THE UNIVERSITY OF MICHIGAN

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AN ANOMALOUS MAGNETIC TRANSITION IN POWDERED MAGNETITE

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TABLE OF CONTENTS

LIST OF FIGURES

AN ANOMALOUS MAGNETIC TRANSITION IN POWDERED MAGNETITE

INTRODUCTION

The presence of the order-disorder low temperature transition for magnetite has been known for a long time.(1) The short-range order for the cubic phase gives way to long-range order in the orthorhombic phase at approximately -153°C for very pure samples of magnetite and at lower temperatures for less pure samples.(2) Verwey et al.(3,4) investigated the feasibility of the control of the order temperature. This idea was suggested by the variance in the recorded ordering temperature for natural magnetites. Controlled oxidation was tried with synthetic magnetites used for thermistors and it was found that both a shift in the ordering temperature and electrical conductivity resulted from the partial oxidation. The theory that electrical conduction resulted from an electronic exchange in the B sublattice between the ferrous and ferric ions is now widely accepted. The short-range order which exists between the order-disorder transition and the Curie point is consistent with magnetite's semiconductor behavior in this range and the long-range order does yield the insulator behavior. The study which will be described started with the assumption that oxidation does alter the characteristics of magnetite but that the oxidation will continue with time and will eventually cause the disappearance of the transition. To examine quasi oxidized magnetite and also to stabilize the oxidation process, very small percentages of lithium were added to the magnetite system and what resulted is unusual.

EXPERIMENTAL

Preparation of Samples

The samples of lithium doped magnetite were powdered polycrystals prepared in the following fashion:

(1) Ferric oxide and varying amounts of lithium carbonate were dry-mixed with mortar and pestle until visually homogeneous. (Samples S35-55, -56a, and -56b, however, were prepared from magnetite and lithium ferrite of varying amounts.)

(2) The mixed powder was pressed into slugs at some fixed pressure with standardized dimensions.

(3) The slugs were then fired at a fixed rate and held at 1450°C for a length of time which insured complete reaction.

(4) The down-leg of the firing process was completed in a reducing atmosphere of dry nitrogen gas.

(5) The final step in the material preparation was to grind up the slugs and pass the grains through a 100 mesh screen.

Besides the doped samples tests were also run on two natural magnetites (one with an extremely high purity and the other very low purity) and on three synthetic magnetites (one with an extremely high purity prepared elsewhere(5) and two prepared in our laboratory).

Magnetic Moment Experiment

The first test run on the different samples was that of finding the magnetic moment per unit density. The powdered samples were weighed out into 4 to 6 milligram samples, placed in glass capillary tubes, and sealed to insure fixed length measurements. The complete description of the moment measuring apparatus and the following screening experiment can be found elsewhere.(6) The conditions imposed on the samples during the testing were essentially the following:

(1) The samples were cooled through the transition temperature region in the absence of a magnetic field (except where noted).

(2) The samples were held in the sub-transition temperature region for a period of about one-half hour without a magnetic field and about one-half hour with the desired field applied.

(3) The samples were then allowed to warm up through the transition region at a rate of approximately 1°C per five minutes. Force measurements were made during this phase on the sample using the balance and techniques described in the cited report.(6)

The test results were reproducible as seen in Figure 2.

Screening Experiment

The differential-thermal-analysis experiment(7) was adapted to low temperature experimentation to eliminate samples which possessed no apparent order-disorder transition. This experiment is also described elsewhere(6) and will not be detailed here. It should be pointed out that the samples could be prepared and run through this simple test in about one-half hour. The detail thermal fluctuations seen in the magnetic moment test cannot be resolved in the crude version of the DTA test which was run. The samples which exhibited no DTA transition showed no magnetic moment transition. Vestigial transitions were observed for some samples on the DTA which did not show up in the moment experiment.

RESULTS AND DISCUSSION

The following table lists the materials that were studied, the nominal mole percents for the magnetite content, the saturation magnetization per unit density at room temperature and the transition temperature measured at the peak of the DTA transition reaction on the warming leg of the test. All the "S" samples were prepared in our laboratory. The high purity synthetic sample is called Westrum(8) and the natural magnetites are Minerville and Kiruna.

SATURATION MOMENT AND DTA TRANSITION TEMPERATURE
FOR MATERIALS UNDER STUDY

Material	Percent Fe_3O_4	σ	Temperature at Peak (DTA), °C
Minerville	100(?)	87.0	-153
Westrum	100	90.4	-156
S32-80	100	88.3	-154
S35-50	100	73.3	-157
S32-66c	99.5	78.5	-158
S32-66b	99.0	67.3	-162
S35-64	98.5	50.8	-163
S35-56b	98.5	70.4	-157
S32-66a	98.0	65.8	-164
S35-63	97.0	66.4	-167
S35-56a	97.0	77.5	-163
S35-62	96.0	73.5	-176
S35-55	96.0	80.6	-167
S32-65c	95.0	78.9	No transition
S32-65b	90.0	72.5	No transition
S32-65aII	50.0	76.8	No transition
Kiruna	100(?)	94.4	No transition

Note that samples S35-55, 56a and 56b were made from the ferrites rather than from the oxide and carbonate. Minerville and Kiruna are both samples of natural magnetite.

In Figure 1 is plotted the DTA transition temperature against the nominal mole percent of magnetite. The top curve with triangular indicators arose from making the samples directly from the ferrites. The three samples indicated were all processed at the same time and indicate a loss of lithium due to its volatility(9) in the form used. The circle and x indicators mark the curve for the materials made in the conventional fashion and fired at the same time. The pluses mark the relative locations of the nominally pure samples prepared on an individual sample basis. In Figures 2 and 3 we have the reduced field magnetization curves for pure magnetite as usually measured(10) but measured in the system just described and using the testing procedures outlined. These curves are partially described in an earlier paper.(11) The counter-force current, ΔI, is the balance current required to null the balance against the force on the magnetic sample in the nonlinear magnetic field. The counter force current alone or divided by the mass of the sample will be proportional to the magnetic moment of the sample.

The curves shown in Figures 4 through 9 are not like those in Figures 2 and 3 in general shape. The normal behavior for magnetite cooled through the transition without a magnetic field applied and warmed in a moderate(11) magnetic field is to start with a low magnetization below the transition and reach the saturation magnetization at the transition point. This is shown in Figure 2. The samples shown in Figures 4 through 9 start at approximately the projected saturation value for magnetite in the low temperature range and then exhibit a decreasing magnetization just before the transition occurs. In Curve B in Figure 4 it will be noted that a magnetic history alters this abnormal low temperature behavior.

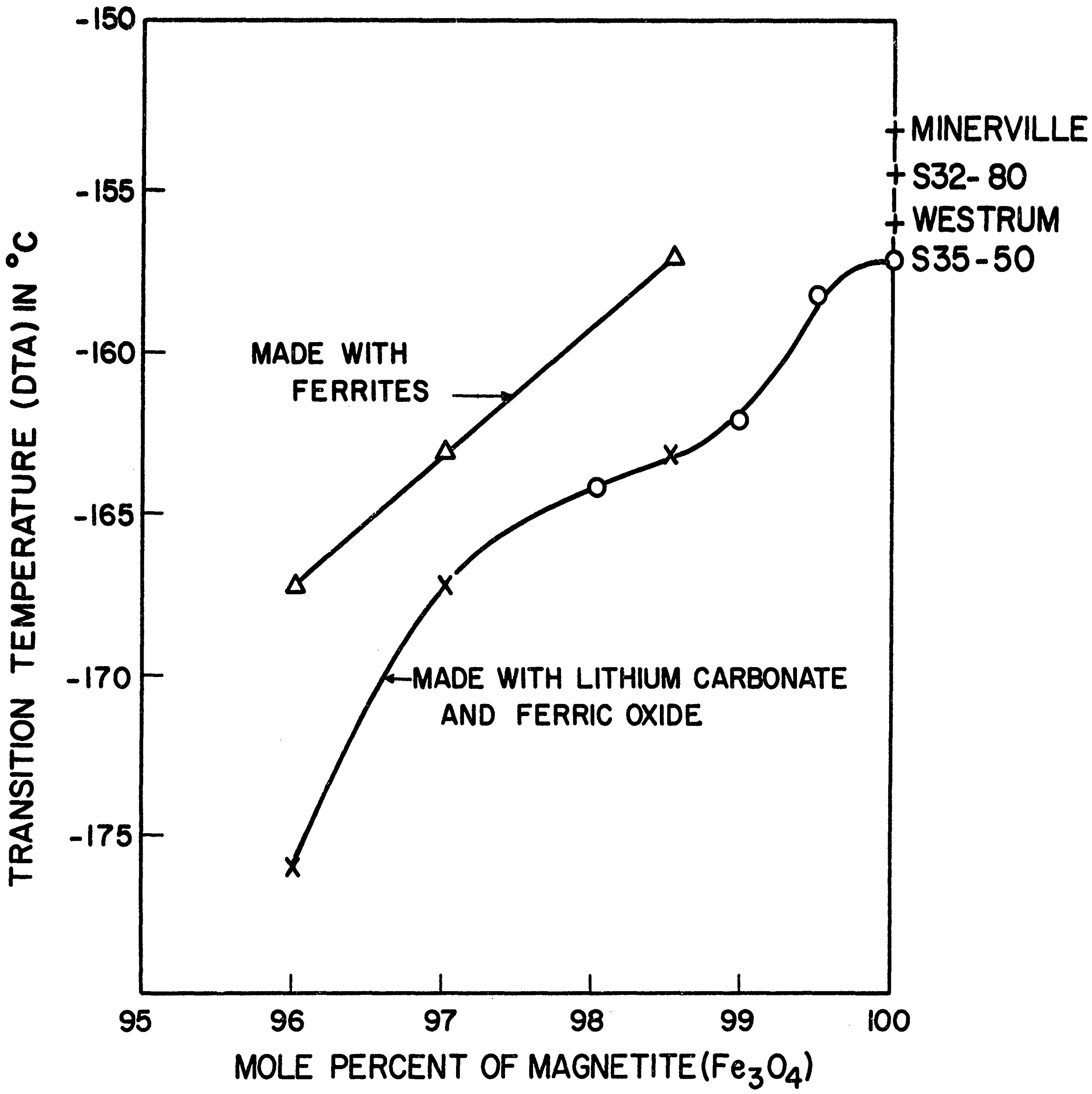

Figure 1. Transition Temperature (temperature at peak of transition on DTA warming cycle) versus Mole Percent of Magnetite.

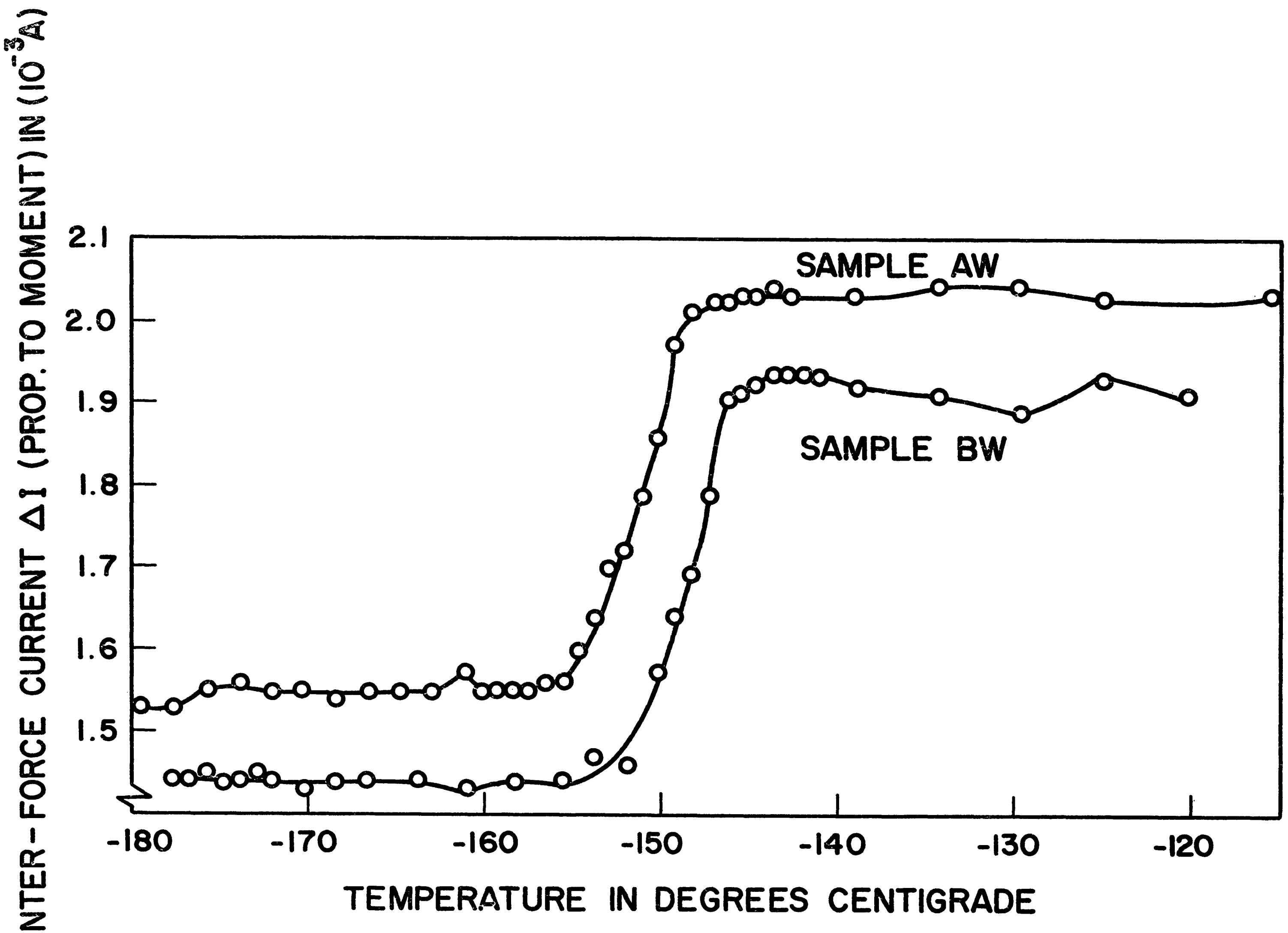

Figure 2. Counter-Force Current versus Temperature for Two Samples of Westrum Magnetite Cooled through Transition without Applied Field and Then Warmed in a Field of 1.04×10^5 A/m. Data obtained on materials just after acquisition.

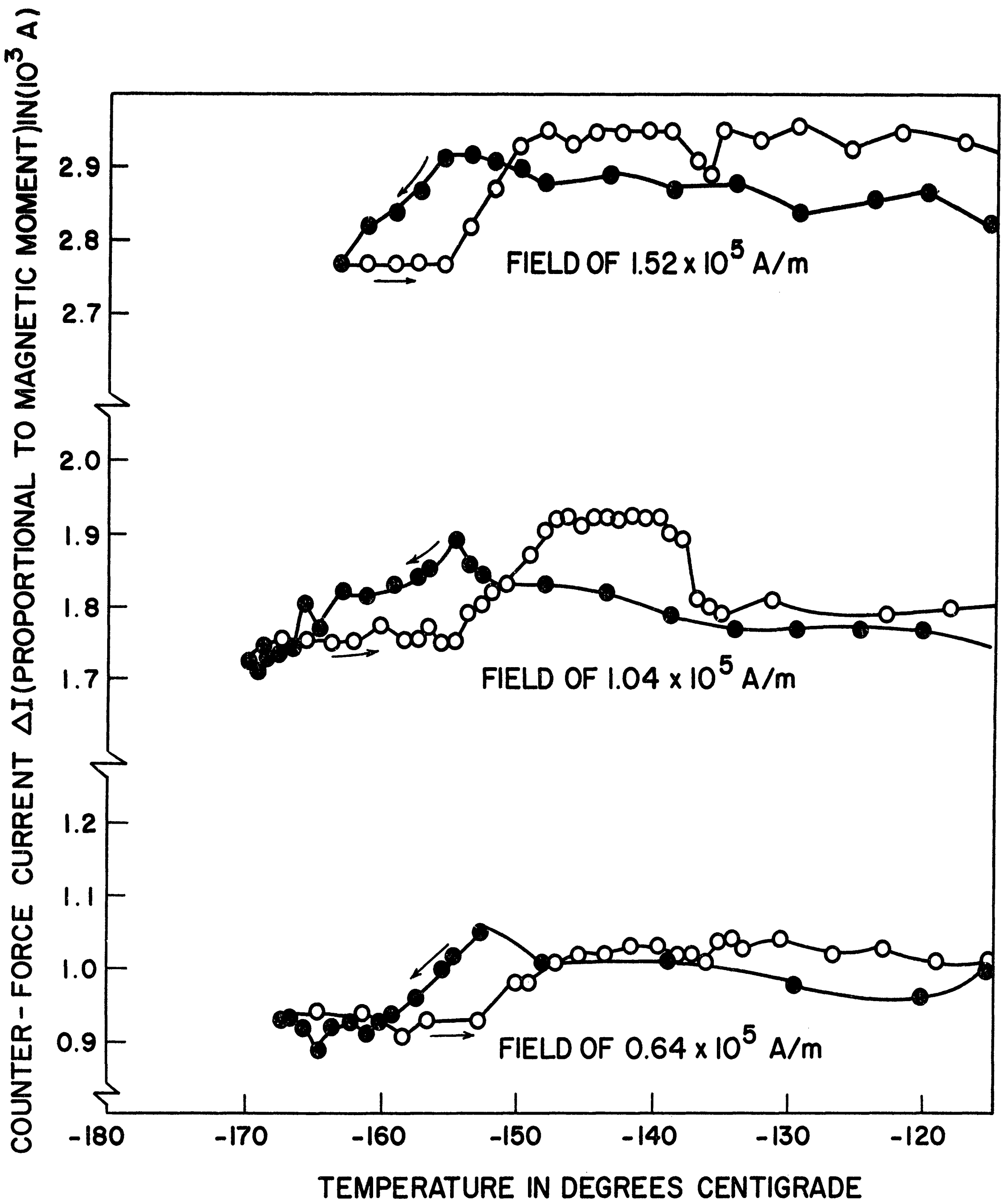

Figure 3. Counter-Force Current versus Temperature for Westrum Magnetite Cooled and Warmed in Fields as Indicated. Data obtained on material just after acquisition.

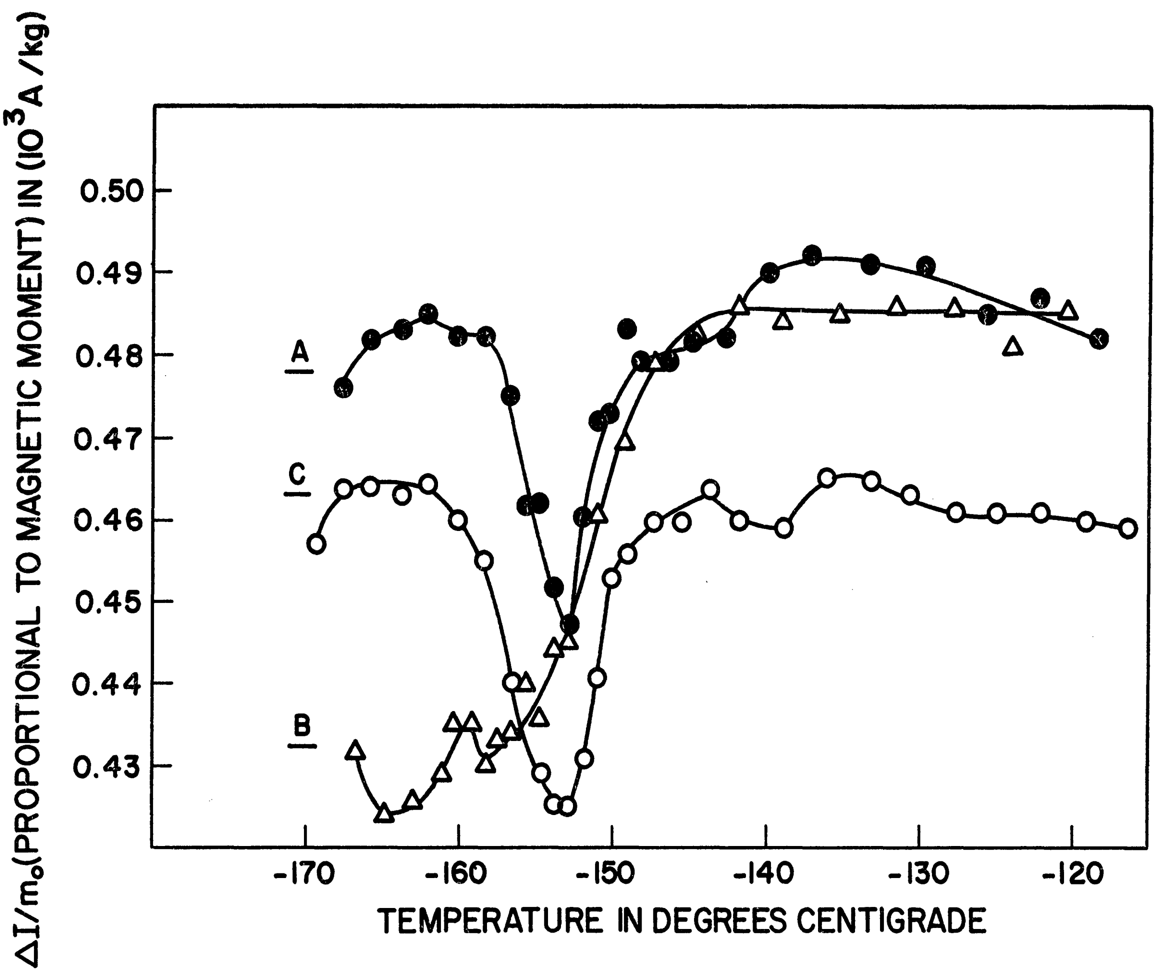

Figure 4. $\Delta I/m_0$ versus Temperature for Minerville Magnetite. Curve A - freshly ground natural magnetite. Curve B - same sample as for curve A but with magnetic history. Curve C - same sample as curve B after randomization by heating. Sample in all cases cooled through the transition region in the absence of a magnetic field and measurements taken at 1.38×10^5 A/m. ΔI is the magnetic balance counter force current and m_0 is the mass of the sample.

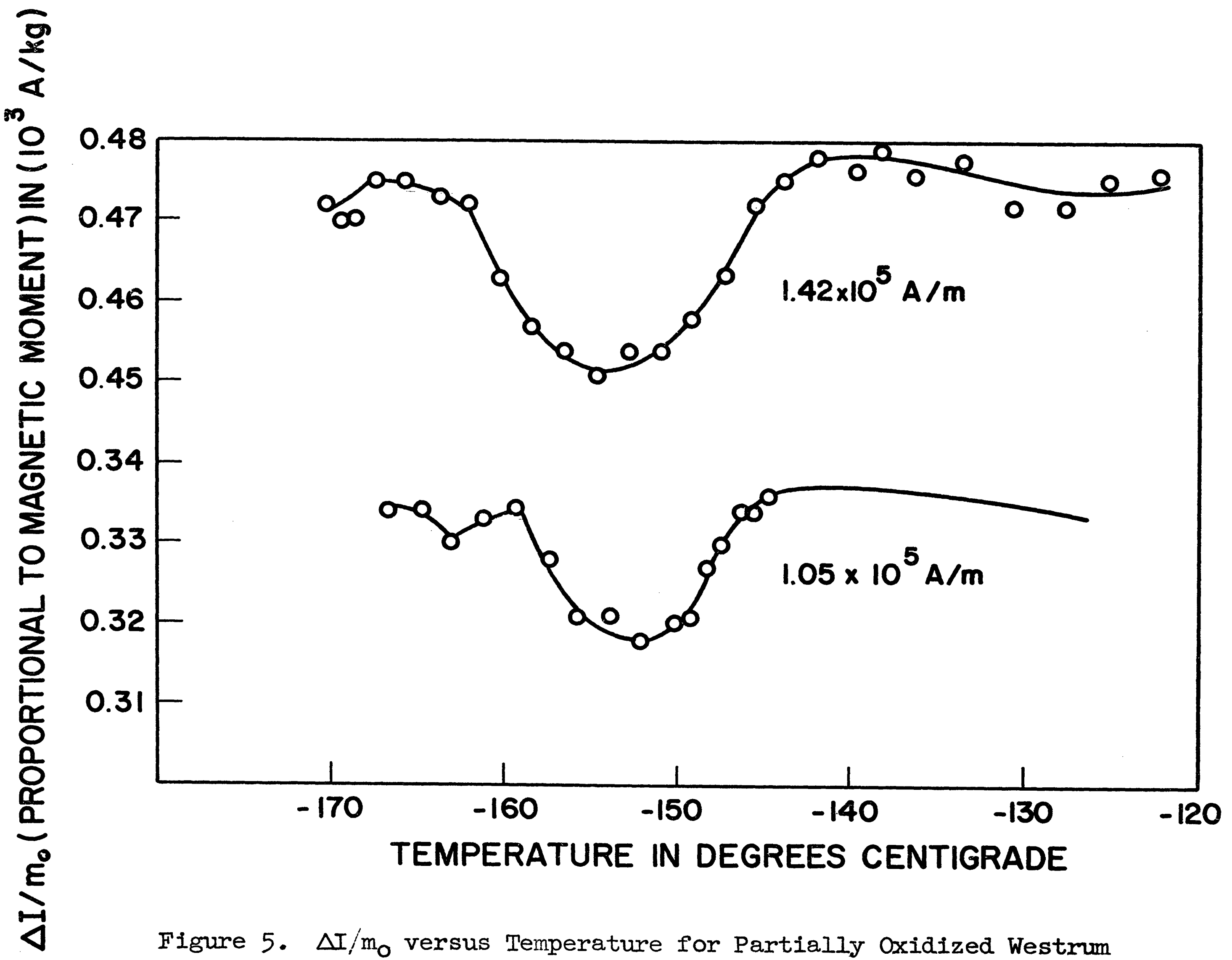

Figure 5. $\Delta I/m_0$ versus Temperature for Partially Oxidized Westrum Magnetite. Both curves the result of cooling through the transition in the absence of an external field and then warming in fields as indicated.

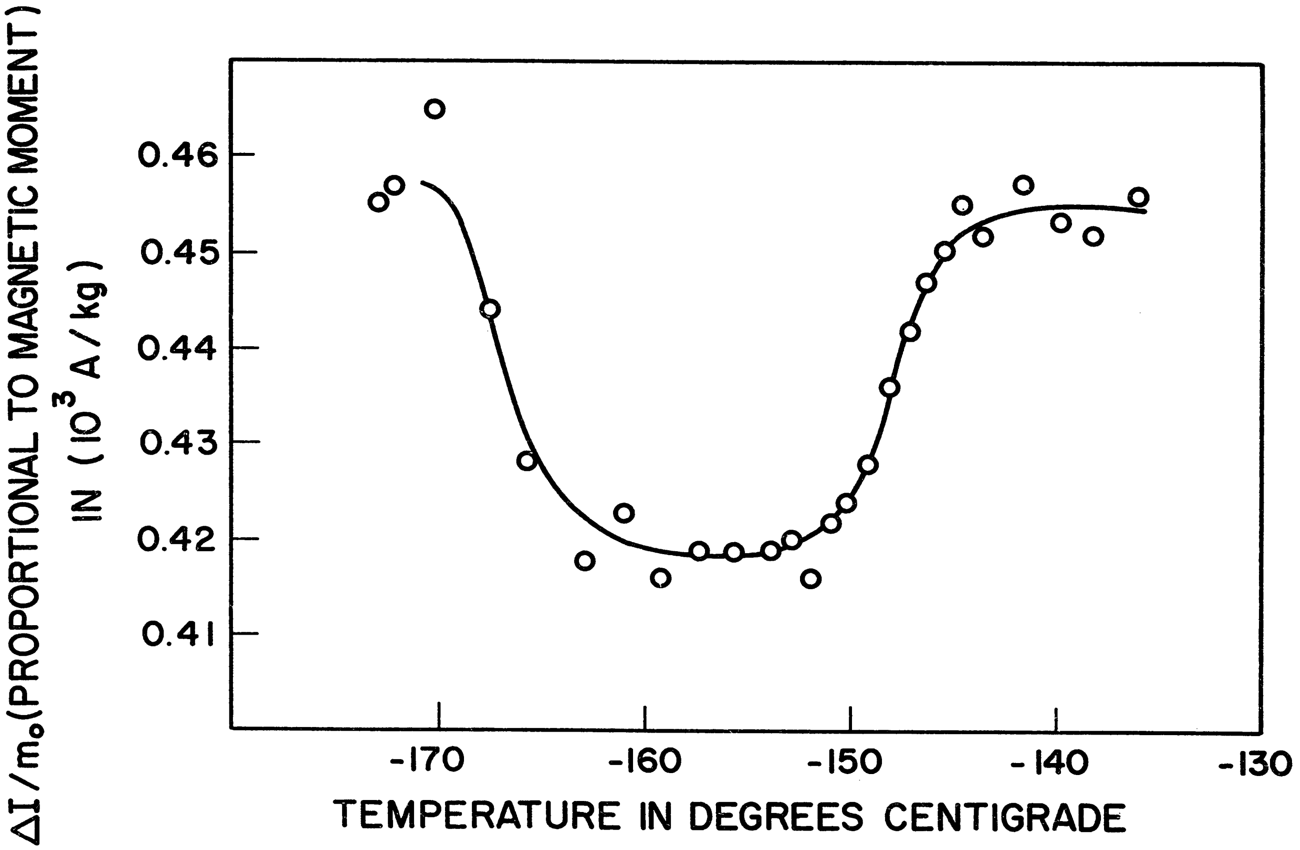

Figure 6. $\Delta I/m_o$ versus Temperature for S32-80. Sample cooled in the absence of an external field and then warmed in a field of 1.38×10^5 A/m.

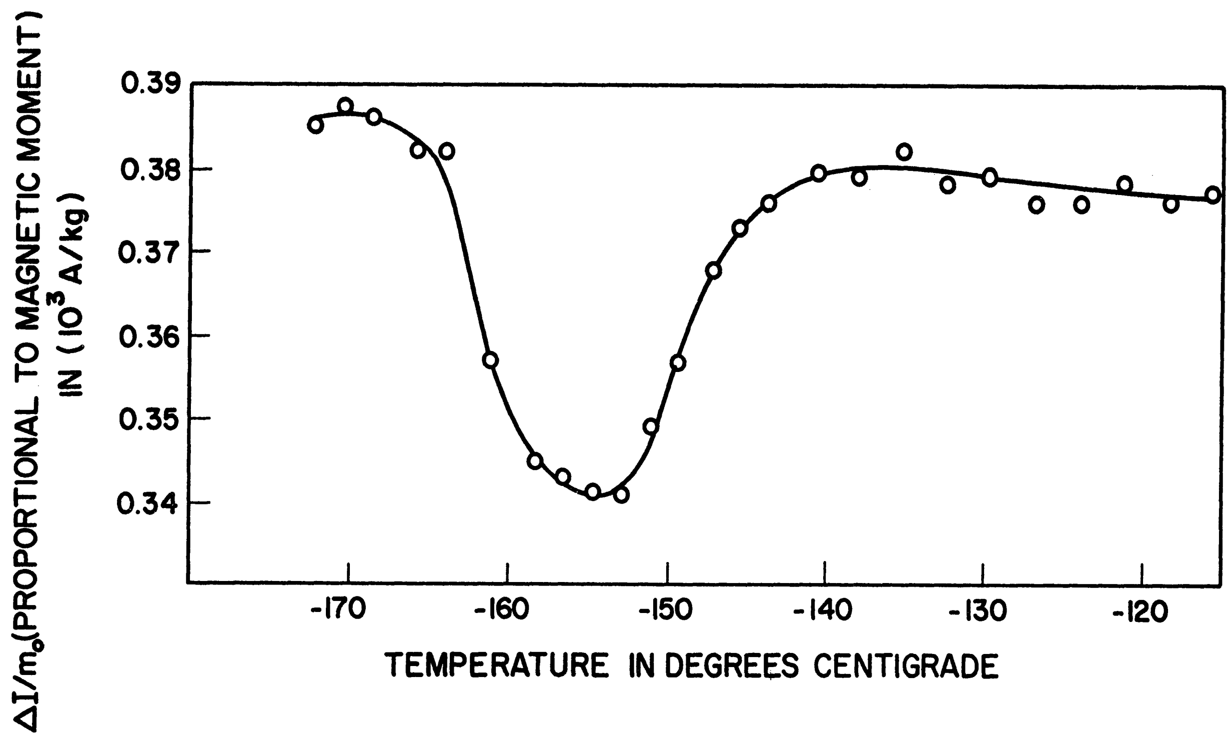

Figure 7. $\Delta I/m_0$ versus Temperature for S35-50. Sample cooled in the absence of an external field and then warmed in a field of 1.38×10^5 A/m.

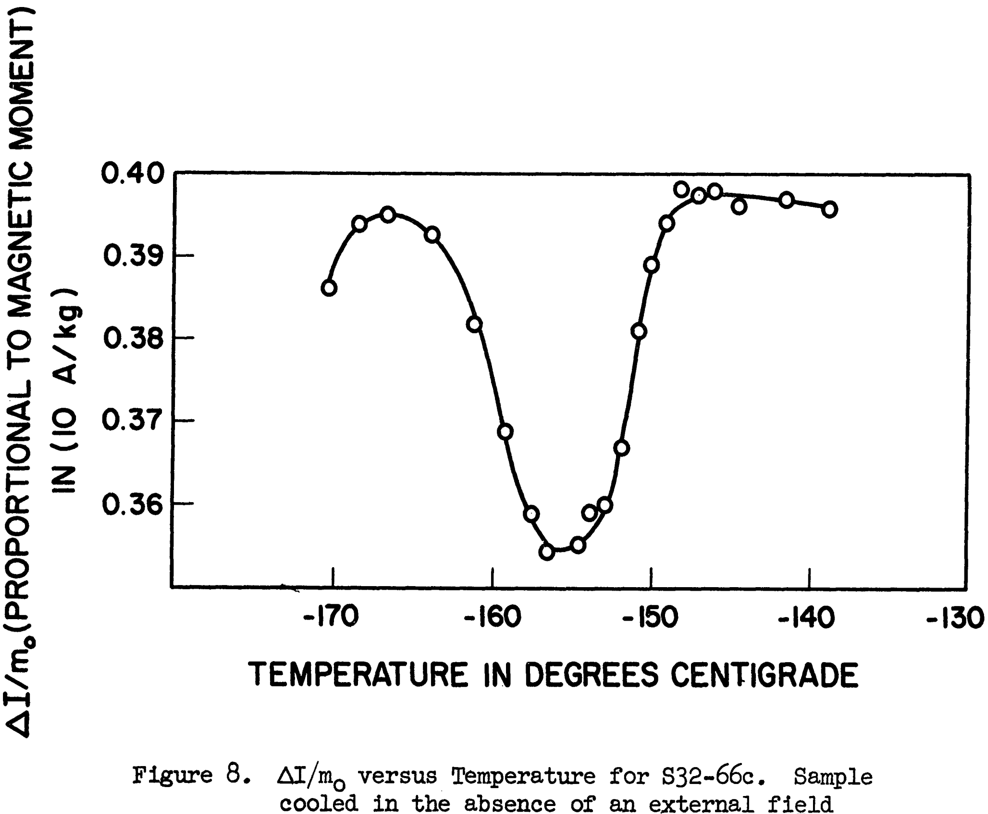

Figure 8. $\Delta I/m_0$ versus Temperature for S32-66c. Sample cooled in the absence of an external field and then warmed in a field of 1.38×10^5 A/m.

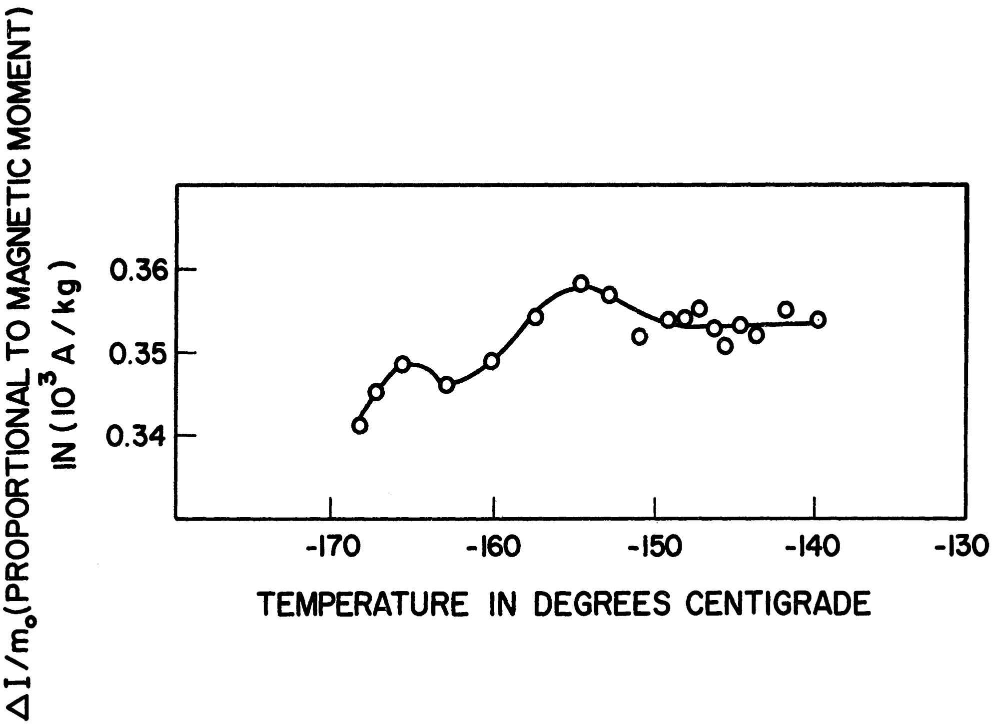

Figure 9. $\Delta I/m_0$ versus Temperature for S32-66b. Sample cooled in the absence of an external field and then warmed in a field of 1.38×10^5 A/m.

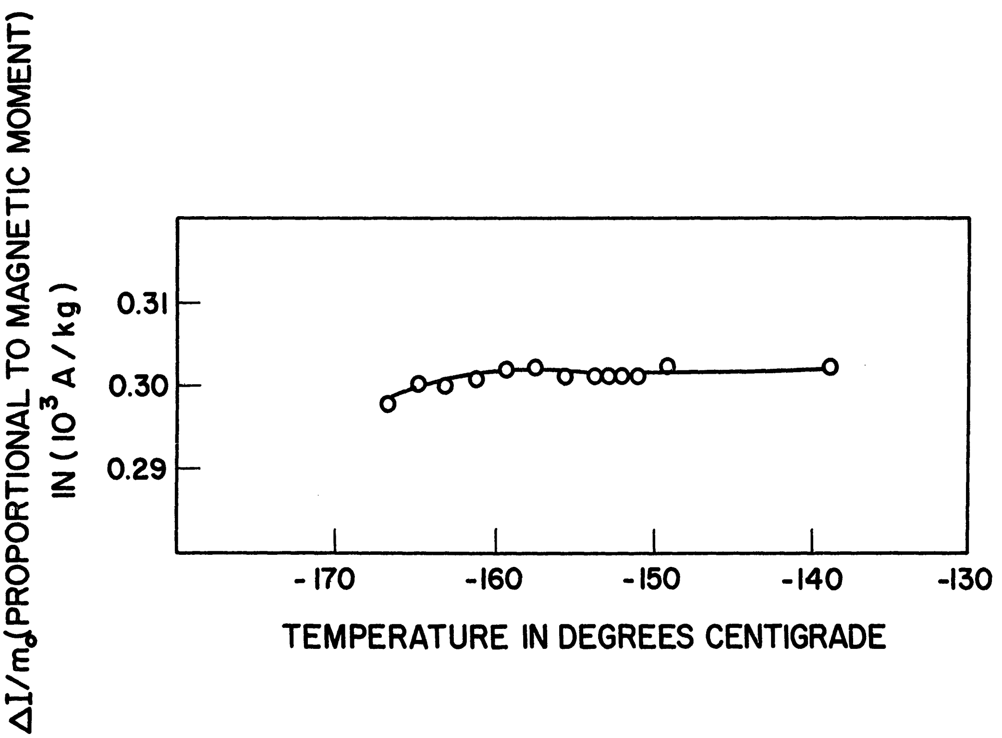

Figure 10. $\Delta I/m_0$ versus Temperature for S35-64. Sample cooled in the absence of an external field and then warmed in a field of 1.38×10^5 A/m.

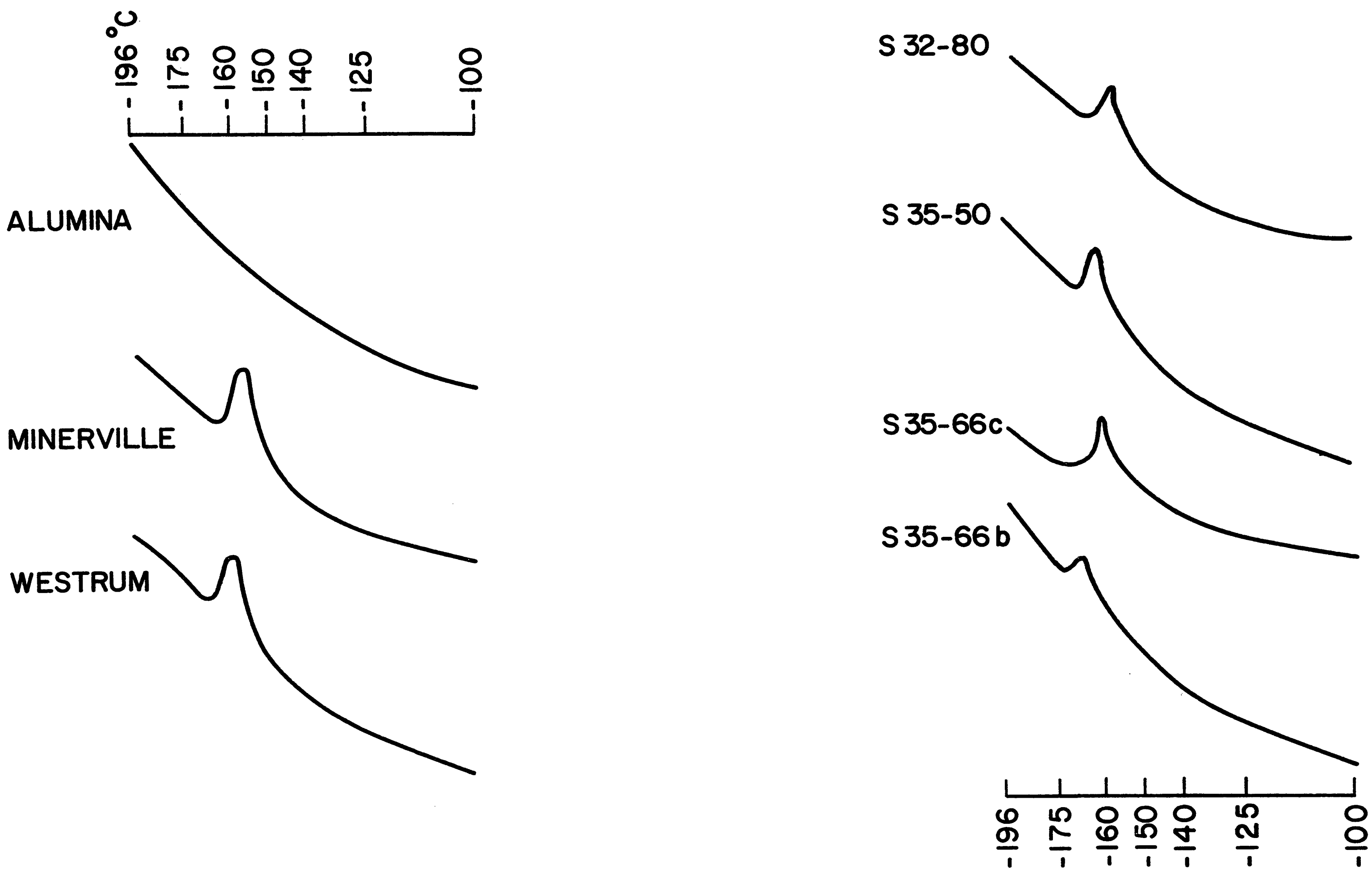

Figure 11. Differential-Thermal-Analysis Records Showing Deflection as a Function of Temperature on the Warming Cycle.

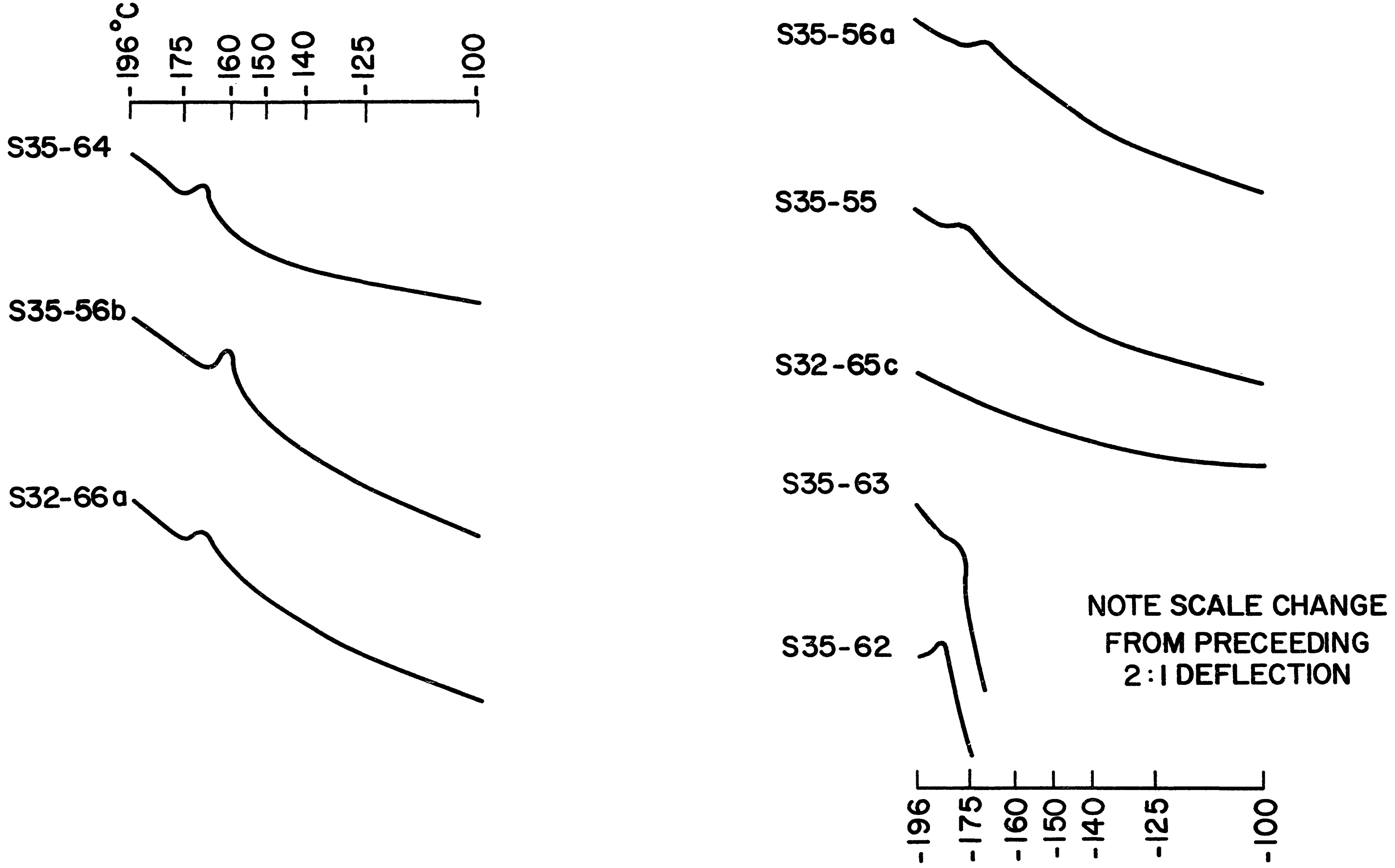

Figure 11. (Continued)

Now it should be recalled that the study of lithium doped magnetite was begun in order to study the effect of quasi oxidation without actually oxidizing the sample. In Figure 5 we see what happened when the very pure synthetic magnetite began to oxidize. It should also be pointed out that the powdered samples are more prone to oxidize than samples studied by other investigators.(10) Figures 6 and 7 show additional evidence of oxidation of a synthetic magnetite. Figures 8, 9 and 10 show effects similar to oxidation brought on by doping with lithium. The effect of doping on the transition as seen through the magnetic moment experiment disappears when the mole percent of magnetite drops below 98.5%. The DTA results which are shown in Figure 11 indicate a trace of a transition down to 96% mole percent of magnetite.

One last comment should be made about the saturation magnetizations per unit density given in the table. Small amounts of non-interacting impurities in the samples will cause what could be called "mass loading." Mass loading amounts to a measured quantity of material larger than the ferrimagnetic portion. This mass discrepancy makes the measured σ smaller than the true σ.

CONCLUSIONS

First, I must point out that I have no positive explanation for the observed anomaly.

The anomalous magnetic transition observed in experimenting with partially oxidized and lithium doped magnetite may simply be a property of the powdered polycrystalline samples used, but the results on the high purity magnetite before oxidation appear to rule out this possibility. What we might be observing is a double transition such as barium titanate(12) undergoes. We might be observing a transition from the orthorhombic to the cubic via a tatragonal intermediate phase. The anomalous magnetic transition does exist and should be investigated in greater detail.

FOOTNOTES

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