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ESR APPLICATIONS TO METEORITE SAMPLES

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Abstract: Electron spin resonance (ESR) measurements were performed on several meteorites. Preliminary results demonstrate some significant features. After the magnetic separation of powdered samples, some of ESR measurements gave ferromagnetic resonance-type spectra similar to the lunar soils. ESR spectra, presumably associated with radiation-induced defects, were observed in Allan Hills-765 and the CAI portion of the Allende meteorite.

1. Introduction

Electron spin resonance (ESR) spectroscopy and thermoluminescence (TL) detection have become powerful tools in geological dating, as well as in radiation dosimetry (IKEYA, 1993). Radiation damages produced in samples as metastable trapped electron centers and hole centers are the objects of these schemes. ESR is especially advantageous in resolution and reproducibility of signals, besides being sensitive to the paramagnetic ions in samples. Few meteorite samples have been investigated because the native iron phases in such samples were considered to disturb ESR measurements. However, ESR studies of lunar soils to determine the state of Fe were conducted early in the Apollo program. TSAY *et al.* (1971a, b, 1973a, b) and others conducted these studies on the state of the iron in the soils. The largest ferromagnetic resonance (FMR) signal was due to metallic $Fe^{(0)}$ present as single domains less than 300 Å in size. This metallic $Fe^{(0)}$ is considered to have formed during micrometeorite-induced impact melting with the presence of reducing solar-wind particles (HOUSLEY *et al.*, 1973). OSTERTAG *et al.* performed ESR measurements on shocked olivine, as well as Mössbauer and optical absorption and explained the results in terms of shock-induced oxidation (OSTERTAG *et al.*, 1984). TOYODA and IKEYA (1989) reported differences in ESR spectrum for terrestrial samples, such as scoria and lavas, as being a function of cooling rates and the coordination of Fe^{3+}.

In this present research, we have studied the ESR spectra for meteorite samples in order to examine two points: 1) the state of Fe and Fe ions which may reflect the reduction/oxidation environment, shock-impact history, and/or cooling rate at formation of minerals; and 2) possible radiation damage in meteorites, which may yield information on radiation environment and thermal history.

2. Samples and ESR Measurements

Table 1 lists the meteorite samples investigated in this study. All samples except the Allende meteorite were received from National Institute of Polar Research (NIPR) as powders of 200 mg each. Before the ESR measurements, magnetic separation was performed on the powder in order to remove large magnetite and metallic iron. This magnetic fraction constituted about half of each sample. In addition, 10 mg of bulk Allende and the CAI portion were also examined. All measurements were performed with a JEOL JES RE-1X X-band ESR spectrometer at room temperature. Measurements were typically performed with a microwave power of 1 mW and field modulation of 0.1–0.63 mT at 100 kHz.

Table 1. List of samples.

Meteorite sample	Class	% Fe_2SiO_4 in olivine	% $FeSiO_3$ in pyroxene
Y-7301,90	H5–6	18.8 (17.9–34.1)	16.5 (16.2–17.0)
Y-7304,96	L6	24.6 (23.2–25.8)	20.9 (20.5–21.1)
Y-7308,106	Howardite	(14.9–33.0)	(20.5–57.0)
Y-74001,90	H5	18.3 (17.2–19.5)	16.1 (15.5–16.6)
ALH-765,89	Eucrite	(82.9)	(34.0–61.9)
Allende	C3		

Ref. "Catalog of the Antarctic Meteorite".

3. Results and Discussion

Figure 1a shows the ESR spectra for Yamato-74001 before and after the magnetic separation. After the magnetic separation of the sample, a broad spectrum with g-value of 2.1 was observed. The width of spectrum (distance between two peaks in the first derivative ESR spectrum) was about 87 mT. This feature is similar to the FMR of fine metallic $Fe^{(0)}$ in lunar soils (Tsay *et al.*, 1971b). Figure 1b also shows the similar ESR spectra of the magnetic fraction of Y-7301, -7304 and -7308. These data suggest the possibility that very fine Fe particles exist in certain meteorites, with analogy of the lunar soils. Fe^{3+} shows the broad ESR spectra around $g=2$; however, the g-value and spectral width vary widely depending on the coordination of Fe ions. From the present study discussed above, the FMR signal is probably due to the fine particle size of the metallic Fe. However, the ESR data do not rule out the possibility of Fe^{3+}. Unfortunately, we have not yet performed Mössbauer spectroscopy to investigate the presence of Fe^{3+} ions. Reduction processes on the Earth are not severe, so that the native Fe formation occurred in space, although the solar wind near meteorite orbitals is not as intense as that on the moon (Zeller *et al.*, 1966). Existing metallic iron cannot form single-domain Fe by simply quenching reduced melt. The solar wind must be dispersed within the melt to ensure extreme reduction on a near atomic scale.

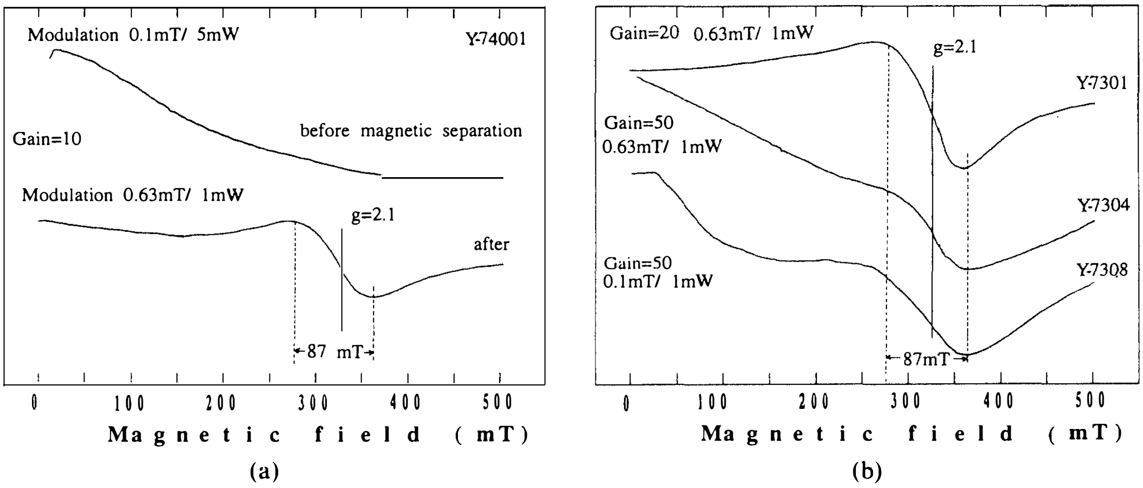

Fig. 1. (a) ESR spectra for Y-74001 before (top) and after (bottom) the magnetic separation. (b) ESR spectra for Y-7301 (top), -7304 (middle) and -7308 (bottom) after the magnetic separation. Gain, modulation and microwave power are indicated in the figure.

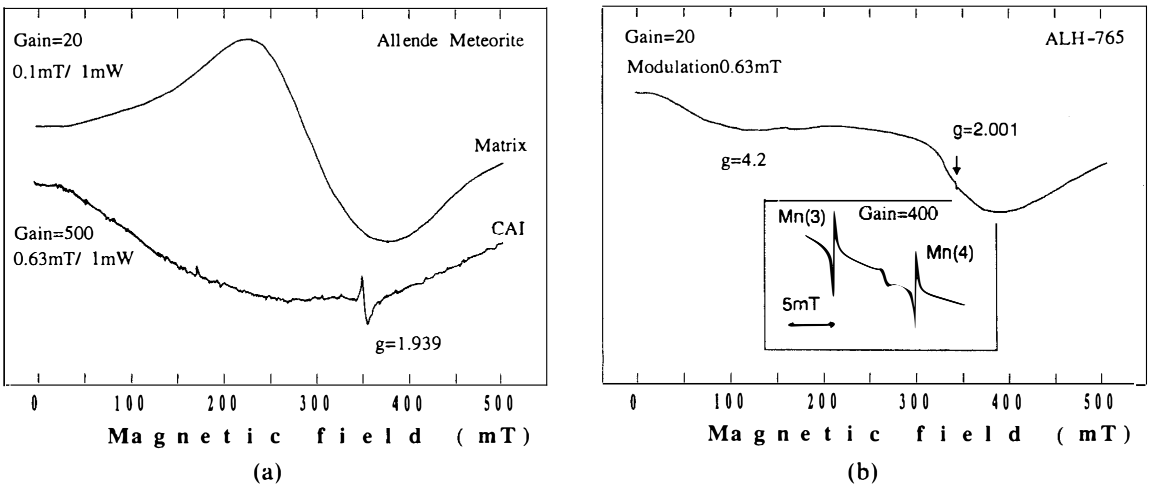

Fig. 2. (a) ESR spectra of Allende meteorite for the matrix (top) and the CAI portion (bottom). Electron center-type ESR signal was seen in the CAI portion at g = 1.939. (b) ESR spectra for ALH-765 meteorite. Hole center-type ESR signal at g = 2.001 is observed. Inset is an enlargement of the signal with manganese markers.

Figure 2a shows the ESR spectra of the Allende meteorite for the matrix and the CAI portion. A broad ESR signal in the matrix is considered due to dispersed Fe^{3+} ion. A sharp ESR signal for the CAI portion at g = 1.939 is probably due to an electron center, possibly formed as a radiation defect. Figure 2b displays the ESR signal obtained from the ALH-765 eucrite. A sharp ESR signal at g = 2.001 is probably a hole-center in the silicate phase.

Figure 3 shows the saturation tendency of the sharp ESR signal in ALH-765 as a function of the microwave power. The ESR signal easily saturates near the 1 mW. This characteristic is very similar to that of the "E′" center in quartz (TOYODA and IKEYA, 1991a). "E′" center is a type of hole center in which an electron is trapped at the oxygen

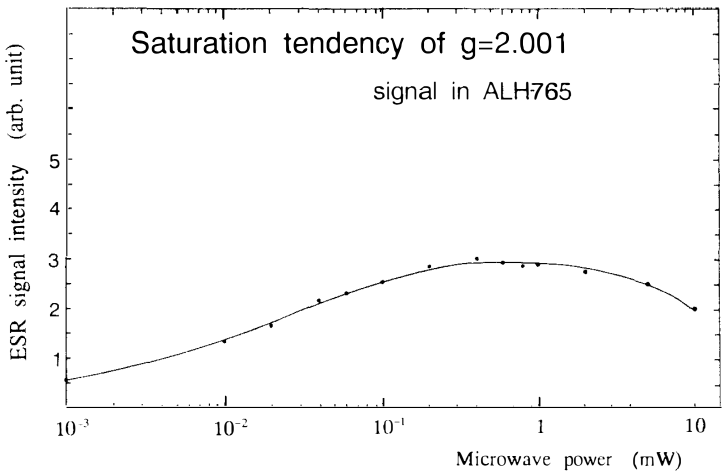

Fig. 3. Saturation tendency of the ESR signal at g = 2.001 to the microwave power in ALH-765 meteorite.

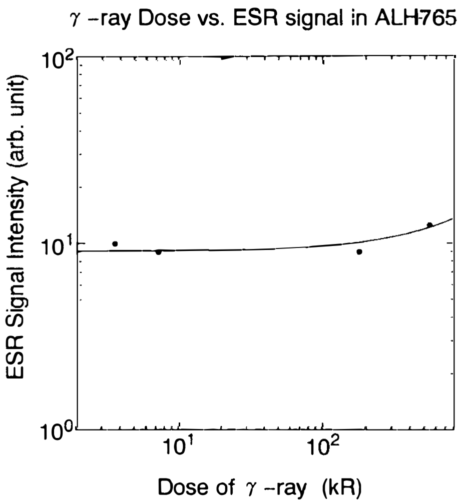

Fig. 4. Growth curve of the ESR signal at g = 2.001 in ALH-765 as a function of γ-ray dose.

vacancy within the silicate structures. In quartz, the ESR signal of the "E′" center was obtained with anisotropic g-values around 2.0003–2.0018. In reality, there are few ESR investigations of radiation defects in silicate minerals except SiO_2; however, "E′" center-type defects can be present in other complicated silicate.

Figure 4 is a growth curve of this signal for irradiation with γ-rays from a ^{60}Co source. The ESR signal at g = 2.001 does not increase with irradiation dose. One reasonable explanation for this result is the lack of available oxygen vacancy to form E′-type defects; *i.e.*, no "E′" center can be formed without an oxygen vacancy. It is considered that oxygen vacancies in silicate minerals can be formed by shock effects or particle irradiation, such as neutron and proton (IKEYA *et al.*, 1992). Therefore, the amount of E′-type center detected by ESR may be closely related to the amount of oxygen vacancy and probably to the cosmic ray exposure age.

Figure 5 shows the results of isochronal heating experiments in air for 20 min to determine the effects on the ESR signal at g = 2.001 in ALH-765. The relaxation

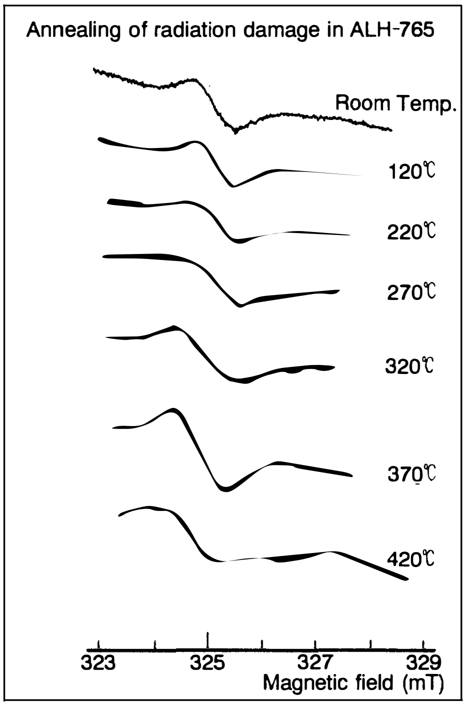

Fig. 5. Thermal stability of the ESR signal at g = 2.001 in ALH-765 after 20 min isochronal experiment in air. Initial signal decays by 270°C, and wider unknown signal appears.

of metastable radiation defects occurs during this thermal activation process. The ESR signal begins to decrease above 120°C and disappears; an unknown wider ESR signal is in its place above 270°C. Assuming a simple thermal activation relaxation process, the stability of this defect at room temperature is estimated to be on the order of a million years. Furthermore, complex ESR signals also appear above 420°C. Although the weak signals, coupled with the limited amount of sample, prevented us from identification of signals, it may be a hyperfine structure of manganese which has diffused away from its initial points of concentration. Significant relaxation of oxygen vacancies in quartz was observed above 400°C (Toyoda and Ikeya, 1991b). Consequently, the decay of ESR signal shown in Fig. 5 is not due to the relaxation of oxygen vacancies but from trapped electron. In any case, it is clear that the sample has not experienced thermal event more than 120°C since its formation (at least after the formation of the defects).

4. Summary

From the preliminary results of this ESR study of meteorites, several interesting observations were made:

1) Very fine particles of metallic iron (< 300 Å) probably exist in several meteorites. Such data from the FMR signal of $Fe^{(0)}$ or from ESR of Fe^{3+} ions may be signatures with which to understand better the environment of formation and subsequent history of meteorites.

2) Sharp signals obtained from the CAI portion of the Allende meteorite, and in ALH-765, are probably considered radiation-induced defects. The ESR signal at g = 2.001 in ALH-765 is considered an "E′" center-type defect from the similarity of

the microwave power dependence. This signal did not increase with the γ-ray irradiation up to 540 kR. Proton irradiation for this sample may increase this ESR signal.

Identification of ESR centers in meteorites samples is unclear at present and requires more investigations. However the data may be used for some simple classification of meteorites.

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