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Electrical conduction of α-Fe_2O_3 colloids

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Aqueous colloidal dispersions of α-Fe_2O_3 particles (average diameter ~ 0.065 μm) have been prepared at different volume concentrations ranging from 0.04 to 4 vol %. The electrical conduction of these colloids at constant $p\mathrm{H} \sim 10$ has been investigated as a function of particle concentration, frequency (including the dc case), temperature (from 77 to 300 K), and magnetic field (up to 7 kOe). The colloid conductivity increases with particle concentration and with temperature. The frequency dependence of conductivity obeys a power law with an index slightly less than unity, and decreasing somewhat with increasing temperature. These observations are consistent with a model of conduction by electron hopping between localized states. Our colloids also show an increase in conductivity with the application of a magnetic field. This conductivity enhancement is believed to result from field-induced agglomeration and particle chaining.

I. INTRODUCTION

The effect of electric and magnetic fields in various configurations on fine particles is of current interest.[1-3] It is known that fine magnetic particles show unique behavior both with and without fields present. In particular, fine iron oxide particles have attracted much attention from a scientific as well as a technological viewpoint. Yet little work exists on colloidal iron oxide particles because of the difficulties in preparation and handling of the colloidal dispersions.

In this paper we report the results of our study of α-Fe_2O_3 colloids in the presence of electric and magnetic fields. The electrical conductivity of α-Fe_2O_3 colloids in concentrations from 0.04 to 4 vol % was investigated. The colloid conductivity as a function of temperature (from 77 to 300 K), frequency (up to 10 kHz), and magnetic field (up to 7 kOe) is reported.

II. PREPARATION AND EXPERIMENT

Polyhedral hematite (α-Fe_2O_3) particles were prepared by combining 0.018 $\mathrm{mol\,dm^{-3}}$ $FeCl_3$ with 1×10^{-3} $\mathrm{mol\,dm^{-3}}$ HCl. The solution was placed in a preheated oven at 100 °C and aged for 24 h. The resulting dispersion was repeatedly washed using doubly distilled water and the particles separated by centrifugation. The final aqueous suspension contained 6.5 $\mathrm{mg/cm^3}$ of α-Fe_2O_3 particles with average diameter 0.065 μm.

After rinsing the dispersion twice with distilled water, the isoelectric point (i.e.p.) of the polyhedral hematite was at pH 4.3. Repeated washing of the powder sample with distilled water raised the i.e.p. to pH 7.5. The electric conductivity measurements were carried out at $p\mathrm{H} \sim 10$, which rendered the hematite negatively charged. The samples were shaken in an ultrasonic bath in order to ensure a uniform concentration throughout. The complete preparation procedure has been described elsewhere.[4]

The dc conductivity measurements were carried out using a Keithley 610 electrometer. The ac measurements were made using the standard technique on samples in a four-terminal geometry. The conductivity was determined by an impedance method to within ±0.94% using two measuring cells designed in our laboratory. The measurements were taken from 77 to 300 K and in the frequency range 50 Hz–10.0 kHz. The low-temperature experiments were carried out in a cryostat which can provide constant temperature to within ±0.01 K from 4 K to 400 K. The temperature was measured by a previously calibrated platinum thermoresistor. Magnetic fields up to 7 kOe were produced by a magnet (type 875) from Cenco Manufacturing and measured with a gaussmeter (model 620, F.W. Bell, Inc.).

An equivalent circuit for the experimental setup is shown in Fig. 1. For this network, the (measured) impedance is related to the equivalent resistance R and capacitance C of the sample as

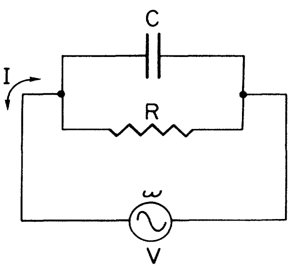

FIG. 1. The equivalent circuit of a sample used in the measurement of ac conductivity.

$$Z=\frac{V}{I}=\left[\left[\frac{1}{R}\right]^2+(\omega C)^2\right]^{-1/2}=\frac{R}{\sqrt{1+(\omega CR)^2}}\ . \tag{1}$$

C was estimated using the relation

$$C=\epsilon\epsilon_0\frac{A}{d}\ ,$$

where ϵ is (the real part of) the dielectric constant of the sample, A the active area of the test cell, and d the thickness of the sample. The (cylindrical) geometry of the test cell is such that $A/d<10^{-3}$ m, and $\epsilon\sim 100$, typically. Thus C is quite small ($\sim 10^{-12}$ F). Moreover, since R is in the range 10^3-10^5 Ω, the term $\omega CR \ll 1$ for $\omega<10$ kHz, and the approximation $Z\approx R$ is a good one even at the highest frequencies studied.

III. RESULTS AND DISCUSSION

A. dc conductivity

The dc conductivity at 77 K of our colloidal samples was measured for α-Fe_2O_3 concentrations of 0.4 and 4 vol %. The conductivity was observed to increase from about 2×10^{-10} to more than 8×10^{-10} S cm^{-1} over this concentration range.

The temperature dependence of dc conductivity $\sigma(0,T)$ for α-Fe_2O_3 colloids in concentrations of 0.4 and 4 vol % is shown in Fig. 2, where $\ln\sigma(0,T)$ is plotted vs $1000/T$. The conductivity of both samples is seen to increase sharply above $T\simeq 210$ K. An exploded view of the curves above and below this temperature is presented in Figs. 3(a) and 3(b), respectively. For temperatures above 210 K, a dc conductivity of the form

$$\sigma_{\mathrm{dc}}=\sigma_0 e^{-\Delta E/kT} \tag{2}$$

is observed, corresponding to activated conduction with activation energy ΔE ranging from 0.687 eV (0.4 vol %) to 1.030 eV (4 vol %). In the temperature regime below 210 K, our data suggest a hopping contribution to the conductivity described by

$$\sigma_{\mathrm{dc}}=\sigma_1 e^{-w/kT}, \tag{3}$$

where $\sigma_1<\sigma_0$ and w is the hopping energy. Such a contribution can be expected whenever localized states are present at the Fermi energy, with w on the order of half the bandwidth for the localized levels.[5,6] For our colloidal samples, the hopping energy varies from 1.810×10^{-4} eV (0.4 vol %) to 2.864×10^{-4} eV (4 vol %). Notice that w is small but increases with Fe_2O_3 content, suggesting that the localized states arise from the dispersed hematite. While the large interparticle separation in the colloid ($\sim 10^3$ Å) would argue against hopping conduction via the dispersed phase alone, we note that

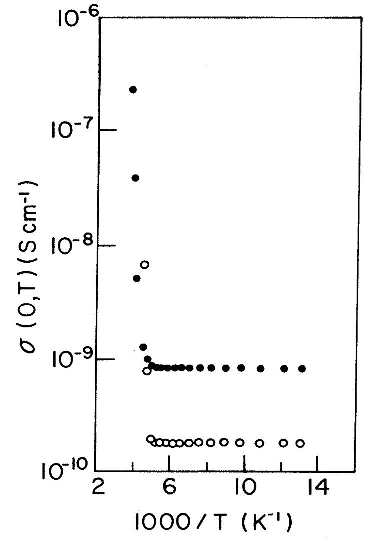

FIG. 2. Temperature dependence of dc conductivity $\sigma(0,T)$ of two α-Fe_2O_3 colloids (○, 0.4 vol %; ●, 4 vol %).

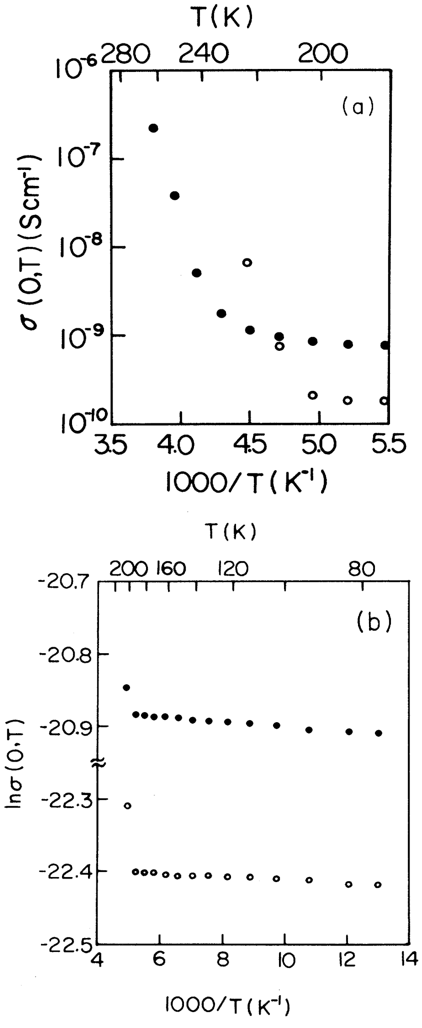

FIG. 3. Exploded view of the dc conductivity of two α-Fe_2O_3 colloids (○, 0.4 vol %; ●, 4 vol %) showing the transition from (a) thermally activated conduction above $T\simeq 210$ K to (b) hopping conduction below this temperature. In both regimes the conductivity varies exponentially with inverse temperature.

this average separation is subject to large statistical fluctuations, i.e., *at the microscopic level, the colloidal dispersion is decidedly nonuniform.* Nor can we discount the presence of the aqueous host, which could facilitate hopping in some (as yet unknown) way. In summary, then, while the data below 210 K speak for some sort of hopping model of dc conduction, the exact hopping mechanism is by no means apparent. By contrast, a hopping mechanism involving only the dispersed hematite can explain the observed ac conductivity dependence on temperature and frequency, as discussed in greater detail below.

B. ac conductivity

Figure 4 shows the volume concentration dependence of the conductivity of our α-Fe_2O_3 colloids at a frequency of 1 kHz. As in the dc case, the conductivity increases with increasing concentration. Notice, however, that the conductivity at 1 kHz is orders of magnitude larger, and the dependence on volume concentration is decidedly nonlinear.

Figure 5 shows the sample conductivity as a function of temperature at fixed frequencies of 50 Hz, 100 Hz, 1 kHz, and 10 kHz for α-Fe_2O_3 colloids at the 0.4 vol % concentration level. In discussing the frequency-dependent response, it has become commonplace to write for the conductivity

$$\sigma(\omega,T)=\sigma_{dc}+\sigma^{p}(\omega),$$

where the first term on the right is the dc conductivity, and σ^p denotes the so-called pair approximation to the frequency-dependent response. The theoretical justification for this decomposition is reviewed by Long.[7] We adopt this convention here, along with the somewhat questionable practice of referring to σ^p as simply the ac conductivity. Essentially, Fig. 5 portrays the ac component σ^p, since the dc conductivity is much smaller than the conductivity actually measured at the frequencies given.

Characteristically, σ^p is much larger than σ_{dc} at most frequencies, but is strongly frequency dependent and vanishes in the dc limit. The frequency dependence of ac conductivity is customarily expressed by a power law of the form

$$\sigma^p \propto \omega^s . \tag{4}$$

Data from this study appear to confirm this relationship over the temperature range 77–233 K. The index s is determined from the log-log plots of Fig. 6, and is found to be slightly less than unity, and increasing with decreasing temperature.

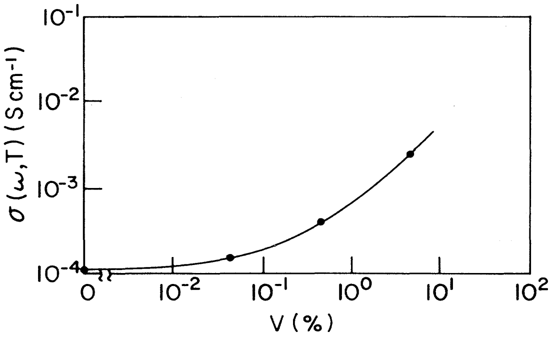

FIG. 4. The ac conductivity $\sigma(\omega,T)$ of α-Fe_2O_3 colloids as a function of particle concentration. The measurements were taken at 1 kHz and 295 K.

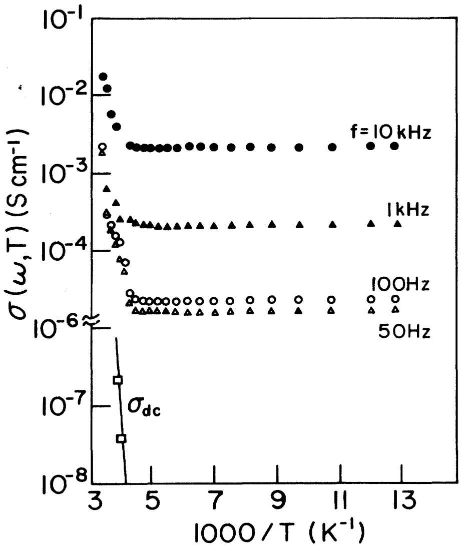

FIG. 5. Temperature dependence of ac conductivity $\sigma(\omega,T)$ of α-Fe_2O_3 colloid at a concentration of 0.4 vol %, for four fixed frequencies (●, 10 kHz; ▲, 1 kHz; ○, 100 Hz; △, 50 Hz).

The observed frequency dependence of the ac conductivity is consistent with the correlated barrier-hopping (CBH) model, first introduced by Pike[8] in the study of

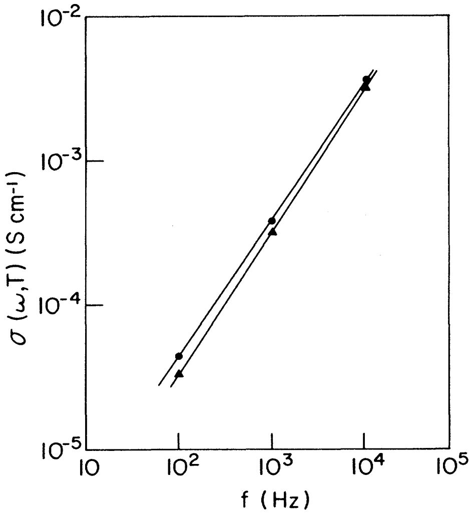

FIG. 6. Frequency dependence of ac conductivity $\sigma(\omega,T)$ of α-Fe_2O_3 colloid at a concentration of 0.4 vol %, at two fixed temperatures (▲, 77 K; ●, 233 K).

scandium oxide films. In CBH the charge carrier (read electron) is assumed to hop *over* the potential barrier separating neighboring localized sites, as opposed to tunneling *through* that barrier. The two alternatives lead to markedly different predictions for s: in the case of tunneling, s ranges somewhere between 0.4 and 0.8, and is temperature independent, while for CBH, s is only slightly less than unity and decreases with increasing temperature. Following Pike, CBH was applied to a variety of systems, and even adapted by Elliott[9,10] to electron *pair* hopping in chalcogenides. Particularly relevant to the present study is the work on iron oxides[11] and borate glasses containing Fe_2O_3.[12] The hopping conductivity in these materials is presumed due to the presence of ferric ions having more than one valency. (For the borates, a band model is assumed for the glass, with localized states residing in the energy gap.) A fraction c of these are occupied by electrons (corresponding to Fe^{2+}) and a fraction $1-c$ are therefore empty (Fe^{3+}). Conduction occurs by an electron hopping directly between occupied $Fe^{2+}$and unoccupied Fe^{3+} sites. The same ideas should apply to our colloids in the frozen state (below 273 K), but with two caveats: first, the mixed valence condition of Fe_2O_3 which fixes the hematite conductivity can result from impurities and/or deviations from stoichiometry, and likely is influenced by the preparation procedure for the hematite particles. Second, since the conductivity of the (aqueous) colloidal matrix is comparable to that of the dispersed hematite, the colloid represents a true multiphase system (composite) with conductivity intermediate between those of its component phases. In what follows, we assume that the observed conductivity *changes* (with temperature, frequency, etc.) can be largely understood in terms of the dispersed hematite alone.

The CBH model gives for the hopping conductivity between localized states forming a narrow band:[7]

$$\sigma^p = \frac{\pi^3}{24} N^2 \epsilon\epsilon_0 \omega R_\omega^6, \tag{5a}$$

with

$$R_\omega = \frac{e^2}{\pi\epsilon\epsilon_0[W_m + kT\ln(\omega\tau_{oh})]}, \tag{5b}$$

a hopping distance varying with both temperature and frequency. Here N is the number density of localized states, W_m the energy required to remove the electron from the site (into extended states), and τ_{oh} a relaxation time for hopping, assumed to be on the order of the inverse Debye frequency. Equations (5) can be coerced into the form of Eq. (4) with

$$s = \frac{\partial(\ln\sigma)}{\partial(\ln\omega)} = 1 - \frac{6kT}{W_m + kT\ln(\omega\tau_{oh})}. \tag{6}$$

This expression for s is consistent with the behavior observed for our α-Fe_2O_3 colloids. The logarithmic term in the denominator is usually ignored in CBH applications, and is arguably small compared to W_m over the range of temperatures and frequencies studied. (Reported values for τ_{oh} range anywhere from 10^{-13} to 10^{-6} s. In the worst case, $\tau_{oh} \sim 10^{-13}$ s and $\omega = 10^4$ Hz, giving $\ln\omega\tau_{oh} \simeq -20$. Actual values could easily be half this, leading to the criterion $W_m \gg 10kT$.) Table I shows the values for s deduced from our measurements at several temperatures. The results are in good agreement with Eq. (6) for $W_m = 2.35 \pm 0.4$ eV. With this value for W_m, a hopping distance can be calculated from Eq. (5b). Notice, however, that the dielectric constant ϵ there is *not* that of the colloid, since hopping presumably occurs between Fe sites of mixed valence, and these might well be found within the same particle. More than likely, we should expect $\epsilon \sim 1-10$, leading to a hopping distance $R_\omega \sim 10$ Å, comparable to the distance between neighboring Fe sites in bulk hematite ($\simeq 3$ Å).

For the temperature dependence of the ac conductivity, the CBH model predicts

$$\sigma^p \propto \omega^s T^n,$$

where the temperature index n is related to the frequency index s at the same temperature and frequency by

$$n = -(1-s)\ln(\omega\tau_{oh}). \tag{7}$$

We see from Table I that s is itself temperature dependent and quite close to unity. This, along with the uncertainty in the value to be used for τ_{oh}, seriously complicates any meaningful comparison of theory with experiment. At low frequencies, we expect n to be quite small ($\sim 10^{-1}$), and this, at least, is in rough accord with our experimental findings.

C. Magnetic-field dependence

The conductivity of α-Fe_2O_3 colloids in the liquid phase shows an interesting magnetic-field dependence. For fields in transverse orientation, the ac conductivity increases with magnetic-field strength. The data of Fig. 7 were gathered as the magnetic field was ramped from 0 to 7.5 kOe continuously at the rate of 5 Oe/s. Data were taken at ≈20 s intervals up to 1 kOe, and at ≈100 s intervals thereafter. The increase in conductivity persisted up to the largest fields studied, but at a pace which progressively diminished, suggesting eventual saturation (see Fig. 7). (Physical limitations made it impossible for us to study the longitudinal configuration, where the applied magnetic field is along the direction of current flow. Previous work[13] suggests the conductivity may be expected to *decrease* in this case.) With increasing particle concentration, the relative change in electric conductivity becomes larger. These phenomena are reproducible.

The response of the α-Fe_2O_3 colloids to changes in

TABLE I. Values for s deduced from different temperature measurements.

T(K)	s
77	0.9823
123	0.9790
213	0.9761
233	0.9496

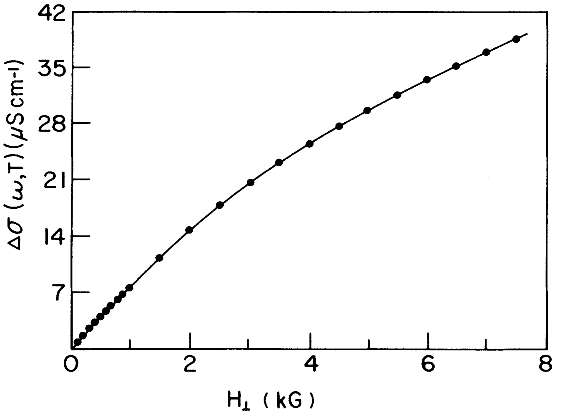

FIG. 7. The change in ac conductivity of α-Fe_2O_3 colloid at a concentration of 4 vol %, in the presence of a transverse magnetic field. These measurements, at 1 kHz and 295 K, were taken at ≈ 1 min intervals as the magnetic field was ramped from 0 to 7.5 kOe at a rate of 5 Oe/s.

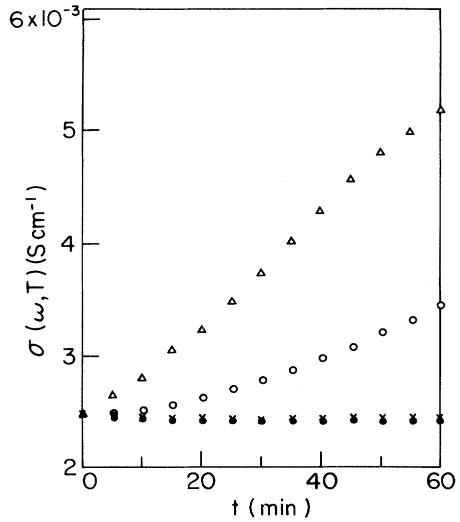

FIG. 8. Variation of ac conductivity with time t for α-Fe_2O_3 colloid at a concentration of 4 vol % subject to a transverse magnetic field (●, $H_\perp = 0$; ×, $H_\perp = 500$ Oe, ○, $H_\perp = 4$ kOe; △, $H_\perp = 5.5$ kOe). All measurements were taken at 1 kHz and 295 K.

magnetic-field strength is very sluggish. Figure 8 shows the conductivity at 1 kHz of the 4 vol % sample as a function of time for magnetic fields of four different strengths, including $H_\perp = 0$. In this connection, we emphasize that the data for Fig. 7 were taken at intervals much shorter than the time scale for the changes depicted in Fig. 8.

Conductivity enhancements resulting from the application of a magnetic field to α-Fe_2O_3 colloids have been reported before, and attributed to an orientational polarization of the dispersed (spindle-shaped) particles, resulting in increased or decreased particle mobility, depending upon the field configuration.[13] No such effect is anticipated in our samples, where the hematite particles are nearly spherical in shape. Moreover, the conductivity changes of Fig. 7 are an order of magnitude larger than those previously reported; the changes seen in Fig. 8 over the long term are much larger still.

However, field-induced particle agglomeration is known to occur in these systems, and is strongly affected by particle size and shape, applied field strength, and ionic strength of the dispersion.[14] According to Chikazumi *et al.*,[15] agglomeration occurs in several stages: the dispersed particles are assumed to be well separated in the colloid when the magnetic field is zero. With the application of a weak magnetic field, the particles tend to form tiny microclusters. Further increase in the field results in the growth and agglomeration of these microclusters to form macroclusters. In a strong magnetic field, the macroclusters continue to enlarge and repel each other to form chains.

We believe our observations are related to such agglomeration and chaining. Since bulk hematite is known to be a semiconductor,[16] ordered chains would provide more effective paths for conduction. Further, such chains, once formed, might not easily be broken, accounting for the sluggish response of the system when the magnetic field is reduced, or even removed. With hematite particle sizes on the order of 0.06 μm, previous work suggests that applied fields in the kOe range will be needed to induce chain formation.[14,17] This estimate is consistent with the data of Fig. 8, where no discernible time dependence is seen in the low-field (500 Oe) case, but is certainly evident at the larger field values ($H_\perp \geq 4$ kOe).

Explaining the data of Fig. 7 is more problematic. Perhaps even the initial stages of agglomeration would enhance the conductivity, but this is by no means obvious.

IV. CONCLUSION

The dc and ac electrical conduction of α-Fe_2O_3 colloids in varying concentration has been reported as a function of frequency, temperature, and strength of applied magnetic field. The measured conductivities are consistent with a model of electron hopping between localized states. The ac conduction obeys a power law of the form $\sigma(\omega, T) \propto \omega^s T^n$, and can be interpreted on the basis of the correlated barrier model discussed by Pike. The effect of a magnetic field applied perpendicular to the current flow is to enhance the electrical conduction. The increased conductivity may result from field-induced agglomeration to form chains, resulting in more effective conducting paths.

ACKNOWLEDGMENT

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