the reduced magnetization of the system. Thus Eq. (11) becomes

$$\Delta\rho/\rho = -(JP/4kT)[m^2(H,T) - m^2(0,T)] . \quad (14)$$

Equation (14) predicts a negative magnetoresistance which is largest at the superparamagnetic-ferromagnetic transition temperature T_M. The peak of the magnetoresistance at T_M becomes more pronounced the smaller the applied magnetic field.

III. EXPERIMENTAL

The samples used in the present study were prepared by co-sputtering of Co and SiO_2. The co-sputtering method, which has been described in detail previously,[1,3] is based on the bombardment of a metal-insulator composite target by Ar ions. In order to get a compositional variation of the metal (vol% Co) along the deposited films, one may use various configurations of the target.[3] For the present work a $\frac{1}{16}$ in.-thick silica plate having a half-disk shape was placed on top of a Co disk of the same diameter (6 in.). The substrate on which the film was deposited was held above the target in a configuration which ensures that one end of the deposited film is metal rich and the other end is insulator rich.[3] We have deposited films which were 2.5–5.5 μm thick and 0.2 in. wide, on two adjacent substrates. One substrate was made of a Pyrex slide (5 in. long, 0.75 in. wide) which had on it Cr-Au contacts to enable transport measurements.[1-3] The other substrate was composed of 0.1 in.-long, 0.2 in.-wide, and 0.01 in.-thick sapphire platelets arranged along the Pyrex slide. The film samples on these platelets were used for the magnetization measurements. Hence the correlation between the magnetization results and the magnetoresistance results for *equal* composition samples could be studied. For comparison of our samples with samples prepared under similar conditions in the RCA laboratories (in which many previous studies were made), we carried out magnetization and magnetoresistance measurements on those samples as well. The results were found to be much the same.

The magnetization was measured in a P.A.R. model 155 vibrating-sample magnetometer which was calibrated by an Ni standard. The sample was introduced into a special Plexiglass sample-holder which was placed in a Janis model 153 variable temperature (4.2–300 K) Dewar. The magnetization versus applied magnetic field was measured at various temperatures for configurations both sample parallel and sample perpendicular to the magnetic field.

The resistance R of the samples was determined by a standard four-probe technique using a stabilized current source and measuring the voltage drop between adjacent Cr-Au contacts (spaced 0.1 in. apart). The magnetoresistance $\Delta\rho/\rho$ was measured with a dc Wheatstone bridge.[5] For the study of the temperature dependence of R and $\Delta\rho/\rho$ the sample was mounted in a dip stick which was placed in a variable temperature (4.2–300 K) Dewar. The tail of the Dewar was centered in a coil which provided fields up to 3 kOe at the sample.

IV. RESULTS

A. Sample characterization

One of the main problems in the characterization of the granular samples is the determination of

the relative composition of the metal and the insulator. The most accepted method is to measure the thickness profile of the sample and to fit this profile with that obtained for the two half-disk sputtering targets, using the sputtering rates as adjustable parameters. Such a fit yields the correct composition within a few percent. As a check and possible correction for this method, Abeles *et al.*[1,3] suggested a comparison of the resistivity-versus-composition curve with the resistivities of a few known compositions. In the present case, however, we are dealing with magnetic specimens and thus the idea immediately occurs of using the saturation magnetic moment as a measure of the cobalt content of the samples. In Fig. 1 we plot this saturation magnetic moment $M_s(x)$ relative to the saturation moment of cobalt $M_s(1)$ as a function of the calculated volume percentage of cobalt.

Inspecting Fig. 1 we see a reasonable agreement between the two methods for composition determination, especially at small Co concentrations. Here the experimental points follow a 45° straight line commencing at the origin. Thus at small Co concentrations the calculated values and those derived from $M_s(x)/M_s(1)$ yield pretty much identical results. At higher ($\gtrsim 50\%$) cobalt concentration, however, the $M_s(x)/M_s(1)$ curve deviates from the straight line and falls somewhat beneath it, yielding a concentration a few percent smaller than the calculated one. As the magnetic method is believed to be more accurate in the regime where the results obtained by the two methods differ, we have chosen the values derived from $M_s(x)$.

To check the electrical behavior of our samples we measure the small-field resistivity ρ of the samples as a function of composition and temperature between room temperature and 50 K. Figure 2 shows ρ as a function of Co composition

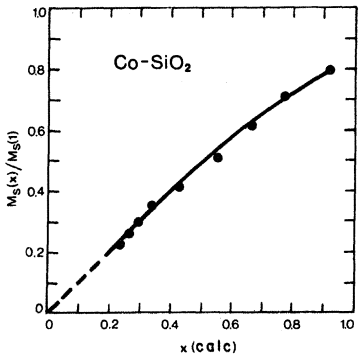

FIG. 1. Saturation magnetic moment $M_s(x)$ at different compositions relative to the saturation moment of pure cobalt, $M_s(1)$, as a function of the calculated volume fraction x of Co.

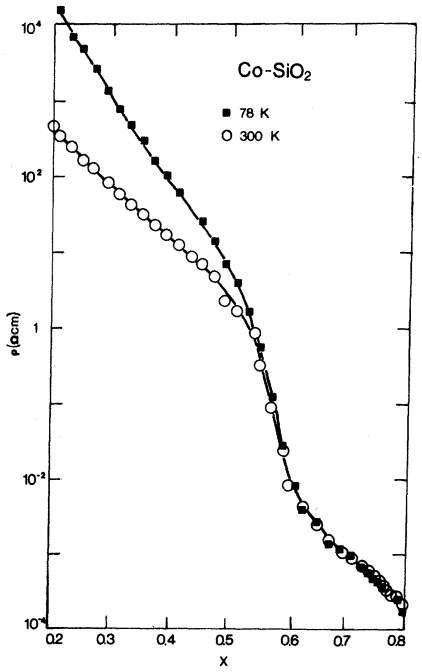

FIG. 2. The resistivity ρ of granular Co-SiO_2 as a function of volume fraction x of cobalt at two temperatures, as marked.

at two temperatures, room temperature and liquid-nitrogen temperature. At around 50–60 vol% Co we see the sharp increase of resistivity characterizing the transition between the metallic and dielectric regime.[1] In this region the temperature coefficient of the resistivity also changes from negative to positive. From ~50 vol% Co and below, the resistivity continues to rise in the dielectric regime, but now much more gradually.

In Fig. 3 we plot the resistivity of a few samples in the dielectric regime as a function of $1/T^{1/2}$. The results are seen to lie on straight lines, just as expected in this regime where the conductance is dominated by tunneling and the charging of the grains [see Eq. (4)]. The tunneling-activation energy values C, derived from the slopes of these curves, are shown by the points in Fig. 4 as a function of composition. The theoretical line in the figure was calculated from Eq. (7) using η as an adjustable parameter. The agreement between experiment and theory is considered satisfactory. The value of η obtained from the fit is $\eta \approx 1$ eV.

B. Magnetization measurements

With the aim of detecting the superparamagnetic-to-ferromagnetic transition temperature T_M, extensive magnetization measurements were performed on samples from 20 to 80 vol% Co content at various temperatures between room temperature and liquid-helium temperature. The mea-

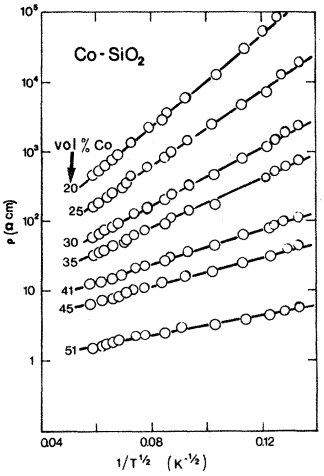

FIG. 3. Semilogarithmic plots of the resistivity ρ of granular Co-SiO_2 as a function of $1/T^{1/2}$ for samples of different cobalt composition, as marked.

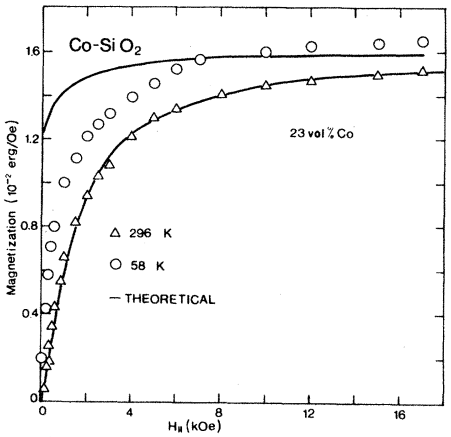

FIG. 5. The measured magnetic moment of a 23 vol % cobalt sample as a function of parallel applied magnetic field $H_{\parallel}$ at two temperatures, as marked. The curves were calculated using the molecular-field theory for $T_M = 95$ K and $\mu = 3.5 \times 10^{-17}$ erg/Oe.

surements were performed as a function of magnetic field with the fields both parallel and perpendicular to the film surface. In Fig. 5 are shown typical magnetization data taken with a parallel field. The cobalt content of this sample was 23 vol% and its transition temperature was found to be around 95 K. The two sets of data in the figure correspond to two temperatures, one at 296 K (triangles) above T_M and one at 58 K (dots) below T_M. One immediately apparent feature of the experimental results is that at 58 K the magnetization barely saturates at the highest field shown (17 kOe). This indicates the presence of a small fraction of superparamagnetic grains even below T_M.

The experimental values of magnetization (such as shown in Fig. 5) were compared to those calculated from the molecular-field theory using

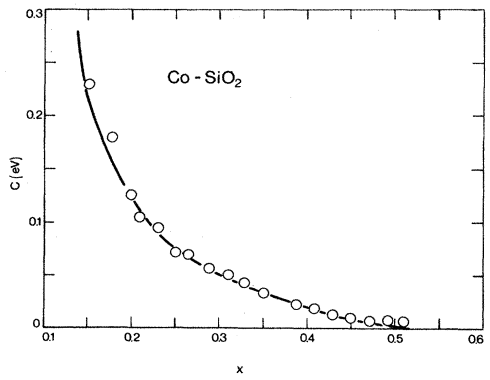

FIG. 4. The tunneling activation energy C (derived from the slopes of lines as in Fig. 3), as a function of the volume fraction x of Co. The curve in the figure was calculated from Eq. (7) with $\eta = 1$ eV.

Langevin's function.[10] It was found that in the superparamagnetic regime the data could be fitted; the higher the temperature, the better the fit. An example of such a fit is shown by the line drawn in Fig. 5 for 296 K. This curve was calculated for a superparamagnetic sample having a transition temperature of 95 K and assuming a uniform grain size with a grain magnetic moment $\mu = 3.5 \times 10^{-17}$ erg/Oe. The agreement between the experimental and calculated values can be seen to be excellent.

The curve for $T = 58$ K in Fig. 5 was calculated using the same parameters as for the curve at the higher temperature. Obviously, this second curve does not fit the experimental results. This was found always to be the case, i.e., the experimental magnetization data below T_M could not be fitted by the molecular-field theory. Even above T_M we find that the molecular-field theory predicts a faster approach to saturation than observed experimentally. Only at high temperatures ($\sim 2T_M$) and above were we able to obtain satisfactory fits.

The temperature dependence of the reciprocal initial susceptibility $1/\chi$ obtained from the magnetization data at parallel fields is plotted in Fig. 6. Results for samples of three different Co compositions are shown in the figure. The dependence exhibited in Fig. 6 is similar to that obtained by Gittleman, Abeles, and Bozowski[6] for the Ni-SiO_2 system and suggest a Curie-Weiss behavior at high temperatures. The intersection with the abscissa of the straight lines drawn through the data at the higher temperatures may thus serve to determine the superparamagnetic-ferromagnetic transition temperatures $T_M(x)$, as illustrated

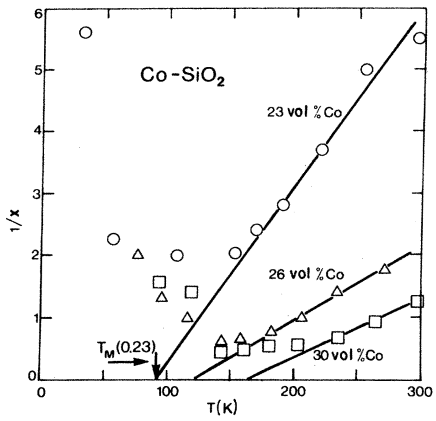

FIG. 6. The reciprocal initial susceptibility $1/\chi$ (obtained from curves as in Fig. 5) as a function of temperature for three Co concentrations, as marked. The extrapolation of the straight lines drawn through the high-temperature points serve to determine T_M as illustrated in the figure.

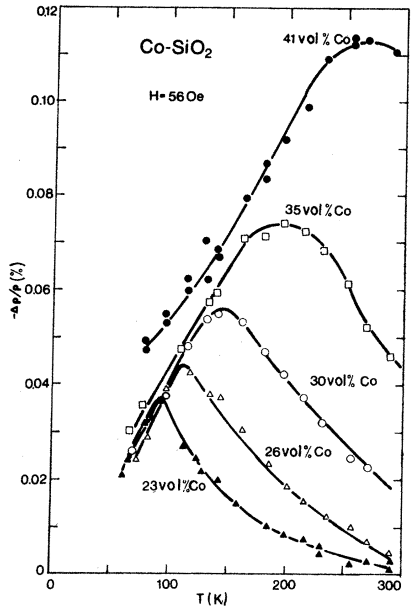

FIG. 7. Negative magnetoresistance $-\Delta\rho/\rho$ as a function of temperature for five volume fractions x of Co, as marked. The data correspond to an applied magnetic field of 56 Oe.

in the figure. Similar results were obtained for higher cobalt concentrations, but since our measurements were limited to below room temperature no T_M could be derived for those samples by this method.

C. Magnetoresistance measurements

Magnetoresistance measurements provide probably the most sensitive means to determine T_M in granular magnetic systems. This was found to be the case in the Ni-SiO_2 system,[4,5] and this is what we also find in the Co-SiO_2 system.

Magnetoresistance measurements on samples whose cobalt composition varied between 20 and 60 vol% showed negative magnetoresistance. The measurements were performed in the temperature range of 50 K to room temperature; the longitudinal magnetoresistance, i.e., the magnetic field parallel to the electric current, was measured.

In Fig. 7 we plot the (negative) magnetoresistance $-\Delta\rho/\rho$ measured at a low magnetic field (56 Oe) as a function of temperature for five sample compositions between 23 and 41 vol% Co. Inspecting the data in Fig. 7 we see that for each composition there appears a maximum in $-\Delta\rho/\rho$ as a function of temperature. These maxima are associated with the transition from the ferromagnetic into the superparamagnetic state and appear at the transition temperature T_M. The maxima appear at lower temperatures the lower the cobalt content, as expected. Comparing the present magnetoresistance results on Co-SiO_2 with those published[4,5] for Ni-SiO_2, we note that the present results are about one order of magnitude higher. Another difference between granular cobalt and nickel is that while in nickel the transition temperature T_M is a very abrupt function of the composition, in cobalt T_M varies much more gradually.

In Figs. 8 and 9 we present magnetoresistance data measured at higher fields (278 and 1000 Oe). We see that the higher the fields, the more obliterated become the maxima. At 278 Oe most of the data still exhibit a broad maximum, while at 1000 Oe the maxima disappear completely.

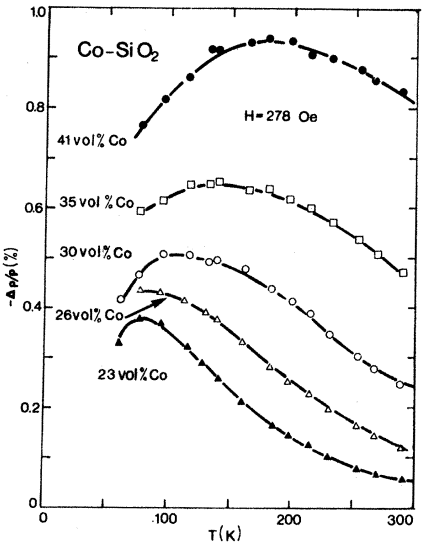

FIG. 8. $-\Delta\rho/\rho$ as a function of T for the same samples as in Fig. 7, but taken in a field of 278 Oe.

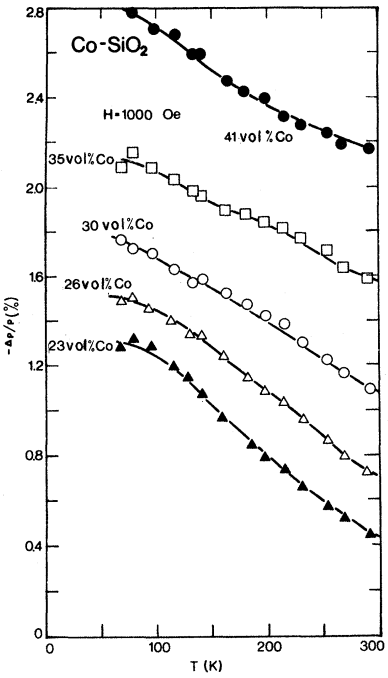

FIG. 9. $-\Delta\rho/\rho$ as a function of T for the same samples as in Figs. 7 and 8, but taken in a field of 1000 Oe.

It should be pointed out, however, that the strong increase of the magnetoresistance observed[4,5] in Ni-SiO_2 at low temperatures and attributed[7] to large paramagnetic grains seems to be absent in the Co-SiO_2 system. If there is a paramagnetic contribution, then it is much smaller than in Ni-SiO_2.

V. DISCUSSION

In this paper we present the first systematic study of the magnetic and magnetotransport properties of a granular magnetic metal performed on identical samples. As was already pointed out in previous sections the magnetoresistance can serve as a sensitive tool to determine T_M. Magnetization measurements provide another independent means of determining T_M. In addition, it is shown here that saturation-magnetization measurements provide an independent and highly reliable method for the evaluation of the sample composition of granular magnetic metals. In fact, it seems to us that at present this is the only reliable physical method of composition determination. Our results show that composition determination by profile fitting[1,3] is quite dependable, apart from the metal-rich end where it apparently overestimates x.

The electrical transport of granular metals has been extensively investigated and is fairly well understood theoretically. In fact, it serves today as a diagnostic tool for checking the quality of granular systems. The results presented in the previous section show that the resistivities of our samples have a "normal" behavior both with respect to composition and temperature dependence. In particular the $1/T^{1/2}$ dependence of ρ shows that a sample of a given composition contains a distribution of metal grain sizes, the usual situation with granular metals. The magnitude and the composition dependence of the tunneling-activation energy C agree well with data published in the literature[1,3] for other granular systems and follow the theoretical line (calculated with $\eta = 1$ eV).

The magnetization data were analyzed on the basis of the molecular-field theory. At high temperatures ($\gtrsim 2T_M$) excellent fits can be obtained for the different compositions using the average grain magnetic moment as an adjustable parameter. The values of μ derived by this fitting are shown in Fig. 10 as a function of x. These values of μ lead to reasonable values for the average grain diameter d, also shown in Fig. 10. The average intergrain distance s was calculated from the values of d and x using Eq. (6) and are shown by the data at the bottom of Fig. 10. We wish to point out, however, that this is the intergrain distance of the average grains and is not to be confused with s_m in Eq. (3) which denotes the distance between the grains that dominate the conductivity at a given composition and temperature.

At low temperatures the magnetization data could not be fitted by the molecular-field theory. We think that there are two possible reasons for this. First, the samples contain various grain sizes, and thus the magnetization theory of such materials should take into account the distribution of barrier thicknesses and a corresponding distribution of exchange-coupling constants between the grains.[11] We expect that such a distribution would lead to a

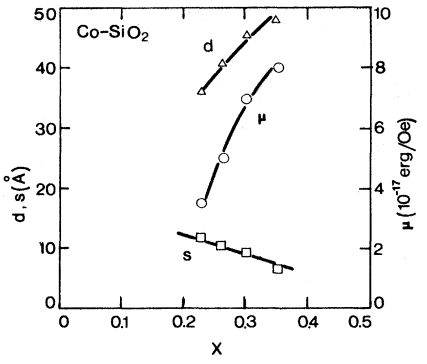

FIG. 10. The individual average-grain magnetic moment μ, diameter d, and average thickness of tunnel barrier s as functions of volume fraction x of Co.

more gradual M versus $H_{\parallel}$ curve. Second, the dipole-dipole magnetic interaction between the grains may not be negligible in cobalt. It is true that in a spherically symmetrical system this interaction cancels out completely. However, a granular sample does not possess locally a complete spherical symmetry, and therefore anisotropic terms in the grain-grain interaction (which are not taken into account by the molecular-field theory) may play a role.

Although the magnetization data cannot be fitted exactly by the molecular-field theory (except at high temperatures), extrapolations of the straight lines drawn through the points at the high-temperature end still lead to values of T_M which are consistent with the values derived from magnetoresistance measurements. In Fig. 11 we show a phase diagram of the Co-SiO_2 system. The transition temperatures T_M were derived both from the magnetoresistance measurements (dots) and the magnetization data (triangles). The data obtained by the two methods are seen to be in excellent agreement. Our results yield the phase transition in the temperature range between 80 and 280 K. The composition dependence of T_M is gradual with a slope $dT_M/dx \approx 9$ K/vol%. This phase diagram for Co-SiO_2 is similar to that found[5,6] for Ni-SiO_2 except that there the composition dependence of T_M is much stronger.

We turn now to the magnetoresistance. The characteristic feature of the low-field magnetoresistance is the pronounced peak which shifts to lower temperatures as the cobalt volume fraction decreases. This structure in the magnetoresistance becomes washed out at higher fields. An attempt was made to fit the experimental $\Delta\rho/\rho$ with the theoretical expression given by Eq. (14) using magnetization values calculated from molecular-field theory. A homogeneous and ordered system was assumed, and for μ we used the value derived from high-temperature magnetization data (see Fig. 10). The results of these fittings are shown in Fig. 12. Here we replotted (on a logarithmic scale) the experimental $\Delta\rho/\rho$ values at three magnetic fields for a 26 vol% Co sample. The above-mentioned theoretical values are shown in Fig. 12 by the dashed lines and were obtained with the value of $JP = 0.7$ meV. Obviously, the dashed theoretical curves do not fit the experimental data either in the structure or the magnitude of the effect. In view of this unsatisfactory fit, and knowing that the molecular-field theory does not predict correctly the magnetization at lower temperatures, we decided to use experimental magnetization values in Eq. (14). A fit obtained in this fashion for the same value of JP is shown in Fig. 12 by the solid curves. These curves reproduce much better the temperature dependence of the magnetoresistance, especially for the low field, as well as the magnitude at different fields. Similar fits for different compositions yielded values of JP in the range of 0.7 to 1.3 meV. Thus our best value for JP is 1.0 $\pm$ 0.3 meV. In comparison, the value of JP found[7] in Ni is 0.35 meV. There is evidence that the tunneling probability of d electrons is about two orders of magnitude smaller than that of free electrons belonging to an s-p band.[12] Thus the product

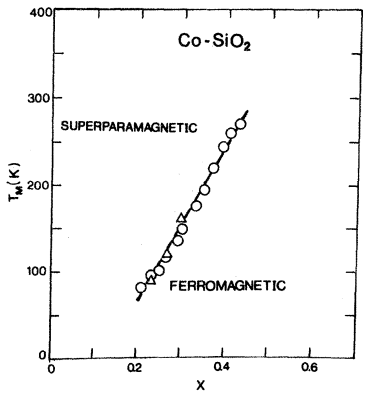

FIG. 11. Phase diagram of the Co-SiO_2 system. T_M is the superparamagnetic-to-ferromagnetic transition temperature; the dots were obtained from magnetoresistance and the triangles from magnetization measurements.

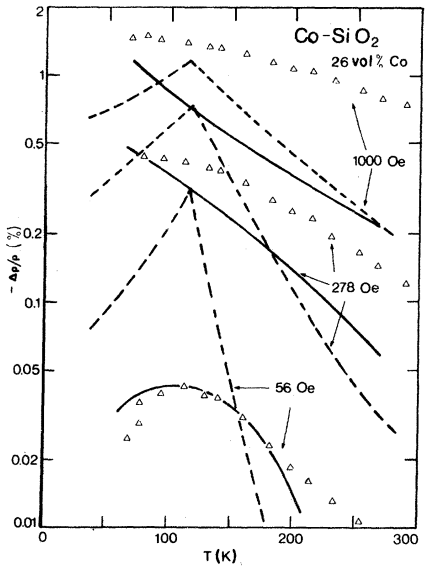

FIG. 12. Measured values of $-\Delta\rho/\rho$ as function of T (triangles) for a 26 vol % Co sample at three magnetic fields, as marked. The dashed curves were calculated from Eq. (14) using molecular-field values for magnetization while, in calculating the solid curves, experimental values of the magnetization were used.

JP obtained by fitting the magnetoresistance of granular magnetic metal systems should closely correspond to that of free s-p electrons. The value of the polarization P for s electrons in magnetic transition metals is estimated[13] to be about 0.1. We expect that the polarization of the tunneling electrons should be the same as those in the metal. Thus from our experimental $JP \approx 1$ meV we obtain $J \approx 10$ meV. This value for J is much smaller than the estimates[13,14] for the full value of the s-d exchange-coupling constant in cobalt. This seems to indicate that the spin-relaxation process occurs somewhat before the tunneling electron reaches the neighboring grain. The exchange constant involved in the process would then correspond to the overlap of the tunneling s electron only with the tail of the d-electrons' wave functions. This would account for the greatly reduced value of J.

The paramagnetic contribution to the magnetoresistance found in Ni at low temperatures seems to be absent in the present data. This indicates that the fraction of large particles (large intergrain distances) that contribute to the conductivity, but are magnetically disconnected from the rest of the sample, is much smaller than in Ni. These magnetically disconnected grains are probably the ones that are responsible for the slow saturation of the magnetization data at low temperatures and high fields. We can estimate the fraction of these grains from the saturation values of the experimental and calculated saturation magnetization at the lowest temperatures (for instance, about 4% for the data at 58 K in Fig. 5).

VI. CONCLUSIONS

Our present results on the Co-SiO_2 system combined with those reported[4-6] for the Ni-SiO_2 system suggest that the superparamagnetic-to-ferromagnetic transition is a general property of granular magnetic metals. The present study shows that the spin-dependent tunneling theory[7] provides not only the essential features of the magnetoresistance of granular magnetic metals but also a fairly good quantitative account of the experimental results.

The electron tunneling is associated with a spin-relaxation process. The experimental value of JP suggests that this spin relaxation occurs before the electrons reach the neighboring grain.

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