CHAPTER VII

COLLOIDS OF CALCIUM FERRITE AND NICKEL FERRITE
CHAPTER VII

COLLOSOLS OF CADMIUM FERRITE AND NICKEL FERRITE

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REFERENCES
So far we have described magneto-optical effects shown by iron oxide sols as well as by copper ferrite and cobalt ferrite colloids. The effects shown by these increase uniformly to a saturation value with increasing field strength and then become practically independent of the applied field. Effects observed in cadmium ferrite and nickel ferrite sols are, however, remarkably different from those mentioned above. In these sols, the magneto-optical effects increase at first to a maximum value, and then decrease with a further increase in the field strength, reach zero and finally reappear with a reversed sign. Figures 45, 46 show the typical effects that were observed in cadmium and nickel ferrite sols. The magnitude of the field strength necessary to obtain maximum effect is denoted by $H_N$ and the field at which the reversal occurs is denoted by $H_{1/2}$; and collectively they may be called the Characteristic fields. These field-strength values (i.e. $H_N$, $H_{1/2}$) are two important parameters useful in subsequent calculations.

Historically, Majorana and number of other workers had observed this type of unusual behaviour especially in iron oxide sols prepared and studied under various conditions. (Ref. 1). Various explanations were put forward but none
convincing except the explanation given by Keller (Ref. 2). Here it should be pointed out that similar type of reversal behaviour was also observed in the electro-optical effects of bentonite suspensions (Ref. 3). Recently Shah has suggested a very convincing explanation for the reversal in electro-optical effects in bentonite suspensions (Ref. 4).

Preparation of Sol.

Cadmium ferrite and nickel ferrite were precipitated by the method described by Scheule and Begtschek (Ref. 5). Thus, in the case of cadmium ferrite sol, an equivalent mixture of the solutions of cadmium chloride and ferric chloride was precipitated by adding a calculated amount of hot sodium hydroxide reagent. Precipitates thus obtained were washed with water in centrifuge. Peptization was done using concentrated hydrochloric acid (2-3 drops only). The peptised sol was agitated on a mechanical shaker for about half an hour. The sol thus prepared was not subjected to dialysis but was stored in a pyrex flask. Similarly nickel ferrite was prepared by employing an equivalent mixture of the solutions of nickel chloride and ferric chloride. The colloids prepared by this method did not show high stability and the sedimentation was observed after six months of storage.

To a considerable extent, the magneto-optical effects
were found to depend on the preparation method adopted and on the ageing procedure. Peptization of freshly precipitated ferrites and subsequent ageing at room temperature gave the sols in which observable effects appear only after a couple of months. Artificial ageing of the precipitates by boiling (along with the reagent in an unwashed state) for an hour and subsequent peptization gave a colloidal sol in which effects were observed much earlier. Effect of similar hydrothermal treatment of precipitates on the magnetic properties of ferrites is also reported by Schuler and Deetschuck who correlates it with the growth in particle size (Ref. 5). In the present work, the fresh precipitates were peptized and the sols were subsequently allowed to age at room temperature, particularly because it was felt desirable to have crystal growth in isothermal equilibrium conditions.

Freshly prepared sols showed neither birefringence nor absorption changes. When observed after four months, appreciable changes were observed in both the cases (figure no. 39 and 40). These figures show that there was no reversal up to 100 k-gauss field; however, the effects show a continuous decrease after reaching a maximum value at around 3.0 k-gauss. Thereafter, reversal would have been observed if larger fields (more than 15.0 k-gauss) were available. After a further ageing of one month the sols started to show reversal phenomenon; the characteristic fieldstrength \( F_N \) being
Cadmium Ferrite

Before and after reversal

$Q \text{ vs. } H \quad \lambda: 5500 \ \text{Å}$

$H$: field strength (in X-gauges)

Longitudinal Relation

Prepared in: Dec. 66

Observed in: 1) March 67; 2) April 67

before reversal after reversal

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<th>$Q$</th>
<th>$H$</th>
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9.0 k-gauss in both the cells for absorption as well as for birefringence measurements. On further ageing, the colloids developed high turbidity and at the same time the colour changed from red to grass yellow. Still further ageing resulted in the phase separation such that the yellow sediment was found at the bottom. The liquid phase was still a colloid with red colour.

The most important feature in the magneto-optical effects in these colloids requiring a particular attention, is the reversal in sign. The two characteristic field strengths $H_1$ and $H_2$ were observed to depend markedly on the temperature at which the experiment was carried out, and also on the size of the particles.

The dependence on the temperature could only be qualitatively investigated, because experimental arrangements to maintain the cell at uniform lower temperature could not be made. Qualitatively the effect was observed at a temperature of $\sim 15^\circ$ C. (room temperature being $35^\circ$ C.). To prevent the formation of dew on the sides of the cooled cell, special design was adopted as shown in margin. Arms $T_1$ and $T_2$, of glass tubing were cemented to the cell in a dessicator after slight heating to drive off all moisture. Windows $W_1$ and $W_2$ remained at around the room temperature but
the specimen cell containing sol was at a lower temperature. The cell was wrapped with iron foil and rigidly fixed to the metal base to ensure good conduction of heat. It was observed that the fields \( H_M \) and \( H_H \) were lower at lower temperature.

After about 12 months of ageing, phase separation was observed in the sol and yellowish sediment collected at the bottom leaving reddish collosol at the top. Both the clear sol as well as the suspension formed by shaking the precipitates showed magneto-optical effects and the reversal in their sign. The field strengths \( H_M \) and \( H_H \) were, however, much different. The suspension formed from the sediment contained presumably coarser particles and showed magneto-optical effects in which \( H_M \) and \( H_H \) were lower than those obtained with the clear sol.

This preliminary study is summarized in a tabular form below:
## Table No. 7.1

**Characteristic fields $H_{II}$ and $H_{III}$ at different periods for Cadmium Ferrite Sol**

(A) Observations at room temperature

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<th>Ageing period</th>
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<th>18 months</th>
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<td>$F_{II}$ (in k-gauss)</td>
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<td>$F_{III}$ (in k-gauss)</td>
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(B) Observations at different temperatures

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<tr>
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<td>(ii)</td>
<td>(iii)</td>
<td>(i)</td>
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<tr>
<td>Temperature (°C)</td>
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<td>$30^\circ$</td>
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<tr>
<td>$F_{II}$ in k-gauss</td>
<td>2.4</td>
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<td>$F_{III}$ in k-gauss</td>
<td>5.7</td>
<td>6.2</td>
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The tables indicate that the field strengths required to attain reversal depends considerably on the size of the particles as well as on the temperature of observation (table B).

As mentioned earlier, reversal in the sign of magneto-optical effects have been also observed for certain specimen of iron oxide sols (Ref. 6). One specimen of the iron oxide sol prepared by peptization (with HCl) of the precipitates obtained by adding NaCl has been studied by Desai in this laboratory showed similar reversal phenomenon, the results of which are discussed in the present thesis (Ref. 7). In electro-optical effects also, a reversal in the sign occurring on increasing the electric field strength has been observed for the suspensions of bentonite (Ref. 3,4). To explain the reversal in the sign of electro-optical effects and magneto-optical effects different workers have suggested a variety of possibilities like:

(i) polydispersity ; (ii) presence of two separate species of particles ; (iii) action of anisotropy and anisotropy ;
(iv) existence of two orthogonal torques etc. (Ref. 8).

Most probable mechanism is the one suggested by Heller (Ref. 8) who considered the simultaneous action of two torques viz. dipolar moment \( \omega \) and the induced anisotropic moment \( \chi = (\chi_0 - \chi_o) \), both being perpendicular to each other. Recently, Shah (Ref. 4) has worked out a
complete theory for such cases to explain the reversal observed in bentonite suspensions. Same theory can also be used here to explain the reversal in magneto-optical effects. Expressions given by Shah are rather complicated and not convenient for calculations. The explicit form of the function given by Shah is (Ref. 4);

\[ \phi = \frac{3}{4h^2} \left[ \frac{\beta^2}{2\gamma^2} + 1 + \frac{\exp\left(\frac{\beta^2}{4\gamma^2} - \eta\right)}{1} \frac{\left(\frac{\beta}{\gamma} + \frac{\beta}{\gamma^2} - 2\sqrt{\eta}\left(\frac{\beta}{\gamma} + \frac{\beta}{\gamma^2}\right)\right)}{1} \right] - \frac{1}{2} \]

where, (i) \( \beta = -\frac{\mu E}{kT} \) (ii) \( \gamma = (\alpha_2 - \alpha_1) \frac{E^2}{kT} \) (iii) \( I = \int \exp(-x^2) dx \)

(iv) \( t_1 = -\frac{\gamma}{2\sqrt{\gamma}} \) (v) \( t_2 = \sqrt{\gamma} - \frac{\beta}{2\sqrt{\gamma}} \) (vi) \( \mu = \text{dipole moment} \)

(vii) \( E \) is the electric field; (viii) \( 2 \cdot 1 \) are the principal components of electrical polarizability.

This expression when written in our notations is:

\[ \phi = \frac{3}{4h^2} \left[ \frac{h_1^2}{2h_2^2} + 1 + \frac{\exp\left(\frac{h_1^2}{4\gamma^2} - \eta\right)}{1} \frac{-h_1 \left(\frac{h_1 - h_2}{2h_2^2} + \frac{h_1 + h_2}{2h_2^2}\right) - h_2^2 (e - e^2)}{E_t} \right] - \frac{1}{2} \]

where, \( h_1 = -\beta \); \( \sqrt{\gamma} = h_2 \); \( I = E_t \)

In place of function \( \phi \) defined above, we have preferred to use a function \( P(h_1, h_2) \) given on the next page. \( P(h_1, h_2) \) function is more convenient for calculations and is also related to \( L(h), M(h) \) functions used in this work (pp. 77).
\[ P(h_1, h_2) = \frac{1}{2h_2^2} \left[ 1 + \frac{(t_1 + t_2)^2}{2} + \frac{t_1 e^{-t_2} - t_2 e^{-t_1}}{h_2} \right] \]

where, (i) \( t_1 = [-h_2 - \frac{h_1}{2h_2}] \); (ii) \( t_2 = [h_2 - \frac{h_1}{2h_2}] \)

(iii) \( E_t = (E_{t_1} - E_{t_2}) = \left[ \int_{0}^{t_1} e^{-x^2} dx \right] - \left[ \int_{0}^{t_2} e^{-x^2} dx \right] \)

(a) \( h_1 = \frac{\omega B}{kT} \); (b) \( h_2 = \left[ \frac{(\chi_0 - \chi_e) \cdot V}{2kT} \right] \cdot h_2 \)

(1) \( B \) = magnetic field; (2) \( \omega \) = dipolar moment;

(3) \( (\chi_0 - \chi_e) \) = induced anisotropic magnetic susceptibility.

This function is used to calculate \( P(h_1, h_2) \) values for different \( h_1/h_2 \) ratios. Calculated values are given in the table no. 5 (pp.219). The figure no. 41 shows these values plotted as \( P(h_1, h_2) \) vs. \( h_2 \).

The relationship between \( \phi \) and \( P(h_1, h_2) \) functions is:

\[ 2\phi = [3P(h_1, h_2) - 1] \]
Determination of $\omega$ and $(\chi_0 - \chi_o)^{1/2}$ from $H_i$ and $H_i^2$

It has already been pointed out that, from the experimentally observed values of $H_i$ and $H_i^2$, one can determine both the magnetic moment $\omega$ per particle and anisotropy parameter $(\chi_0 - \chi_o)^{1/2}$ per particle. Procedure is explained below:

The family of curves $P(h_1, h_2)$ vs. $h_2$ (figure 41) for different ratios $h_1/h_2$ shows one pair of points $(h_1, h_2)$ at which $P(h_1, h_2)$ attains a maximum value and another pair of $(h_1', h_2)$ at which $P(h_1, h_2)$ is $1/3$. The second pair indicates a point at which the magneto-optical effects temporarily vanish i.e. the reversal point. We can, therefore, plot two loci as $h_1$ vs. $h_2$ plots.

(i) locus for points $h_1, h_2$ appropriate to maximum in the magneto-optical effects.

(ii) locus for points $h_1', h_2'$ appropriate to reversal of sign in the magneto-optical effects. (figure no. 42).

Now both $h_1$ and $h_2$ are proportional to $H$. Therefore, of all the pair of points on the locus of reversal graph, if a particular set of $h_1, h_2$ is appropriate to the field strength $H_i^2$, then multiplying them by $H_i^2/H_i$ we should get a set $h_1', h_2'$ which is on the locus $P(h_1', h_2') = \text{maximum}$. To obtain therefore, a graphical solution of the problem, following
## TABLE No. 5.

Table of $P(h_1, h_2)$ vs. $h_2$ for different values of the ratio $\frac{h_1}{h_2}$

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<th>$\frac{h_1}{h_2}$</th>
<th>$h_2$</th>
<th>$P(h_1, h_2)$</th>
<th>$\frac{h_1}{h_2}$</th>
<th>$h_2$</th>
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procedure can be adopted:

(i) locus of points $h_1, h_2$ appropriate to $P(h_1, h_2) = \text{maximum}$ is first plotted.

(ii) pairs of points $h_1, h_2$ appropriate to reversal i.e. $P(h_1, h_2) = 1/3$ are multiplied by $\frac{H_{13}}{H_{12}}$ and a reduced pairs of points $h'_1 = h_1(\frac{H_{13}}{H_{12}})$ and $h'_2 = h_2(\frac{H_{13}}{H_{12}})$ are obtained.

Curve of the points $h'_1, h'_2$ is then plotted which is, thus, locus of the reversal points plotted on a scale reduced by $h'_1/h'_2$. The intersection of this curve with the curve of $P(h'_1, h'_2) = \text{maximum}$ give a set $h'_1, h'_2$ which is correct set appropriate to the field strength $F_M$ (figure no. 47). Using the relations:

$$h'_1 = \frac{\omega \cdot H_{13}}{H_{12}}$$
$$h'_2 = \left[ \frac{(\chi_0 - \chi_c) \cdot V}{2kT} \cdot H_{12}^2 \right]^{1/2}$$

and $(\chi_0 - \chi_c) \cdot V$ are calculated.

**Determination of shape-factor**

To obtain particle shape one needs the values $(Q_L - Q_R)_\infty$ and $(\delta)_\infty$ to start with. Since in this case the magneto-optical effects do not increase uniformly to the saturation value on increasing the field strength, the saturation values can not be extrapolated merely by extrapolation $H \rightarrow \infty$ of the experimental data. Following
modification of the comparison of log-log graphs of theoretical expressions and experimental data can, however, be used to determine the saturation magneto-optical effects.

Intersection points \( h_1^0, h_2^0 \) in the figure 47 give \( h_1, h_2 \) appropriate to the field strength \( H_1 \). It also gives the ratio \( h_1/h_2 \) appropriate to a particular sol under study.

We, now select the graph \( P(h_1, h_2) \) vs. \( h_2 \) appropriate to this ratio \( h_1/h_2 \) (figure no. 41) and convert \( h_2 \) values to \( H \) values multiplying them by \( H_1/h_2^0 \). We thus get a graph of \( P(h_1, h_2) \) vs. \( H \) with \( h_1/h_2 \) appropriate to the observed ratio and in which the points \( P(h_1, h_2) = \text{maximum} \) and \( P(h_1, h_2) = 1/3 \) are matched to the fields \( H_M \) and \( H_A \) on the experimental graph.

Now we plot:

(i) \( \log_{10} \left[ P(h_1, h_2) - 1 \right] \) vs. \( \log_{10} H \); and

(ii) \( \log_{10}(Q_L - Q_R) \) vs. \( \log_{10} H \) or

\( \log_{10} \delta \) vs. \( \log_{10} H \)

Abscissae of the two graphs are already matched now and only the ordinate shift is required to superpose theoretical graph on experimental graph. The shift \( \bar{Y} \) along the ordinate necessary for superposition can be used to determine saturation values. Thus

\[ \text{antilog } \bar{Y} = (Q_L - Q_R) \text{ or } (\delta)_{\infty} \]
**RESULTS**

Figure 39 shows the changes in the optical absorption of cadmium ferrite sol observed at 5500 Å. The curve (i) refers to the sol studied after four months of ageing; the effects exhibit maximum but no reversal. The second set of curves (i.e. curve (ii)) refer to the same sample studied after five months of ageing. The effects are distinctly better developed and show a maximum as well as the reversal in sign.

Figure 40 shows similar graphs for colloidal of nickel ferrite. The graph (i) refers to the effects observed after five months of preparation, while graph (ii) refers to the effect observed after eight months of ageing.

Figure 43 shows birefringence in the cadmium ferrite sol aged four months. The values of maximum and reversal fields are the same as those observed for the changes in the optical absorption.

In the case of nickel ferrite sol, birefringence was studied when the ageing was incomplete (viz. five months) and the results are shown in the figure 44.

Figure 45 shows the changes in the optical
Figure No. 44(a)

Nickel ferrite

$\delta$ vs $H$ before reversal

$H$: field strength (in $\text{Ko}$.gauss).

Figure No. 44(b)

(i) $\log_{10} \delta$ vs $\log_{10} H$

$\lambda$: 5893 Å

(ii) $\log_{10} (Q_i - Q_p)$ vs $\log_{10} H$

$\lambda$: 6500 Å

Nickel ferrite

Only experimental values are plotted in this figure in order to show the nature of the log-log curve.
absorption of cadmium ferrite at different wavelengths. The magnitudes of the effect observed at different wavelengths do not differ appreciably and the differences observed can be accounted for by an experimental error, mainly due to the error in the value of the extinction cross-section $C_0$ used for calculations of $Q$. This fact is supported by the nickel ferrite sol in which the absorption changes were measured at two different wavelengths. The magnitudes of effect were found to be equal which can be easily verified from the figure no. 46.

The results observed at two different periods of ageing are shown mainly for qualitative comparison and further calculations given below pertain only to the results obtained with the sols aged for not less than five months. The results are summarized in the tabular form as given below:

**TABLE No. 7.2**

**CHARACTERISTIC FIELDSTRENGTHS**

<table>
<thead>
<tr>
<th>Sol</th>
<th>Observation</th>
<th>$H_{11}$ (in k-gauss)</th>
<th>$H_N$</th>
<th>$H_{11}/H_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO₆Fe₂O₃</td>
<td>Abs. change</td>
<td>2.95</td>
<td>9.0</td>
<td>0.33</td>
</tr>
<tr>
<td>CdO₆Fe₂O₃</td>
<td>Birefringence</td>
<td>2.95</td>
<td>9.0</td>
<td>0.33</td>
</tr>
<tr>
<td>Ni₆Fe₂O₃</td>
<td>Abs. change</td>
<td>3.4</td>
<td>9.0</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Concerning the applicability of Rayleigh theory, we note that $Q_X$ and $Q_R$ were found to be only approximately equal (figure is not given); but Langevin relation is obeyed viz.

For, (i) CdO·Fe$_2$O$_3$  
\[ Q_L = \frac{1}{1} - Q_R = 2.4 \]

(ii) NiO·Fe$_2$O$_3$  
\[ Q_L = \frac{1}{1} - Q_R = 2.4 \]

The colloidal particles may therefore be considered as Rayleigh scatterers to a reasonably satisfactory approximation.

Calculation of $\omega$ and $(X_0 - X_0)\cdot V$

Figure 47 shows the graphs of (a) $P(h_1, h_2) = \text{maximum}$ and (b) $P(h_1, h_2) = 1/3$ on a scale reduced by $I_H'/I_H'$. The point of intersection gives following results:

\[
\omega \quad \text{and} \quad (X_0 - X_0)\cdot V \quad \text{from intercepts on the graph (Fig. 46)}
\]

\[
\begin{array}{ccccccc}
\text{Sample} & h_1 & h_2 & H_{||} & \omega & (X_0 - X_0)\cdot V \\
\hline
\text{CdO·Fe}_2\text{O}_3 & 20.01 & 2.46 & 2.95 & 281 \times 10^{-13} & 5.76 \times 10^{-20} \\
\text{NiO·Fe}_2\text{O}_3 & 11.4 & 1.94 & 3.4 & 135.2 \times 10^{-18} & 2.7 \times 10^{-20} \\
\end{array}
\]
Figure No. 47.

Determination of $h_1$ and $h_2$

using $P(h_1, h_2)$ maximum & $P(h_1, h_2)$ reversal graphs

\[ h_1 \]

\[ h_2 \]

--- 

Ni O Fe$_2$O$_3$

Cd O Fe$_2$O$_3$
Determination of particle size

Knowledge of particle size or volume is necessary if the saturation magnetization \( I_0 \) or the magnetic anisotropy \( (\chi_e - \chi_o) \) are required. Hence, the particle sizes were estimated by methods described earlier, viz. (i) extinction method, (ii) dissymmetry ratio method, (iii) angular Rayleigh ratio \( (R_{90^\circ}) \) method. Results are summarized in a table below:

<table>
<thead>
<tr>
<th>TABLE No. 7.1</th>
</tr>
</thead>
</table>

PARTICLE SIZE BY LIGHT SCATTERING METHODS

(radius \( r \) in cm.)

<table>
<thead>
<tr>
<th>Extinction method</th>
<th>Dissymmetry method</th>
<th>( R_{90^\circ} ) scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (1) ) ( \text{CdO}_{2}\text{Fe}_2\text{O}_3 ) (a) ( 235 \times 10^{-8} )</td>
<td>( 605 \times 10^{-3} )</td>
<td>( 304 \times 10^{-3} )</td>
</tr>
<tr>
<td>(b) ( 294 \times 10^{-3} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( (ii) ) ( \text{MnO}_{2}\text{Fe}_2\text{O}_3 ) (a) ( 323 \times 10^{-8} )</td>
<td>( 467 \times 10^{-3} )</td>
<td>( 298 \times 10^{-3} )</td>
</tr>
<tr>
<td>(b) ( 395 \times 10^{-8} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a), (b): Values determined at different periods of ageing

The saturation magnetization \( (I_0) \) and anisotropic susceptibility \( (\chi_e - \chi_o) \) are calculated using the volume \( (V) \)
of the particle as determined by extinction method. The results are given below:

<table>
<thead>
<tr>
<th>Volume (V)</th>
<th>( \chi_0 - \chi_e )</th>
<th>( I_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO.Fe(_2)O(_3)</td>
<td>(1.07 \times 10^{-13} \text{ cc.} )</td>
<td>(5.38 \times 10^{-4} )</td>
</tr>
<tr>
<td>NiO.Fe(_2)O(_3)</td>
<td>(2.53 \times 10^{-13} \text{ cc.} )</td>
<td>(1.05 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

**Determination of particle shape-factor**

For cadmium ferrite, the intersection method gives \( h_1/h_2 = 8.14 \); and for nickel ferrite it gives \( h_1/h_2 = 5.72 \).

Figures 43, 49 compare the graphs of

(i) (a) \( \log(\epsilon_0 - \epsilon_R) \) vs. \( \log \epsilon_1 \) (experimental)
(b) \( \log \delta \) vs. \( \log \epsilon_1 \) (experimental)
(ii) \( \log \left[ 3P(h_1,h_2) - 1 \right] \) vs. \( \log \epsilon_1 \)

(theoretical for \( h_1/h_2 = 8.14 \) and 5.72.)
where the value of \( B \) in curve (ii) are calculated from corresponding \( h_2 \) such that the maximum in \( P(h_1, h_2) \) will occur at \( h_1 = 2.95 \) (p. 227).

Figure 49 shows similar graph for nickel ferrite with \( h_1/h_2 = 5.72 \), and \( h_1 = 3.4 \) k-gauss.

In both the cases, the shift \( \bar{y} \) along ordinate leads to the following values:

### TABLE No. 2.6

**SATURATION MAGNETO-OPTICAL EFFECTS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \bar{y} )-shift</th>
<th>( (Q_L - Q_R)_{\infty} )</th>
<th>( (\delta)_{\infty} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) ( \text{CdO}_x\text{Fe}_2\text{O}_3(q) )</td>
<td>-1.16</td>
<td>0.69x10^{-1}</td>
<td>-</td>
</tr>
<tr>
<td>(ii) ( \text{Mn}_x\text{Fe}_2\text{O}_3(q) )</td>
<td>-0.53</td>
<td>2.95x10^{-1}</td>
<td>-</td>
</tr>
</tbody>
</table>

Assuming the particles to be optically isotropic, particle shapes are worked out and are given in the following table; larger magnitude of effects in cadmium ferrite sol indicate fairly elongated particles.
Figure No. 48

$\log_e (Q_Q_0) = \log_e H$

Cadmium ferrite

$\lambda 6000 \AA$

Scale for experimental graph

$\log_e (Q_Q_0)$ vs. $\log_e H$ Experimental,

$\log_e [1 + \sin(\omega t)]$ vs. $\log_e H$ Theoretical

prepared in Dec. 68
observed in April 67
Figure No. 49
Cadmium ferrite

Scale for experimental graph:

$\log_{10} \delta$ vs. $\log_{10} H$ (experimental).

$\log_{10}[3P(h, k, l) - 1]$ vs. $\log_{10} H$ (theoretical).

Prepared in Dec. 66.
Observed in April 67.
Figure No 50

Nickel ferrite

\[ \log_{10}(Q_{L} - Q_{R}) \text{ vs. } \log_{10}H \]

\[ \times 5500, 4500 \text{ cu.} \]

- Scale for experimental graph:

- prepared in: Oct '66
- observed in: May '67

- \[ \log_{10}(Q_{L} - Q_{R}) + 0.53 \text{ Y-axis} \]
**TABLE No. 7.7**

<table>
<thead>
<tr>
<th>Sol</th>
<th>$(Q_L - Q_R)_0$</th>
<th>$(\delta)_0$</th>
<th>$\frac{\text{Im} \alpha}{\text{Im} \alpha_0}$</th>
<th>$\text{Re}(\alpha - \alpha_0)$</th>
<th>$L_0$</th>
<th>$a/b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) CaO·Fe$_2$O$_3$</td>
<td>-0.069</td>
<td>0.23</td>
<td>1.14</td>
<td>0.134</td>
<td>(Q) 0.305</td>
<td>1:11</td>
</tr>
<tr>
<td>(11) NiO·Fe$_2$O$_3$</td>
<td>-0.295</td>
<td>-</td>
<td>1.75</td>
<td>-</td>
<td>(δ) 0.275</td>
<td>1:24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.215</td>
</tr>
</tbody>
</table>

$a/b = \text{major/minor axis}$

**DISCUSSION**

The colloids of cadmium and nickel ferrites, thus, exhibit remarkable magneto-optical effects vis. with an increase in the field strength the effect reaches maximum and then starts decreasing and finally undergoes reversal.

In the theory presented above and the calculations described, it is assumed that the reversal in the magneto-optical effects is a consequence of an actual reversal in the orientation of the particles brought about by the action of
two orthogonal torques. However, alternative possibilities should also be considered.

Such reversal in the magneto-optical effects can also occur if the dispersed system is a mixture of two types of particles - one fraction showing a positive magneto-optical effect and the other fraction showing negative effect. Then, if the net effect (i.e., saturation value) of the fraction which requires comparatively larger fields for orientation then a reversal in the sign of magneto-optical effect may be observed (Ref. 8). This possibility appears unlikely in the present case for the following reasons:

(i) Relative contribution to birefringence and dichroism for two fractions will not be the same in general. Hence the field strength $H_M$ at which the effects are maximum and the field strength $H_B$ at which the reversal occurs will in general be different for the experiments involving measurements of transmission changes than those observed in the experiment involving the measurement of birefringence.

(ii) Similarly, since the two fractions will have, in general different spectral properties, the characteristic values $H_M$ and $H_B$ may also be expected to depend upon the wavelength of observation.

Since our observations clearly show that the fields $H_M$ and $H_B$ are the same whether one studies birefringence or absorption changes, and also they are independent of the wavelength of observation, we conclude that the observed
reversal in magneto-optical effect is a consequence of actual reversal in the orientation of individual particles themselves.

The above argument also rules out the possibility of reversal being the result of polydispersity of the particles—coarser particles being oriented orthogonally w.r.t. the finer particles. Our studies on other collosols (Ref. 9) indicate that coarser particles of absorbing nature show strong dichroism but weak birefringence whereas finer particles show both dichroism and birefringence. Under such conditions one would expect \( L_{\parallel} \) and \( L_{\perp} \) to be different for birefringence and for absorption changes.

(iii) Considering the reversal in the orientation of individual particles, it has also been suggested (Ref. 3) that such a reversal can be due to a torque due to anisometry acting orthogonal to the torque due to anisotropic magnetic susceptibility.

Expression for the potential energy of an anisotropic spheroid is given by the expression:

\[
U_\theta = -\frac{M}{2} \left[ (\chi_e - \chi_o) + 4\chi_o \cdot \chi_e \cdot (L_o - L_e) \right] \cdot \cos^2 \phi
\]

First term is the contribution of anisotropy and the second term gives the contribution of anisometry. Since \( \chi_o, \chi_e \) are the order of \( 10^{-5} \) to \( 10^{-6} \), second term is far too small to give significant orientation at fields of the
order of few kilogauss viz. In graphite dispersions (Ref. 9),
\[\chi_C \chi_C = 10^{-12}, \quad (\chi_C - \chi_C) = 4 \times 10^{-7}, \quad (L_C - L_C)\]
can assume a maximum value of unity only.

Further, both the torques depend on the square of the field strength \(H\); hence even when they are comparable and opposite, reversal in orientation will not occur unless two fractions in the dispersed system are assumed with different properties.

To compare, the expression for the potential energy of a dipole anisotropic particle is:

\[U = -\omega \mu \cos \theta + \left[\frac{(\chi_C - \chi_C)}{2} \cdot \mu H^2 \cdot \sin^2 \theta\right]\]

Here reversal becomes possible because part I is proportional to \(H\); whereas part II is proportional to \(H^2\).

Considering all these aspects it seems most appropriate to use the model of dipolar anisotropic particle to explain the observed magneto-optical effects in colloids of cadmium and nickel ferrites.

Lastly, the size-dependence and the temperature dependence of the characteristic values \(H_{II}\) and \(H_{II}\) may be considered.

Observations at two different temperatures give \(\omega\)
and \( \chi_0 - \chi_e \), \( V \). Of these, \( \omega \) is expected to be independent of the temperature, but the anisotropy \( \chi_0 - \chi_e \) will, in general, be temperature dependent (Ref. 10). Following table compares \( \omega \) and \( (\chi_0 - \chi_e), V \) observed at two different temperatures for the sols of the same age.

### TABLE No. 7.8

**EFFECT OF TEMPERATURE ON MAGNETIC MOMENTS OF THE PARTICLES**

**\( \text{Cdo. Fe}_2\text{O}_3 \text{ SOL} \)**

<table>
<thead>
<tr>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( h_1 )</td>
<td>( h_2 )</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>300°K</td>
<td>10.7</td>
</tr>
<tr>
<td>285°K</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Regarding size dependence we have:

1. \( h_1 = \frac{\omega H}{kT} = \frac{[\chi_0 - \chi_e] V/kT}{H_M} \)
2. \( h_2 = \left[ \frac{(\chi_0 - \chi_e) V}{2kT} \right] \cdot H_M \)
Therefore, if $I_0$ and $(\chi_0 - \chi_c)$ are independent of the temperature, the ratio $\frac{h_4}{h_2}$ will be larger for the coarser particles. This need not hold good however, since both $I_0$ and $(\chi_0 - \chi_c)$ will depend, in general, on the particle size also.

**Iron Oxide Precipitated by NaCl**

In earlier studies on the magneto-optical effects carried out in this laboratory it was observed that a sample of iron oxide sol prepared and studied by Desal (Ref. 11) showed similar reversal in the magneto-optical effects (figure no. 51). This colloidal was prepared by peptization method. Iron oxide was precipitated by adding NaCl to the concentrated solution of ferric chloride. The freshly precipitated oxide was washed repeatedly and finally peptized using minimum quantity of HCl. The solution was dialysed and then stocked (Thesis pp. 31). The observations were taken after two months of ageing. Changes in the optical transmission were only studied, and are shown in the figure which is reproduced from the Ph.D. thesis of Desal (Thesis pp. 106).
Graph of $Q$ vs. $H$

Iron Oxide Sol

Field Strength $H$ (in k-gauss)

Reproduced from: Ph.D. thesis of

Re$O_3$ prepared by precipitation by $NaOH$;

peptized with $HCl$;

and observed after 2 months of aging

Qesal J.N. (1964)

submitted to Gujarat University.
In his thesis Desai suggests that this type of behaviour can be due to the presence of at least two chemically different types of suspended particles, probably $\alpha$-$\text{Fe}_2\text{O}_3$ and $\alpha$-$\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (Thesis pp. 107). In the light of our results on cadmium ferrite and nickel ferrite it appears more likely that in this case also joint action of the two torques — one due to permanent moment and the other due to induced moment — can give more satisfactory explanation. Calculations carried out on this basis are summarized below.

The nature of $Q$ vs. $H$ curve is quite similar to that observed in cadmium ferrite and nickel ferrite sols (Figure no. 51). Here field strength $H_1 = 1.95$ and $H_2 = 4.2$ k-gauss; it gives the ratio $h_1^2/h_2^2 = 0.464$. Proceeding as shown on the page 218, $h_1$ and $h_2$ were calculated and came out to be 11.8 and 3.12 respectively. Particle size being unknown, only $\omega$ and $(\chi_0 - \chi_e) V$ could be determined. With $h_1 = 11.8$; $h_2 = 3.12$ at $H_1 = 1.95$ k-gauss, one gets $\omega = 251 \times 10^{-13}$; $(\chi_0 - \chi_e) V = 21.2 \times 10^{-20}$.

Saturation value of $(Q_L - Q_R)$ was also determined by the method described on pp. 222. The individual values of $h_1$ and $h_2$ mentioned in the above paragraph gives the ratio $h_1/h_2 = 3.8 \times P(h_1, h_2)$ function corresponding to this ratio $h_1/h_2$ is calculated (pp. 219 for values). Using these values the theoretical graph of $\log_{10} \left[3P(h_1, h_2) - 1\right]$ vs. $\log_{10} H$
Iron Oxide penetration method.

Graph of:

\[ \log_{10} \left( \frac{3P_{f} \beta h_{1}}{l} \right) = \log_{10} H \]

\[ \log_{10} \left( \frac{Q_{1} - Q_{w}}{Q_{w}} \right) = \log_{10} H \]

Scale for experimental graph:

- \( \log_{10} (Q_{1} - Q_{w}) + 1.6 \) vs \( H \)
is drawn exactly as for cadmium ferrite and nickel ferrite. The experimental values are plotted as $\log_{10}(Q_L - Q_H)$ vs. $\log_{10}H$ and superposed on the theoretical graph after an appropriate shift $\bar{Y}$ along the ordinate. Figure 52 gives $\bar{Y} = -1.16$ which gives $(Q_L - Q_H)_{\infty} = 0.069$. Using this saturation value, the shape-factor is derived.

Low field direction of orientation is with the magnetic moment parallel to the field and at higher fields induced moment dominates and orienting particles with their permanent moment orthogonal to the field.

Since hematite crystals are known to carry residual magnetization in the basal plane i.e. perpendicular to the symmetry axis (Ref. 12); we assume here that at saturation, the colloidal particles are oriented with their symmetry axis parallel to the field i.e. permanent moment is orthogonal to the field. $Q_H > Q_L$ means that the symmetry axis is the shorter dimension of the particle i.e. the particles are oblate spheroids.

$(Q_H - Q_L)_{\infty} = 0.069$ gives $\frac{\ln \alpha}{\ln \alpha_0} = 0.936$

For optically anisotropic hematite crystals, this corresponds to

$L_e = 0.375; L_o = 0.313$ and $\frac{\text{minor axis}}{\text{major axis}} = \frac{a}{b} = 0.86$

It is clearly recognised that uncertainty in the
precise knowledge regarding the orientation of the direction of the permanent moment with respect to the geometrical symmetry axis of the particle does not permit unique interpretation of the results in terms of its shape. Some results could alternatively be explained by assuming the particles to be elongated along the symmetry axis (i.e., prolate spheroids) if the moment is assumed to be parallel to the symmetry axis. It seems highly desirable to develop some alternative method to decide a priori, whether the particles are flattened or elongated. Magneto-optical effects can then give the exact degree of flattening or elongation, where the necessary facility exists electron microscopy can, of course, give this information. But it seems desirable to develop some alternative method requiring simple experimental set-up.
REFERENCES

1. (a) (1) Majorana, Q. R. Accademia Nazionale d. Lincei II, 1° Sem. 374, 467, 470; 2° Sem. 90, 139 (1902).
   (ii) Dwell, A.W. Phys. Rev. (1903), 12, 292.
   (iii) Heller, W.
       (a) Kolloid Beilhefte (1933), 32, 1
   (iv) Heller, W. Compt. Rend. (1933), 206, 64.

(b) Tobacco mosaic virus suspensions show similar type of effects:
   Zimm, B.H.


   (ii) also refer 3 (ii)


8. (a) Polydispersity:

(i) Majorana, Q. Ref 1(a), (i).

(b) Separate species:

(ii) Heller, W. refer 1(a), (iii).

(c) Anisometry and anisotropy:


(d) Two orthogonal torques:

(ii) Shah, M.J. et al. refer (4)

(e) Other explanations:


He considers the change in the sign of magnetic anisotropy as the probable cause of orientation.
(ii) Sakamann, B.W. refer 3(i)

(iii) C'Konski, C.T.
Haltner, J.J.


(ii), (iii) consider it a cause of interaction between the particles at high concentrations.

9. (i) Shah, H.S.
Desai, J.N.
Naik, Y.C.


(ii) Desai, J.N.


10. Junjiro Kanamori


11. Desai, J.N.


Ch. 4, pp. 104-107.