From: AMORPHOUS MAGNETISM II
Edited by R.A. Levy, and R. Hasegawa
(Plenum Press, 1977)

CHARACTERIZATION OF FERROMAGNETIC PRECIPITATES IN GLASSES BY FERROMAGNETIC RESONANCE

E.J. Friebele and D.L. Griscom

Naval Research Laboratory, Washington, D.C. 20375

C.E. Patton

Colorado State University, Ft. Collins, Co. 80523

ABSTRACT

Ferromagnetic phases precipitated from iron-containing silicate glasses have been identified and characterized by studying the integrated intensity of the ferromagnetic resonance (FMR) as a function of sample temperature. The data show a completely different character for metallic iron precipitates and ferric iron spinel precipitates -- a result which is important because these phases may be indistinguishable in conventional magnetic experiments such as FMR lineshape, Mössbauer, static magnetic analysis, etc. The different behaviors make it possible to determine the relative amounts of the two phases if they are co-present in one sample. The data also show that the temperature variation of the microwave skin depth provides a way to estimate particle sizes for the precipitates.

INTRODUCTION

The ferromagnetic phases which are precipitated from iron-containing silicate glasses may be divided into 3 catagories -- fine particle metallic Fe, coarse particle Fe, and ferric iron spinels. The latter include both stoichiometric and nonstoichiometric Fe_3O_4 and "polluted" magnetite-like phases with other transition metal ions substituting for the iron ions in the spinel lattice.

In concept, it should be possible to discriminate between these three ferromagnetic phases by several methods. In practice, however, complications arise. Magnetite is stable below 600 C under even extreme reducing conditions,[1] so that it is impossible to determine a priori what phases have precipitated. The identification of the phases is further complicated because bcc metallic iron is often indistinguishable from ferric iron spinel phases by static thermomagnetic analysis.[2] The ferromagnetic resonance lineshape is also of little use since FMR spectra characterized by a positive magnetocrystalline anisotropy constant, which is the normal case for bcc metallic iron, have also been observed in magnetite-like phases and nonstoichiometric Fe_3O_4.[3,4] Finally, up to 0.1 wt % large grained ferric iron spinel precipitates can escape detection by Mössbauer techniques,[5] while superparamagnetic particles of both metallic iron and magnetite give rise to an excess area near zero velocity in the γ ray resonance absorption spectrum.[6] Thus, the present study was undertaken to find a simple and reliable way to detect fine-grained metallic iron and ferric iron spinel phases precipitated from iron-containing glassy matrices and to discriminate between them.

EXPERIMENTAL

FMR spectra were obtained using a Varian E-9 electron spin resonance spectrometer operating at X-band (9 GHz). Sample temperatures were varied between 90-573 K by means of a Varian variable temperature accessory and between 4.2-140 K by means of an Air Products LTD-3 Helitran apparatus.

A complete description of the samples used in this study and the preparation techniques involved has appeared elsewhere.[7] With the exception of a sample of crushed mineral Fe_3O_4 (OKA-B) dispersed in powdered SiO_2, all ferromagnetic phases were produced by nucleation and precipitation from glasses which were initially homogeneous. Sample 2.1-600-16 was derived from a calcium aluminoborosilicate glass which as-quenched contained both Fe^{2+} and Fe^{3+} ions. X-ray and electron diffraction studies and transmission electron microscopy of this sample revealed the presence of spherical precipitates $\sim 100\text{Å}$ characterized by a lattice constant close to that of γ-Fe_2O_3.[4] On the other hand, glass CG-820-74-810-36 was shown[8] to contain metallic iron precipitates $\sim 150\text{Å}$.

The method used in the present study is critically dependent on obtaining a reliable determination of the integrated FMR intensity. Because the first derivative of the FMR absorption is experimentally observed, it is necessary to perform a double integration of the spectra to obtain the intensity. When the resonance is narrow with respect to the mean resonance field, the method is straightforward, but in the present case when the intensity extends

to zero field, reproducible
when sufficient care is take
level.[7] The integrations ca
hand[7] or by a computer,[9] but
tive level be established (b
for example).

Partially because of th
zero level, it is of value t
tion of the area under the a
straight line intersecting t
the curve near 5-6 kG (i.e.,
row integral is obtained by

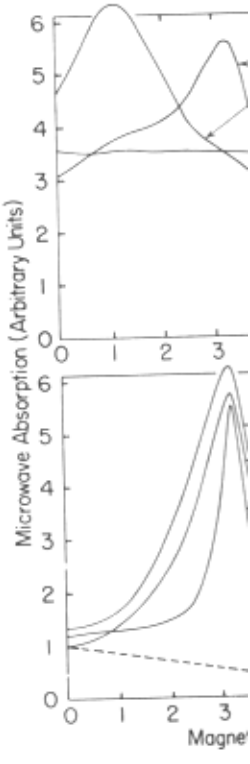

Fig. 1. X-band FMR absorp
(b) ferric iron s

to zero field, reproducible total intensities can be obtained only when sufficient care is taken to establish the zero derivative level.[7] The integrations can be performed numerically either by hand[7] or by a computer,[9] but in any case require that a zero derivative level be established (by running an empty sample tube spectrum, for example).

Partially because of the difficulty in establishing a reliable zero level, it is of value to define a narrow integral as that portion of the area under the absorption curve which lies above a straight line intersecting the curve near zero field and tangent to the curve near 5-6 kG (i.e., the dashed line in Fig. 1). This narrow integral is obtained by making a guess of the zero derivative

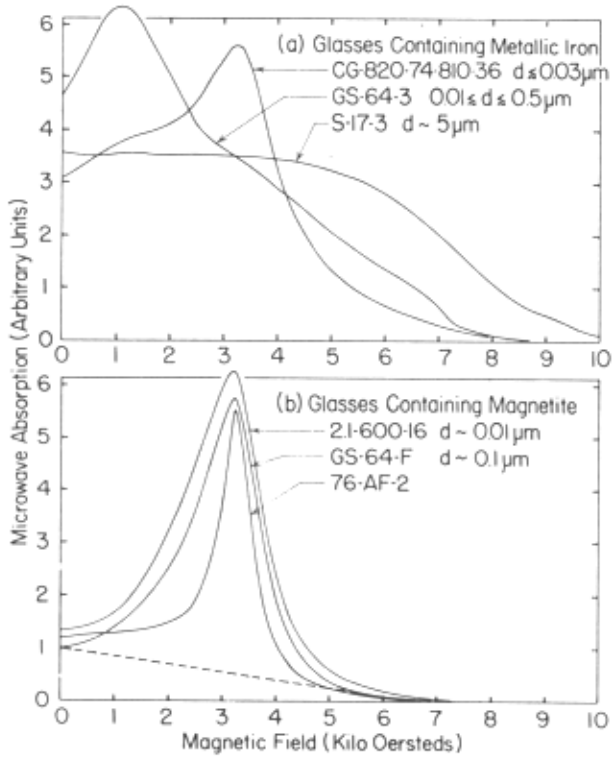

Fig. 1. X-band FMR absorption curves for (a) metallic iron and (b) ferric iron spinel precipitates in glass.

level and then treating the low field part of the FMR absorption as baseline drift in the method outlined by Ayscough.[10] Experience has shown that this method is operationally quite simple and highly reproducible provided the guessed zero derivative level is reasonably good.[7] As discussed below, similar results are obtained with both the total and narrow integrals.

RESULTS AND DISCUSSION

It is possible to qualitatively associate the broad and narrow FMR spectra with different configurations of ferromagnetic precipitates. In principle, multidomain configurations give rise to broad backgrounds which peak at zero field due to the Polder-Smit low field loss which occurs whenever the condition $\omega \gg \omega_m$ is not satisfied, where ω is the microwave frequency and $\omega_m = 4\pi|\gamma|M_s$, where γ is the gyromagnetic ratio and M_s is the saturation magnetization.[11]

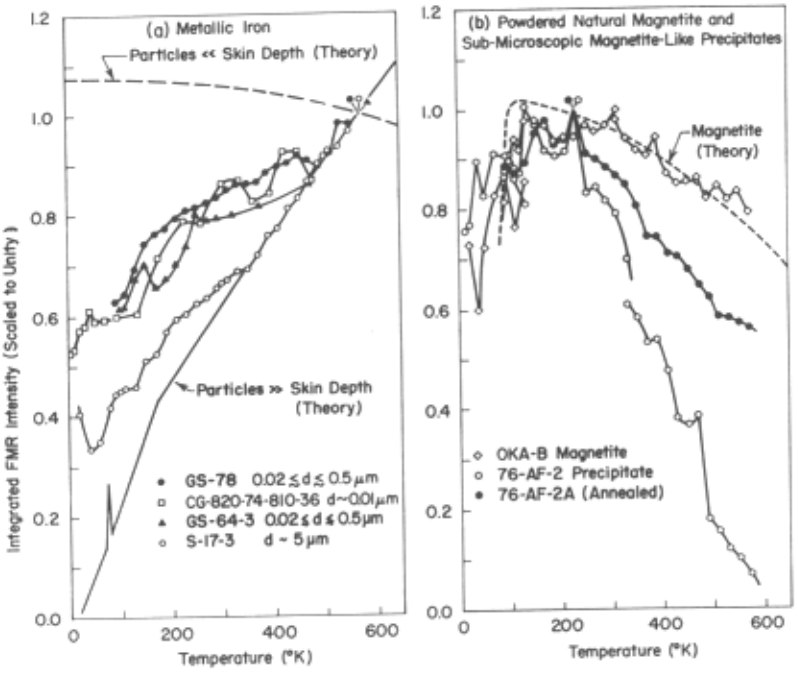

Fig. 2. Total FMR intensity vs. temperature for (a) metallic iron and (b) magnetite and ferric iron spinel precipitates in glass.

For iron and magnetite at ro
≈ 17 GHz respectively,[11] as
Thus, Polder-Smit losses are
larger effect predicted in t
together with the shape anis
most probably responsible fo
for a wide variety of ferror
In contrast, single-domain
resonances.[15,16] Examples
where it can be seen that th
either iron or magnetite may
part. This is further evide
like phases cannot be identi
alone.

The FMR intensity can
component of the susceptibi
ials and spherical single d

$$\chi_e'' = \alpha\,\omega\,\omega_m / [(\omega_{res} -$$

where $\omega_{res} = |\gamma|H_{app}$, H_{app}
the Landau-Lifshitz damping

$$I = \int_0^\infty \chi_e''\, dH_{app} = 4\pi M_s$$

Thus, in the usual case whe

$$I = 4\pi^2 M_s = \pi\omega_m/|\gamma|$$

and the integrated intensit
magnetization. If the part
skin depth of the microwave
tation occurs, the temperat
be the same as the temperat
Fig. 2a as the theoretical
On the other hand, for meta
wave skin depth $\delta = 1/\sqrt{\pi\sigma\mu}$
the permeability, and ν is
intensity would also be pro
volume being penetrated.
size, one obtains

$$I \propto M_s\delta \propto M_s/\sqrt{\sigma}\ .$$

Equation (4) should p
perature dependence of the
particles in this category
metallic iron is shown in
Depth."

For iron and magnetite at room temperature $\omega_m/2\pi \approx 61$ GHz and ≈ 17 GHz respectively,[11] as compared to $\omega/2\pi \approx 9$ GHz at X band. Thus, Polder-Smit losses are expected for both materials, with a larger effect predicted in the case of iron. These domain effects, together with the shape anisotropy of non-spherical particles, are most probably responsible for the zero-field absorption observed for a wide variety of ferromagnetic precipitates in glasses.[12-14] In contrast, single-domain equant particles give rise to narrow resonances.[15,16] Examples of these resonances are shown in Fig. 1 where it can be seen that the FMR absorption of samples containing either iron or magnetite may consist of both a narrow and broad part. This is further evidence that metallic iron and magnetite-like phases cannot be identified on the basis of the FMR lineshape alone.

The FMR intensity can be determined by integration of the loss component of the susceptibility χ_e'' assuming insulator-type materials and spherical single domain particles:

$$\chi_e'' = \alpha \omega \omega_m / [(\omega_{res} - \omega)^2 + \alpha^2\omega^2)] \quad (1)$$

where $\omega_{res} = |\gamma|H_{app}$, H_{app} is the applied magnetic field, and α is the Landau-Lifshitz damping factor. The FMR intensity is then

$$I = \int_o^\infty \chi_e'' \, dH_{app} = 4\pi M_s [\pi/2 + \tan^{-1}(1/\alpha)] \quad . \quad (2)$$

Thus, in the usual case when $\alpha \sim 0.01$, Eq. (2) reduces to

$$I = 4\pi^2 M_s = \pi\omega_m/|\gamma| \quad (3)$$

and the integrated intensity depends linearly upon the saturation magnetization. If the particles are sufficiently smaller than the skin depth of the microwave radiation so that total particle excitation occurs, the temperature dependence of the FMR intensity will be the same as the temperature dependence of M_s. This is shown in Fig. 2a as the theoretical curve for "Particles $\ll$ Skin Depth".[17] On the other hand, for metallic particles larger than the microwave skin depth $\delta = 1/\sqrt{\pi\sigma\mu\nu}$, where σ is the conductivity, μ is the permeability, and ν is the frequency (mks units), the FMR intensity would also be proportional to the fractional particle volume being penetrated. For δ much smaller than the particle size, one obtains

$$I \propto M_s\delta \propto M_s/\sqrt{\sigma} \quad . \quad (4)$$

Equation (4) should provide a first approximation for the temperature dependence of the integrated intensity for magnetic particles in this category. A normalized plot of $M_s/\sqrt{\sigma}$ versus T for metallic iron is shown in Fig. 2a as the curve "Particles $\gg$ Skin Depth."

As shown in Fig. 2a, there is good agreement between the theory for "size $\gg \delta$" and the data of S-17-3, which is consistent with the belief that $\delta < 5\mu m$ for metallic iron. For smaller particles whose size is intermediate between the two limiting cases, the FMR intensity behavior falls between the two theoretical boundaries (Fig. 2a). However, the total FMR intensity of all metallic iron-containing samples is seen to be an increasing function of temperature, even for particles as small as $0.015\mu m$ (CG-820-74-810-36). This result is evidence that metallic effects are important in the FMR of fine-grained iron precipitates.

Thus, the lower theoretical curve in Fig. 2a represents a semiquantitative lower bound for the integrated FMR intensity versus temperature for metallic iron. Several rather extensive modifications would be necessary to perform more quantitative calculations. In the first place, the μ parameter in the skin depth expression is not a simple scalar number for ferromagnetic metals. For such materials, μ has a tensor form and depends on particle orientation relative to the applied field, as well as other factors. In the second place, the classical skin depth δ as defined by Eq. (3) is only a crude approximation for the actual skin depth of the modes participating in metallic FMR. The effective penetration depth of these modes can vary substantially as the applied magnetic field passes through the region of FMR. The boundary conditions at the surface of the particles are also extremely important and determine the mixture of normal modes in the FMR response. Detailed consideration of these effects can be done with ease only for a planar geometry.[18] However, the general results should apply: the effective skin depth at resonance can be much smaller than δ calculated from Eq. (3) with the static (dc) values of σ and hence the condition "size $\ll \delta$" is not really adequate to justify the assumption of total particle excitation.

Because magnetite has a conductivity substantially less than that of iron, the microwave skin depth calculated from Eq. (3) is relatively large -- $\sim 200\ \mu m$ for $T < 120$ K and $\sim 5\mu m$ at higher temperatures. Thus, the effect of the skin depth on the FMR intensity can be neglected for ferric iron spinel particles $< 5\mu m$, and the intensity will be expected to vary as M_s. Furthermore, it is expected that there will be a drop of $\sim 20\%$ in the FMR intensity upon cooling the sample below 120K since the induced magnetization of magnetite measured in static fields ~ 3 kG is known to drop $\sim 20\%$ as the sample is cooled through the Verwey temperature (~ 120 K).[19] These expectations are incorporated into the theory curve shown in Fig. 2b.[19,20]

The agreement between the theory and experimental results for OKA-B magnetite is quite good. The FMR intensity of the ferric iron spinel precipitates decreases more rapidly than that of the Fe_3O_4

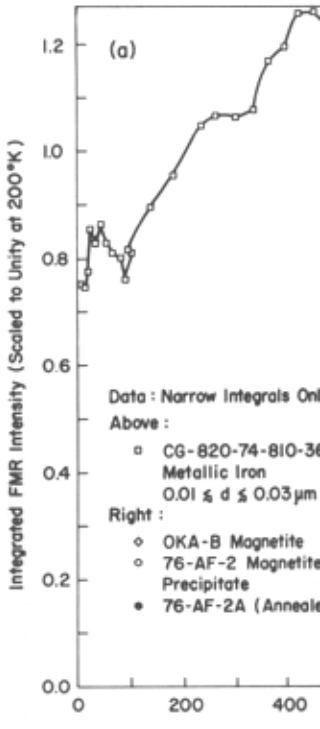

Fig. 3. Narrow integral int
ferric iron spinel

sample with increasing tempe
a lower Curie temperature in
magnetite precipitates than
ples display the characteris
temperature.

The data shown in Fig.
under the FMR absorption cur
tinguishing between fine-gra
However, as discussed above,
tensity of only the narrow p
integral can be obtained for
single domain Fe precipitate
temperature dependence is si
Likewise, the narrow integra
spinel precipitates in Fig.
intensity below the Verwey t
broad absorption (the triang
Fig. 1) of the latter sample

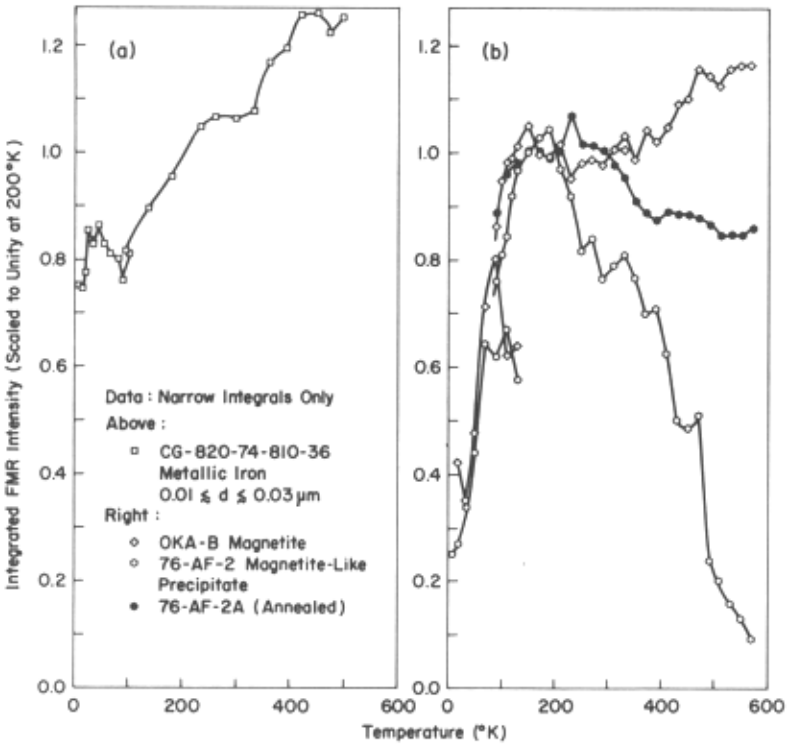

Fig. 3. Narrow integral intensity for (a) metallic iron and (b) ferric iron spinel precipitates.

sample with increasing temperature, which is probably a result of a lower Curie temperature in the "polluted" or nonstoichiometric magnetite precipitates than in pure magnetite. However, all samples display the characteristic drop in intensity near the Verwey temperature.

The data shown in Fig. 2 are derived from the total areas under the FMR absorption curves and provide a clear means for distinguishing between fine-grained iron and fine-grained magnetite. However, as discussed above, it is often easier to obtain the intensity of only the narrow part of a resonance. When the narrow integral can be obtained for an iron-containing sample (e.g. for single domain Fe precipitates), it can be seen in Fig. 3a that the temperature dependence is similar to that of the total integral. Likewise, the narrow integral of samples containing ferric iron spinel precipitates in Fig. 3b display the characteristic drop in intensity below the Verwey temperature.[7] As shown in Fig. 4, the broad absorption (the triangular wedge below the dashed line in Fig. 1) of the latter samples actually gains intensity upon cooling.

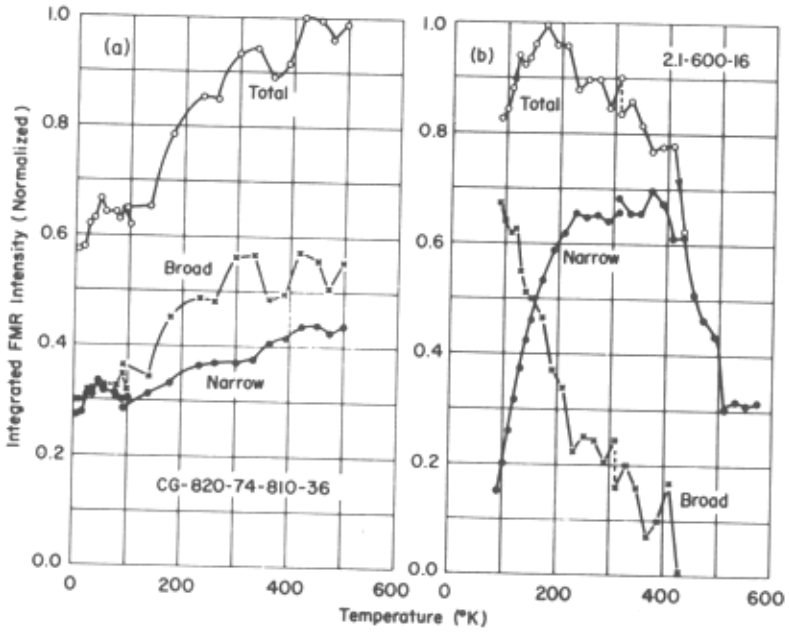

Fig. 4. FMR intensity vs. temperature for (a) metallic iron and (b) magnetite precipitates in glass.

This effect is also observed in Fe_3O_4 where the FMR absorption near g=2 (narrow part) shifts to lower fields (broad part) due to a cubic to uniaxial symmetry change upon cooling through the Verwey temperature.[21] Thus, the drop in the narrow integral of the spinel-containing sample of Figs. 3b and 4b is greater than that of the total integral. The narrow and broad parts of the resonance for metallic iron precipitates (Figs.3a and 4a) monotonically lose intensity upon cooling, in contrast to the behavior of the spinel precipitates. It should be pointed out that at the present time there is no quantitative theory for the temperature dependence of the narrow integrals; the usefulness of this simpler technique rests on the empirical evidence that it behaves in a manner which is similar to the total integral method.[7]

By using the techniques outlined above, it is possible to distinguish between precipitated iron and/or ferric iron spinels (or magnetite) in glass. A sample which displays an inverted-U-shape FMR intensity vs. temperature behavior in the range 4.2 - 600K can be inferred to contain ferric iron spinel precipitates whether or not metallic iron is present. As little as ∿0.1 wt % spinel phase has been detected in the presence of ∿ 1.0 wt % metallic iron, detected by conventional spectroscopic techniques.[7]

In conclusion, the tec
pendence of the FMR intensi
for detecting and identifyi
tates in glass, even when t
means. In addition, it is
phases in the presence of a

1. R.J. Williams, and E.K
84 (1972).
2. D.L. Griscom, E.J. Fri
T. Nagata, EOS, Trans.
3. D.L. Griscom, Geochim.
4. M.P. O'Horo, Bull. Am.
these proceedings.
5. D.W. Forester, Geochim
2697 (1973).
6. R.M. Housley, R.W. Gra
Cosmochim. Acta, Suppl.
7. D.L. Griscom, C.L. Mar
Res. 80, 2935 (1975).
8. G.W. Pearce, R.J. Will
17, 95 (1972).
9. E.H. Cirlin, I.B. Goldb
R. Perhac, Geochim. Cos
10. P.B. Ayscough, Electron
(London) 1967, p. 442.
11. J. Smit and H.P.J. Wijn
1959, pp 22, 82 ff, 157
12. D.L. Griscom, C.L. Marg
Earth Planet. Sci. Lett
13. R.A. Weeks, J.L. Kolopu
Cosmochim. Acta, Suppl.
14. E.J. Friebele, D.L. Gri
D. Prestel, Geochim. Co
2729 (1974).
15. F.D. Tsay, S.I. Chan an
Acta 35, 865 (1971).
16. D.L. Griscom, E.J. Frie
Cosmochim. Acta, Suppl.
17. A.H. Morrish, The Physi
Wiley (New York), 1965.
18. For example, see C. Vit
Appl. Phys. 40, 1561 (1
19. C.A. Domenicali, Phys.
20. Handbook of Chemistry a
Chemical Rubber Publ. C
21. L.R. Bickford, Jr., Phy

In conclusion, the technique of studying the temperature dependence of the FMR intensity has been shown to be a powerful tool for detecting and identifying fine-grained ferromagnetic precipitates in glass, even when they may escape detection by conventional means. In addition, it is possible to detect ferric iron spinel phases in the presence of as much as 10 times more metallic iron.

REFERENCES

1. R.J. Williams, and E.K. Gibson, Earth Planet. Sci. Lett. 17, 84 (1972).
2. D.L. Griscom, E.J. Friebele, C.L. Marquardt, N. Sugiura and T. Nagata, EOS, Trans. Am. Geophys. Union 55, 329 (1974).
3. D.L. Griscom, Geochim. Cosmochim. Acta 38, 1509 (1974).
4. M.P. O'Horo, Bull. Am. Ceram. Soc. 53, 324 and 356 (1974), and these proceedings.
5. D.W. Forester, Geochim. Cosmochim. Acta, Suppl. 4, Vol. 3, 2697 (1973).
6. R.M. Housley, R.W. Grant, and M. Abdel-Gawad, Geochim. Cosmochim. Acta, Suppl. 4, Vol. 1, 1065 (1972).
7. D.L. Griscom, C.L. Marquardt and E.J. Friebele, J. Geophys. Res. 80, 2935 (1975).
8. G.W. Pearce, R.J. Williams and D.S. McKay, Earth Planet. Sci. 17, 95 (1972).
9. E.H. Cirlin, I.B. Goldberg, R.M. Housley, R.A. Weeks and R. Perhac, Geochim. Cosmochim. Acta, Suppl. 6, Vol. 3 (1975).
10. P.B. Ayscough, Electron Spin Resonance in Chemistry, Methuen (London) 1967, p. 442.
11. J. Smit and H.P.J. Wijn, Ferrites, John Wiley (New York), 1959, pp 22, 82 ff, 157.
12. D.L. Griscom, C.L. Marquardt, E.J. Friebele, and D.J. Dunlop, Earth Planet. Sci. Lett. 24, 78 (1974).
13. R.A. Weeks, J.L. Kolopus, D. Kline and A. Chatelain, Geochim. Cosmochim. Acta, Suppl. 3, Vol. 1, 797 (1970).
14. E.J. Friebele, D.L. Griscom, C.L. Marquardt, R.A. Weeks and D. Prestel, Geochim. Cosmochim. Acta, Suppl. 5, Vol. 3, 2729 (1974).
15. F.D. Tsay, S.I. Chan and S.L. Manatt, Geochim. Cosmochim. Acta 35, 865 (1971).
16. D.L. Griscom, E.J. Friebele, and C.L. Marquardt, Geochim. Cosmochim. Acta, Suppl. 4, Vol. 3, 2709 (1973).
17. A.H. Morrish, The Physical Principles of Magnetism, John Wiley (New York), 1965.
18. For example, see C. Vittoria, R.C. Barker, and H. Yelon, J. Appl. Phys. 40, 1561 (1969).
19. C.A. Domenicali, Phys. Rev. 78, 458 (1950).
20. Handbook of Chemistry and Physics (1956), C.D. Hodgman, ed. Chemical Rubber Publ. Co., p. 2362.
21. L.R. Bickford, Jr., Phys. Rev. 78, 449 (1950).