Detection of diluted marine tertiary tephra by electron spin resonance and magnetic measurements

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SUMMARY
Oligocene sediments from ODP leg 115 (South Indian Ocean), Site 709 and Site 711, have been investigated using electron spin resonance (ESR) and magnetic susceptibility measurements, to detect volcanic tephra layers of supposed Ethiopian traps origin. The results obtained at room temperature, without separating the volcanic material from the bulk sediment, show that the ash-content strongly influences the lineshape and intensity of the ESR signal. As a result, the ESR alone, can be used as a powerful tool for characterizing the diluted ash-content of marine sediments. We have also found a strong similarity between the ESR spectra of the same tephra layers from the two sites.

Key words: ESR, magnetic susceptibility, marine sediments, tephras, volcanic ash layers.

1 INTRODUCTION
Electron spin resonance (ESR) is a very sensitive and discriminating spectroscopic technique for probing paramagnetic ions as well as the symmetry of their crystallographic sites (Abragam & Bleaney 1970). It is also very efficient for the study of magnetically ordered phases (Griscom 1984). Moreover, among the methods giving a direct access to the knowing of the ‘magnetic composition’ of the materials, ESR is very complementary to more conventional magnetic techniques like hysteresis loop and susceptibility measurements. In the last decades, ESR has been used along with classical magnetic methods to characterize clays and volcanic materials, mainly glasses (Bart et al. 1982; Bonnin et al. 1982; Schlinger et al. 1988; Pawse et al. 1998; Balan et al. 1999). From a previous study of ash emitted by known volcanic eruptions of the last century, it appears that the magnetic hysteresis properties and ESR signals can be distinct for each eruption (Pawse et al. 1998). Both techniques are sensitive to various parameters (chemical environment, oxidation state, composition, grain size and shape, etc.) which vary from one eruption to another, even if bulk chemistry is similar. These techniques can thus be of general interest for tephrrostratigraphy. Indeed, some recent ash layers are not unambiguously attributed to a well-known historical event (Rose et al. 1981), and are difficult to discriminate based on their chemistry (Palias et al. 1990).

There is a need for techniques that can characterize diluted tephra material in a sedimentary sequence, without separating the volcanic material from the bulk sediment. In case of long distance transport, i.e. when the source volcano is less easy to identify, only minute amounts of volcanic material are deposited and can be mixed with other particles during bioturbation. From an investigation of ESR signature versus distance to eruptive event in a single ash fall (Fuego volcano in Guatemala), Pawse et al. (1998) show that above 30 km distance the ESR ash signal does not depend on the distance for that eruption.

Ethiopian traps have emitted at least $6 \times 10^5$ km$^3$ of volcanic product in less than one Myr based on combined radiochronology and magnetostratigraphy of traps sequences (Rochette et al. 1998). Ethiopian traps have recorded three polarities within Chron 11 according to the $^{40}$Ar/$^{39}$Ar ages, which cluster around 30 $\pm$ 1 Ma (Rochette et al. 1998; Hofmann et al. 1997). Between 10 and 20 per cent of the total volume is composed of ignimbritic material (rhyolite). The Si-rich composition implies explosive eruptions and production of ash.

In the marine sedimentary records of Leg 115 (South Indian Ocean), four susceptibility peaks have been identified and attributed to four different ash layers. They were notably recognized in Site 709 and Site 711. Dating, chemical and isotopic analyses argue for an Ethiopian origin of these volcanic deposits (Touchard et al. 2002) and confirm that the four ash layers are the same in both sites.

The purpose of our study is to measure, for the first time with the help of the ESR technique, the magnetic response of bulk marine sediment containing small and varying amounts of ancient volcanic ashes. The main aim is to show that the volcanic component of the ESR signal can be discriminated from the total ESR signal without a prior extraction. Extraction is a problem because it may lead to modification of the ash.
2 TECHNIQUES

2.1 Susceptibility measurements and magnetization

In 1987, whole-core volume magnetic susceptibility measurements were performed on the ship using a Bartington Susceptibility Meter (Model MS1) in which the whole-core was passed through a sensor coil of 80 mm inner diameter (Model MS2C) (Backman et al. 1988). The sediment was then kept in a moist atmosphere at 4°C until 1998. For the present study, the sediment was dried at 40°C during 24 hr and sampled in cubic boxes of average 8 cm³ volume. Further room temperature ac susceptibility measurements at 920 Hz frequency were completed using an AGICO Kappabridge KLY-2 (0.37 mT rms field strength) susceptometer. Hysteresis curves on small samples (m ≈ 0.3 g) were obtained using a Micromag Vibrating Sample Magnetometer (VSM) with 0.1 s averaging time and 8 mT field increment.

2.2 Electron spin resonance spectroscopy

The basics of ESR can be found for instance in Abragam & Bleaney (1970) and are briefly recalled in the appendix A.

The experiments were carried out using a Bruker EMX 10/12 spectrometer operating at ν₀ = 9.63 GHz. This frequency corresponds to a 'measuring time' τ_m ≈ 10⁻¹⁰ s. The cavity, excited on the TE₁₀₂ mode, was irradiated with a microwave power of 1 mW. The static field B was modulated sinusoidally at a frequency ν_m = 100 kHz with an amplitude of 5 × 10⁻⁴ T. For ν₀ = 9.63 GHz, the resonance for g = 2 (free spin) occurs at B_r ≈ 0.3464 T. The spectra have been recorded at T = 295 K from B = 0 up to 0.895 T with a resolution of 4096 points. Typical field sweep time is about 3 mn. Each spectrum was normalized to the spectrometer gain and sample mass (typically 5 mg).

3 SEDIMENT DESCRIPTION AND SAMPLING

Site 709 and 711 (Fig. 1) are located at 03°54.9′S; 60°33.1′E and 02°44.5′S; 61°09.7′E (Backman et al. 1988). They are 158 km apart from each other and about 2500 km S-E from the Ethiopian traps. For the present study a set of discrete samples (36 for Site 709 and 54 for Site 711) was obtained from a few meters on either side of the four tephra layers, with a mean sampling interval of 10 cm. At Site 709, around 235 meters below sea floor (mbsf), the bulk sediment is a homogeneous nanofossil chalk with an average carbonate content of 91 per cent in mass (Backman et al. 1988). At Site 711, around 118 mbsf, the lithology is homogeneous and composed of clay bearing nanofossil ooze with a carbonate content of 85 per cent in mass (Backman et al. 1988). Tephra grains are distributed in this sediment and never represent more than 20 per cent of the total mass. Physical separation of ash particles from the tephra layers was performed using the following procedure: first, an one molar concentration acetic acid leaching of the bulk sediment allows to eliminate carbonate material. Secondly, a defloculation agent, a 5 g/l solution of hexametaphosphate of sodium, is added to the remaining sediment and agitated during 24 hr to dissociate clay clusters. Then, the procedure is completed by a clay separation (<2 μm) achieved after repeated settling periods of 24 hr on deflocculated material. Observation under the optical microscope reveals that minor amounts of radiolarian tests (amorphous silica) are associated with the volcanic particles in such extracts. The volcanic material is composed essentially of glass shards (size between 10–100 μm) and some plagioclases. Very rare clinopyroxenes are the only mafic minerals of these layers. This composition is in accordance with segregation process during atmospheric fall out. Actually, denser volcanic material, represented by phenocrysts, could be recognized in proximal sites from the volcanic source but this proportion tends
to decrease with distance (Carey & Sigurdsson 1982; Sparks et al. 1997). Major elements and isotopes analyses show a very similar composition for the three oldest volcanic deposits, close to the one of Ethiopian rhyolites. The major elements composition of the volcanic glass from the youngest deposit exhibit a chemical trend resulting of the evolution of a magmatic chamber by fractional crystallization. Nevertheless, major element compositions are compatible with the one of Ethiopian rhyolite. Indeed, isotopes analysis confirm their Ethiopian origin (Touchard et al. 2002). The common composition of the three oldest tephra is typical of rhyolite. Fe and Mn are the only magnetic elements present in non negligible amounts, 2.23 and 0.14 atomic weight per cent respectively.

The Oligocene record of Site 711 has provided a very reliable magnetostratigraphy. The youngest ash layer occurs in chron C11n.1 and the oldest in chron C11n.1r which is in perfect agreement with the age of the acidic products in the Ethiopian traps. Calcareous nannofossil stratigraphy confirms the magnetostratigraphic interpretation, with the NP23-24 limit dated at 29.9 Ma right within the tephra layers. The Site 709 confirms Site 711 results (Touchard et al. 2002).

4 RESULTS

4.1 Magnetic properties

The reliability of continuous magnetic susceptibility versus depth curves obtained on board was confirmed by our discrete sample measurements. Fig. 2 shows both data sets with on board data adjusted to account for the change from wet volume units to dry mass units. For sediments we used a dry density of 670 kg m$^{-3}$ for Site 711 and 980 kg m$^{-3}$ for Site 709 (Backman et al. 1988). Dry mass susceptibility means of 5 10$^{-8}$ m$^{3}$ kg$^{-1}$ for Site 709 and of 2 10$^{-7}$ m$^{3}$ kg$^{-1}$ for Site 711 are observed for the background signal. These weak magnetic susceptibility values are common for a carbonate lithology. Four susceptibility peaks stand out against these backgrounds. These four peaks are interpreted as indicating the presence of four Ethiopian traps ash layers. The presence of volcanic ash within a marine core locally modifies the magnetic properties of the sediment (Kennett 1981) depending on the proportion of volcanic material and the susceptibility difference between the volcanic and background material. Magnetic susceptibility measurements on volcanic material extracted from the susceptibility peaks (from 0.85 to 1.96 10$^{-6}$ m$^{3}$ kg$^{-1}$), as well as on Ethiopian ignimbritic ashes (from 0.84 to 17 10$^{-6}$ m$^{3}$ kg$^{-1}$ (Rochette et al. 1998)) confirm this interpretation. The widths of susceptibility peaks represent the dispersion by bioturbation of the ash layer in the sedimentary record. All peaks at both sites have the same thickness. Therefore, the depth of mixing which is about 30 cm depends on bioturbation rather than duration of the ash fall. For Site 709, the susceptibility peaks are further apart than in Site 711, in accordance with a higher sedimentation rate in Site 709 than in Site 711. The sedimentation rate in Site 711, according to magnetostratigraphic interpretation (Touchard et al. 2002), is around 6 m Myr$^{-1}$. In the following and for both sites, peak-1 represents the shallowest peak (i.e. the youngest volcanic event), and higher numbers increasingly older layers: peaks-2, -3 and -4 (Fig. 2).

Hysteresis of separated ashes has been measured at room temperature. Fig. 3 presents the data obtained with a representative sample of peak-1 in Site 711, located at $d = 118.84$ mbsf. This figure displays two components: first, a low-field hysteresis and secondly, a high-field linear contribution with a slope of $86.4 \times 10^{-9}$ m$^{3}$ kg$^{-1}$ due...
to the paramagnetic Fe and Mn ions. Assuming that all Fe and Mn are in paramagnetic non interacting state, it is possible to compute a theoretical high-field susceptibility using the Fe and Mn contents of the ash. For example, the computed range of 67–89 \(10^{-9}\) m\(^3\) kg\(^{-1}\), depending on the Fe\(^{3+}\)/Fe\(^{2+}\) ratio from 0 to 1, is compatible with the measured susceptibility. This indicates that most Fe (and Mn) is in paramagnetic form, diluted in the silicate glass.

However a large ferrimagnetic signal is still visible in the hysteresis loop obtained after subtraction of the linear contribution (inset of Fig. 3). It is responsible for 94 per cent of the low-field susceptibility. The saturation magnetization \(M_s = 0.125\) Am\(^2\) kg\(^{-1}\) corresponds to an equivalent amount of magnetite of 0.14 wt per cent. The ratio \(M_r/M_s = 0.30\) (\(M_r\) is the remanent magnetization) and a coercive magnetic field \(B_c = 23\) mT, are consistent with the presence of pseudo-single domain (i.e. micron sized) titanomagnetite particles within the glass shards. Such grains were already observed by Schlinger \textit{et al.} (1988) for the KBS tuff. High temperature susceptibility measurements were carried out on the same ash-sample in order to determine the Curie temperature. Fig. 4 shows that the susceptibility decreases over a broad temperature range above \(\approx\)550 K; this behaviour is consistent with the presence of Fe\(_{1-x}\)Ti\(_x\)O\(_4\) ferrites. The critical temperatures of \(\approx\)590 K and 765 K, indicated by the vertical arrows in Fig. 4 correspond to an estimated high Ti content of \(x \approx 0.45\) and to a low Ti content of \(x \approx 0.2\) respectively (Dunlop & Ozdemir 1997), if we neglect the possible partial oxidation toward titanomaghemite and irreversible change during heating.

4.2 ESR Spectra

ESR spectra were made on a selection of samples corresponding to:
(i) the background where sediments have low susceptibility and are thought to be free of ash (Fig. 2).
(ii) the zone of the four \(\chi\)-peaks.
(iii) tephra layers and corresponding separated ashes.

Background samples are located far from the four \(\chi\)-peaks (Fig. 2). For each site, one of these samples was taken as back-

\[ \chi(a.u.) \]

\[ T(K) \]

\[ \text{separated ash} \]

\[ 118.84 \text{ mbsf} \]

\[ \text{Site 711} \]

\[ \text{ref-709} \]

\[ 239.83 \text{ mbsf} \]

\[ \text{ref-711} \]

\[ 136.49 \text{ mbsf} \]

\[ B(\text{T}) \]

\[ 0 \text{ to } 0.8 \]

\[ \text{ground reference: } d = 239.83\text{ mbsf in Site 709 and 136.49 mbsf in Site 711 (respectively noted ref-709 and ref-711). Samples at the four }\chi\text{-peaks, corresponding to }\chi\text{ maxima have been measured as well as samples having intermediate }\chi\text{-values, in between two peaks.} \]

4.2.1 Free-of-ash sediments

For the two sites, the ESR spectra of free-of-ash sediments (FOA-sediments) display some similarities as shown in Fig. 5 for ref-709 and ref-711. Their salient feature is a broad line characterized by an asymmetric shape, a positive extreme at \(B = 0.3\) T and two negative extremes at \(B = 0.374\) T and 0.408 T. Between \(B = 0.20\) T and \(B = 0.42\) T a multitude of narrow resonance lines, with weak amplitudes, are superimposed on the broadest component. Six of them exhibit larger amplitudes than the others but their integrated intensity is several orders of magnitude weaker than the one of the broadest line.

4.2.2 Tephra layers

Fig. 6 presents three spectra of specimens from Site 711: the ref-711 sample \((d = 136.49\text{ mbsf}, \chi = 5 \times 10^{-8}\text{ m}^3\text{ kg}^{-1})\) and two samples containing an increasing amount of volcanic ashes \((d = 119.37\text{ mbsf}, \chi = 54 \times 10^{-8}\text{ m}^3\text{ kg}^{-1}\) and \(d = 118.99\text{ mbsf}, \chi = 146 \times 10^{-8}\text{ m}^3\text{ kg}^{-1})\). Ref-711 shows the characteristic features of the FOA sediment as described above. Sample 2, located between peak-1 and peak-2 \((d = 119.37\text{ mbsf})\) has a \(\chi\)-value which reveals the presence of volcanic ashes. Its ESR spectrum is more intense than that of the FOA-sediment. Sample 2 has a broad, asymmetric curve with a characteristic positive extreme at \(B = 0.27\) T; it exhibits a weak...
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The spectra of the separated ash from the ash rich layers are similar to that of bulk sediment (Fig. 8). However, some resonances around $B = 0.22–0.25$ T appear in the spectrum of separated ashes and not in the tephra layer. After chemical treatment, to remove the carbonate and clays, the 6 narrow lines signal around $B_r = 0.34$ T disappears. This confirms our interpretation that the 6 narrow lines are caused by the non volcanic material (carbonates and clays) and that the rest of the ESR signal is of volcanic origin. It is highly unlikely that these lines correspond to absorbed volcanic ions on the material backed by the chemical treatment due to the small specific surface of the glass shards.

5 DISCUSSION

The similarities between tephra layer bulk material and separated volcanic material demonstrate that it is not necessary to perform tedious extraction of ashes to characterize the volcanic material diluted in the sediments when using ESR. Furthermore, use of the bulk sample avoids the possibility of alteration of the original signal by chemical treatment during extraction and allows analysis of small quantities of sediments. Indeed, an efficient extraction may need tons of grams of sediment.

Generally, the ESR signal is the sum of signals produced by each magnetic phase. ESR lineshape and intensity of FOA-sediment have to be carefully characterized in order to reveal the presence of small amounts of ash. In the FOA-sediment (Fig. 5), the multitude of narrow lines located between $B = 0.20$ T and $B = 0.42$ T can be interpreted using a powder spectra model of isolated paramagnetic...
Mn$^{2+}$ ions, with electron spin $S = 5/2$ and nuclear spin $I = 5/2$ (Griscom 1980a), interacting with a crystalline electric field of axial symmetry (Gratchev, unpublished data, 2001). The lines are due to the Mn$^{2+}$ ions in interstitial sites or in substitution in diamagnetic CaCO$_3$. Concentrated paramagnetic Mn$^{2+}$ would give a larger linewidth due to Mn–Mn dipole interactions. In Fig. 5, the broad line with the two distinct minima is probably caused by Fe$^{3+}$ paramagnetic ions in phyllosilicates and carbonates as well as ferrimagnetic grains.

Whatever the sample depth, the response of the FOA-sediment is always identifiable in the spectra. For samples containing volcanic ash, the FOA signature may represent only a small fraction of the overall response (Figs 6 and 7). The superimposed tephra ESR intensity is proportional to the susceptibility value. Therefore the spectra of samples with the largest susceptibilities (peaks-1, -2, -3 and -4) are the most representative of each ash layer. For both sites, these spectra are gathered in Fig. 9. In Site 711, spectra of the four peaks exhibit some similarities. This is also true for the 3 more recent events in Site 709, except for peak-4 which displays a noticeable discrepancy. Measurements performed on several subsamples of peak-4 reveal slightly different lineshapes. This difference can be explained by a sample inhomogeneity, as, in fact, we visually note for this specimen. Moreover, the ESR responses corresponding to ash layers 1, 2 and 3 in the two sites are comparable.

However, the data of Fig. 9 are perhaps not representative of all the magnetic phases included in the tephras, since many paramagnetic ions and also ferromagnetic compounds may be ESR silent at this experimental frequency. The ESR intensities, obtained by double integration of the derivative signal, are proportional to the susceptibility (appendix A). With the aim of comparing the results obtained using the two methods, the ESR intensity data have been plotted with the $\chi$-data measured on the ship (Figs 10a and b) for Site 709 and Site 711. A good agreement is obtained between ESR intensities and the $\chi$ data of Figs 2(a) and (b). The four ESR data points of peak-1, Site 709 (Fig. 10a) correspond to four independent measurements performed on three different subsamples ($d = 235.5 \text{ mbsf}$). The scatter of these data is due to the sample inhomogeneity as well as the experimental uncertainty. The results presented in Figs 10(a) and (b) suggest that the low field magnetic susceptibility and the ESR intensities are produced by the same mineralogical sources (i.e. $\mu$m sized titanomagnetite inclusions in glass shards). However we cannot exclude that the sources are different but both proportional to the amount of volcanic material. From these data, we can estimate...
that ESR allows detection of small ash-content as low as 1–2 per cent in bulk marine sediment.

Concerning the origin of the tephra ESR absorption, two distinct signals at $g \approx 4.3$ and $g \approx 2.0$ are evidenced in the spectra. The $g \approx 4.3$ intensity is negligibly small with respect to the total intensity and is due to isolated Fe$^{3+}$ ions in low symmetry crystal field (Castner et al. 1966; Asaa 1970; Ja 1972; Scala et al. 1978; Menil et al. 1979; Muller & Calas 1993; Gaite et al. 1993; Balan et al. 1999). Such a resonance appears in Figs 6, 8 and 9 as a small shoulder at $B_\| \approx 0.16$ T. The weak intensity of the $g \approx 4.3$ line does not mean that isolated Fe$^{3+}$ ions responsible of this signal represent a small fraction of the total Fe content. Indeed, as Griscom (1980b) and Schlinger et al. (1988) outlined, a number N of ferromagnetically coupled spins may produce at 300 K an ESR absorption several orders of magnitude larger than the EPR absorption caused by an equivalent number of uncoupled spins.

The broad asymmetric signal at $g \approx 2$ ($B_\| \approx 0.34$ T) is representative of the totality of the ESR absorption. A similar signal has been already observed in some volcanic glasses (Bart et al. 1982; Schlinger et al. 1988; Pawse et al. 1998) while its origin is not well established and can be due to small clusters and/or single-domain particles (Griscom 1984; Schlinger et al. 1988). The correlation established in Figs 10(a) and (b) and the study of the temperature dependence of the ESR intensity are in favour of a FMR origin of the broad asymmetric component (Ananou et al. 2002) presumably coming from spherical single-domain ferrimagnetic particles (Griscom 1980b; Griscom 1984; Schlinger et al. 1988). This suggestion is consistent with our preliminary High Resolution Transmission Microscopy observations which reveal in these tephas a population of embedded quasi-spherical grains with a wide distribution in size (from 60 nm to 200 nm); these grains present a crystalline composition as ring and bright spots were observed in selected area diffraction.

The FMR lineshape of small ferrimagnetic particles, randomly oriented, may be influenced by the shape anisotropy, the grain size (domains) and the intrinsic anisotropy field. Shape anisotropy can be neglected in the case of nearly spherical particles. Domains effects are not expected because the hysteresis cycle presented in Fig. 3 shows that, in a field of $B \approx 0.3$ T corresponding to the mean resonance field, the ferrimagnetic particles should behave like single domains ones (Griscom 1984). The superparamagnetism is not expected with ESR because the measuring time $\tau_m = 10^{-10}$ s is much smaller than the relaxation time $\tau$ of the particles’ magnetic moments (Griscom 1980b). Thus, on the timescale of the spectrometer, the ferrimagnetic particles contributing to the ESR intensity are in the single domain and not in the superparamagnetic state. However the hysteresis loop (inset Fig. 3) has the so-called wasp-waisted shape (Roberts et al. 1995; Tauxe et al. 1996) expected when either ferrites with widely different coercivities or superparamagnetic/single domain grains are co-present. Since titanomagnetics with $x = 0.2$ and $x = 0.45$ Ti content cannot lead to wasp-waisted loop because their coercivities are too close to each other, it is likely that these tephas are composed of ferrimagnetic grains with wide distribution of sizes.

6 CONCLUSION

We report on the ESR and magnetic susceptibility measurements performed on ancient marine sediments containing volcanic ash deposited approximately 30 Myr ago. The samples are from sites 709 and 711 of the ODP leg 115 (South Indian Ocean). We show that the ash-content attributed to the Ethiopian traps strongly influences the ESR lineshape and intensity. The free of ash sediment and the volcanic material have very distinct ESR responses.

An important result is the strong similarity which exists between the ESR spectra of ashes deposited in the two sites studied in this work. This result validates the use of the ESR method for the investigation of other sites containing only small amounts of ash. Finally we show a good agreement between the ESR and magnetic susceptibility measurements.

The ESR technique, because of its high sensitivity, easily detects and characterizes small quantities of volcanic ash present in the sediments. In contrast, Mossbauer technique needs a Fe concentration of at least a few percent to be exploitable and microscopy requires time consuming statistical studies of the Fe-rich grains (size, composition, high resolution imaging).

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REFERENCES


APPENDIX A: ELECTRON SPIN RESONANCE SPECTROSCOPY (ESR)

A1 Electron Paramagnetic Resonance (EPR)

Electron Paramagnetic Resonance (EPR) can be experimentally detected in samples containing ions or molecules having incomplete electronic shell. EPR spectroscopy allows us to probe the energy differences between electronic states split by an homogeneous applied magnetic field $B$. Let us consider a spin system (for example $S = 1/2$). In the absence of any applied magnetic field, the two energy states corresponding to $m_s = ±1/2$, where $m_s$ is the magnetic quantum number, are degenerate. A non-zero external field $B$ splits the two levels by an amount $E = g\mu_B B$ where $g$ is $g$-factor ($g = 2.0023$ for a free electron spin), $\mu_B$ is Bohr magneton and $B$ is the Planck constant. This is the Zeeman effect schematized in Fig. A1(a). In presence of a spatially homogeneous magnetic field $B$ (0, 0, $B_z$), the equation of motion for the magnetic moment $M$ (with its quantum number $M_s$) of a substance

$$E = g\mu_B B/2$$

$$\Delta E = h\nu_0$$

$$E = -g\mu_B B/2$$

$\Delta B$

$$dA/dB$$

Figure A1. (a) Zeeman effect for $S = 1/2$. (b) ESR absorption curve $A(B)$. (c) Experimental spectrum corresponding to the first derivative of $A(B)$.© 2003 RAS, GJI, 155, 341–349
consisting of free magnetic dipoles is

$$d\mathbf{M}/dt = \gamma (\mathbf{M} \wedge \mathbf{B})$$  \hspace{1cm} (A1)

where $\gamma = 2g\mu_B/h$. It implies that $\mathbf{M} = (M_0 \cos \omega t, M_0 \sin \omega t, M_z)$ where $M_z$ is a constant. We consider now that an oscillating magnetic field $\mathbf{b} = (b_0 \cos \omega t, b_0 \sin \omega t, 0)$ with $b_0 \ll B$ is superimposed to the static one. When the EPR condition is fulfilled the magnetic moment precesses around the field direction with an angular frequency $\omega_0 = 2\pi \nu_0 = \gamma B_0$. The energy transitions with $\Delta M_z = \pm 1$ will be induced by this oscillating field when the resonance condition $\nu = \nu_0$ is established. But since both transitions occur with the same probability, no noticeable absorption of energy from the alternating field can be detected. In real samples, individual magnetic moments interact with each other and also with the lattice. Due to these relaxation phenomena, the transition probability for $\Delta M_z = +1$ is higher than for $\Delta M_z = -1$. The oscillating field transfers quanta of energy $h\nu_0$ to the spin system and this energy is continuously yielded to the lattice by a relaxation mechanism.

A substantial absorption of energy is then experimentally detected. Generally, EPR spectra represent the absorption of energy per unit time as a function of the applied static field $B$, $\nu_0$ being kept as constant. However, many ions may be EPR silent even if they have a measurable magnetic susceptibility. For instance, this may be the case when their zero field splitting is too high or when excessive line-width caused by a short relaxation time occurs.

Fig. A1(b) shows the shape of the typical absorption curve $\Delta A(B)$. It is characterized by: (i) the resonance field $B_0$, field for which $A(B)$ passes through a maximum; it allows to calculate the $g$-factor from the resonance relation, $h\nu_0 = g \mu_B B_0$; (ii) the linewidth $\Delta B$ which gives informations on the spin dynamics; (iii) the line intensity $I = \int_0^\infty A(B - B_0) dB$. This last parameter is important and is exploited in the present study because, at a given temperature $T$, it is proportional to the static susceptibility of the sample $\chi = \mu_0 M/B$ (measured in a static field $B_0$), where $M$ is the magnetization and $\mu_0$ the vacuum permeability.

A2 Ferromagnetic resonance (FMR)

The theory of ferromagnetic resonance (FMR) is not fundamentally different from EPR (Kittel 1998). It can be applied when compounds have a non zero spontaneous magnetization, namely ferro- or ferrimagnets. In this case, the spins not only experience the applied magnetic field $B$ but also the internal anisotropy field $B_A$ and the demagnetizing field $B_d$ which may be strong in ferromagnetic substances. The total magnetic moment precesses around the effective field $B_{eff}$ which is a such function of $B$, $B_A$ and $B_d$ that in the absence of $B$, $B_{eff} \neq 0$. Therefore FMR can be detected without applying any external field. This implies the existence of a gap $\nu_g$ in the ferromagnetic resonance spectrum. The second important point is related to the temperature dependence of this gap $\nu_g(T)$ which exists in a ferromagnetic substance below the Curie temperature $T_C$. If $\nu_g < \nu_g(T)$, FMR may be undetectable with the available field range at a given temperature. However, most of the natural ferromagnetic iron-rich compounds, when they exist under the form of spherical particles (Griscom 1984), are expected to display an FMR absorption because their anisotropy field is smaller than $B_0 = h\nu_0 / g \mu_B$ ($g \approx 2$). Indeed, for the spherical shape, the demagnetizing field $B_d$ has no effect.

A3 Technique

EPR and FMR experiments are performed on the same ESR spectrometer. The ESR spectrometer is essentially composed of a microwave source, a resonant cavity and a detector connected to each other via a waveguide. The sample placed at the centre of the resonant cavity is irradiated with a microwave field $B$. The resonant cavity is dimensioned so that the microwave magnetic field is maximum at the sample position while the associated microwave electric field is zero. In the absence of any sample absorption, the waveguide and the cavity are critically coupled so that a maximum of microwave energy is stored inside the cavity, while the amount of the reflected energy in the waveguide is minimum. When the sample absorbs some energy because the resonance condition is established, this coupling is no longer critical and some microwave energy is reflected back in the waveguide. This reflected radiation is entirely directed on the detector which converts the incident power into a dc-signal.

To increase the sensitivity of the spectrometer, a phase sensitive detection technique is used. The magnetic field $B$ produced by a laboratory electromagnet is modulated at a frequency $\nu_m$ using small coils located on the cavity sides. Thus, the detector output is an alternative signal of frequency $\nu_m$ which amplitude can be accurately measured using a lock-in amplifier. The shape of the measured signal is schematized in Fig. A1(c). Usually the modulation amplitude of the static field is small compared with the linewidth $\Delta B$. In this case, the shape of the experimental spectrum represents the first derivative of the absorption curve $A(B)$. Graphs containing ESR spectrums are often presented, as it is the case in this article, without vertical axis.