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ELECTRON SPIN RESONANCE (ESR) MICROSCOPES AS A 2D-IMAGING

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Abstract. Microscopic imaging of the concentration of unpaired electron spins or paramagnetic ions has been obtained with the electron spin resonance (ESR). The intense magnetic field gradient method employed in the conventional magnetic resonance imaging (MRI) is realized at a pin-hole site. New methods to employ the scanning of the localized magnetic field at a pin-hole region and of the localized microwave field are introduced to obtain the surface image. Present state of ESR imaging especially microscopic imaging (microscope) is reviewed briefly.

INTRODUCTION

Electron spin resonance (ESR) is a microwave absorption spectroscopy to detect states of unpaired electron spins and absorption measurement. The principle resembles that of nuclear magnetic resonance (NMR) in which the electromagnetic wave is absorbed by the transitions between the Zeeman energy states of nuclear spin magnetic moment under the external magnetic field. The similar transition between the Zeeman splittings of electron spin magnetic moment is called ESR. ESR is now used as a method of dating in geoscience, archaeology, anthropology, preservation science and forensic science as well as a method of radiation dosimetry (Ikeya: 1986, 1988; Ikeya & Miki: 1985).

The principle of ESR dating is to utilize the accumulated electron spins created by natural radiation or by chemical reaction. In some case the requirement to determine the age locally for the determination of a growth of a stalactite or a shell for example (Ikeya: 1975) forced us to establish the ESR dating in an image. However, little work has been made in ESR imaging in microscopic scale. Magnetic resonance imaging (MRI) used in hospitals is a computer tomography (CT) of nuclear magnetic resonance (NMR). It employs the method of magnetic field gradient so that the spatial resolution of NMR in realized (Lautebur: 1973). Most

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ESR imaging studies employs this method. One of the disadvantage is the broad linewidth of ESR signal. Although the microscopic resolution of 10 μm is possible in NMR microscope, the conventional magnetic field gradient of 2 mT/cm (0.2 T/m) make the resolution of about 1~0.1 mm for the ESR signal with the linewidth of less than 1 mT.

The spatial resolution of ESR imaging suggested by Lauterbur (1973) was examined theoretically as to have a maximum of about 10 μm (Karthe & Wehrdolfer: 1979). The paramagnetic centers in diamond was demonstrated with the magnetic field gradient of 5 mT/cm (Hoch & Day: 1978). Several trials to develop ESR imaging based on the magnetic field gradient method was made (Eaton & Eaton: 1984; Nishikawa *et al.*: 1985) as reviewed by Ohno (1986, 1987). The low frequency of L-band (1~2 GHz) is used as the main interest in the field of biology is the detection of superoxide in vivo and cancer studies: the microwave loss is the small and the penetration depth is appropriate at this frequency. ESR imaging of a rat brain and a plant stem with a stable nitrogen radical involvement is demonstrated.

Present paper describe the microscopic ESR imaging studies with several other principles especially with the method of scanning local magnetic field and localized microwave field. The ESR microscope to detect radicals and paramagnetic ions will be widely used in physics, chemistry, biology, clinical medicine and mineral sciences.

A METHOD OF CT-ESR MICROSCOPE

The conventional technique of ESR imaging employs the field gradient coils in addition to the uniform static magnetic field created by the usual electromagnet. The field at the spatial site (x, y, z) is expressed as

$$H(x, y, z) = H_S + (\partial H/\partial x)x + (\partial H/\partial y)y + (\partial H/\partial z)z \qquad (1)$$

were $\partial H/\partial x$, $\partial H/\partial y$ and $\partial H/\partial z$ are the field gradient produced by the field gradient coils, H_s is the uniform field produced by the electromagnet. The resonance occurs at the magnetic field H_0, for the microwave frequency of ν ($h\nu = g\beta H_0$). Hence, the signal position obtained by sweeping the uniform magnetic field H_s is indicative of the spin positions as shown in Fig. 1(a) and Fig. 1(b). The ESR spectrum under the field gradient is expressed as a convolution

$$g(H) = \int_0^\infty r(H - H')f(H')\mathrm{d}H' \qquad (2)$$

where $f(x)$ is the distribution of the spin concentration, $r(H)$ is the shape function under the uniform homogeneous magnetic field.

The Fourier transform of convolution integral in the Equation (2) is given as

$$G(\omega) = R(\omega)F(\omega). \qquad (3)$$

Hence the distribution of the spin concentration is given using the experimentally

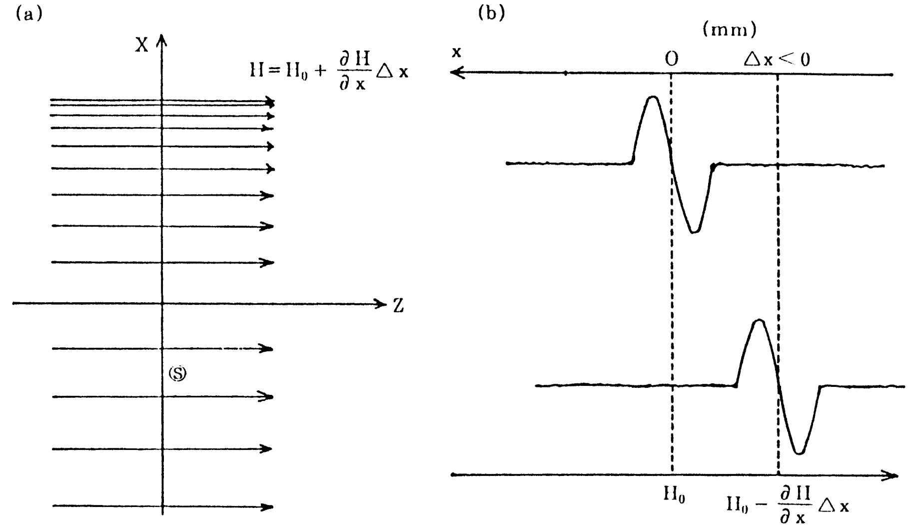


Fig. 1. (a) Magnetic field gradient ($\partial H/\partial x$) created by the 8-shaped coil pairs. (b) The shift of the ESR signal by the application of the magnetic field gradient. The shift in the resonance is directly related to the position. Anti Helmhol & coil pairs create the gradient $\partial H/\partial z$.

determined $g(x)$ and $r(x)$

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G(\omega)/R(\omega)\exp(i\omega x)d\omega. \tag{4}$$

Main difficulties of this method as a microscope is the necessity of high field gradient for ESR signal with a large linewidth. The problem was solved by making a sample holder with small field gradient coils that can be inserted into a microwave resonator (cavity) (Ikeya & Miki: 1987). The effort up to now was to make field gradient coils cooled by insulator oils and to employ the pulse operation to avoid heating (Ohno: 1986).

The antihelmholtz coil pairs produce the magnetic field gradient along the uniform field direction (z direction). The letter 8 shaped coils create the field gradient along x or y directions.

Figure 2(a) shows a typical example of the one-dimensional ESR microscope arrangement with a commercial cylindrical microwave cavity TE_{011}. A test sample of organic diphenyl-picryl-hydrazil (DPPH) particles separated about 50 μm by a mylar foil and sandwitched with other polystyrene is used to check the field gradient. Figure 2(b) shows the ESR signal change by applying the current to the field gradient coils. It is clear that the separation of 50 μm is clearly seen. The resolution of a few μm is practical with this method without the deconvolution.

An example of one-dimensional ESR imaging to study the microdosimetry is shown in Fig. 3. A single crystal of NaCl was irradiated by soft X-rays. The signal intensity of defects with and without the field gradient are shown in (a) and (b). The

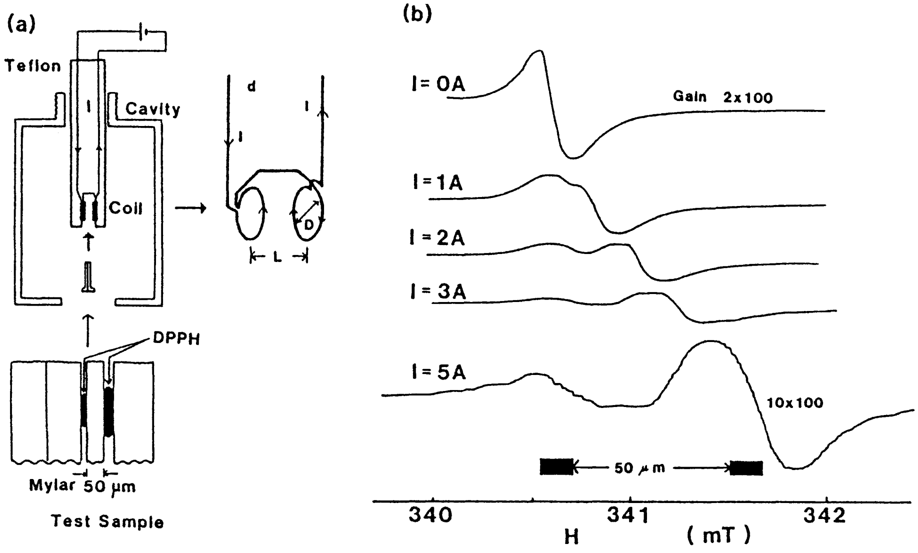


Fig. 2. (a) An ESR cylindrical cavity of TE_{011} mode and the sample holder with a test sample of DPPH separated by 50 μm mylar sheet. (b) ESR spectra with the current to the anti-Helmholtz coil. The field gradient of 20 T/m (2 KG/cm) is clear from the signal separation (Ikeya & Miki: 1978).

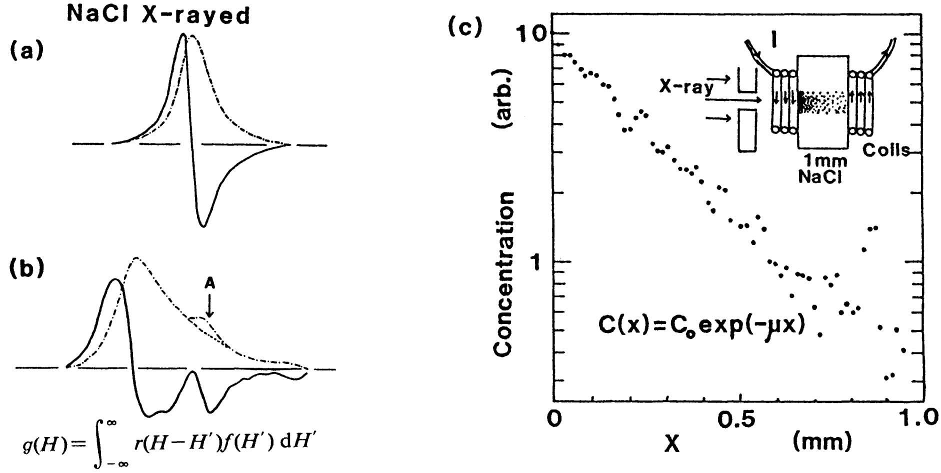


Fig. 3. ESR derivative spectra of NaCl X-irradiated from one side and the integrated one (dashed curve), (a) without the field gradient, $r(H)$ and (b) with the field gradient, $g(H)$, (c) An exponential decay of the spin concentration from the surface is obtained following the Fourier Transformation (Ikeya & Miki: 1978).

one dimensional distribution obtained by the Fast Fourier Transform (FFT) is shown in (c). The exponential decrease of the defect concentration clearly indicates the attenuation of X-rays.

The advantage of the method is that the low cost current & voltage source is sufficient to produce a field gradient of 2 kG/cm (20 T/m) at the small site. Main obstacle of this method was the microwave loss by the insertion of the coils. Orientation of the sample is made to get two or three dimensional images using the sample holder.

SCANNING LOCALIZED FIELD

A part from the conventional ESR imaging studies using the commercial field gradient coils and magnet attachment, the basic idea to create the magnetic field at a pin-hole region with microfabricated coils in a microwave cavity has lead to an invention of the "scanning ESR microscope". The localized field of both the alternative modulation field and the static resonance field are employed in these studies.

1. Localized modulation field

The magnetic field modulation of 100 kHz is applied in ESR measurement to enhance the sensitivity with phase-sensitive lock-in-amplifier system. If the modulation is localized at a pin-hole region, one can detect magnetic resonance at the pin-hole region. The scanning of the modulation field at the surface of the sample give the magnetic resonance image of the surface (Miki & Ikeya: 1987).

The schematic illustration of the scanning ESR microscope was shown in Fig. 4(a). The microcoils for 100 kHz field modulation is scanned mechanically to obtain

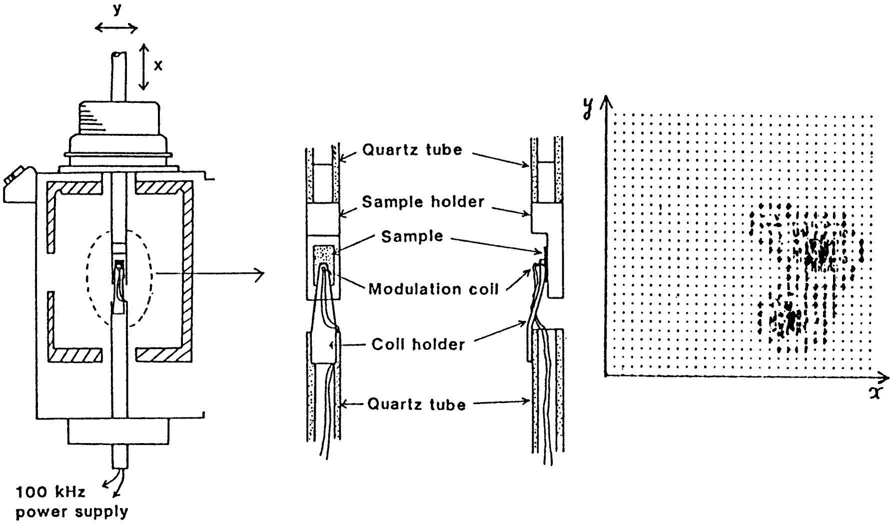


Fig. 4. (a) A schematic illustration of the scanning surface microscope with mechanical site scanning the modulation field, (b) The image of three DPPH particles in X-Y plane (Miki & Ikeya: 1978).

the surface image using the stepping the motor and X-Y stage. The scanning is actually made by moving the sample rather than the modulation coil so that the frequency change of the resonant cavity by the movement of the coil is avoided. Figure 4(b) shows a typical result of three DPPH particles in X-Y plane. The ESR signal at several points in the X-Y plane gives the two dimensional image of the spin distribution.

Figure 5(a) shows the differential modulation method. The surface modulation wire produces the field along z-direction. However, the positions before and after the coil experience the field in opposite direction. The phase is 180 different. Hence, what one can obtain by scanning the coil along x-direction is the difference or a differential form $\mathrm{d}f(x, y)/\mathrm{d}x$. Actual spin distribution must be obtained by integrating along x-direction (Miki and Ikeya: 1988).

Figure 5(b) shows a typical example of microdosimetry using alanine powder casted with paraffine which is widely used as ESR dosimeter elements. The alanine pellet was exposed to X-rays through pin-holes of a lead plate. ESR imaging of the irradiated part is obtained.

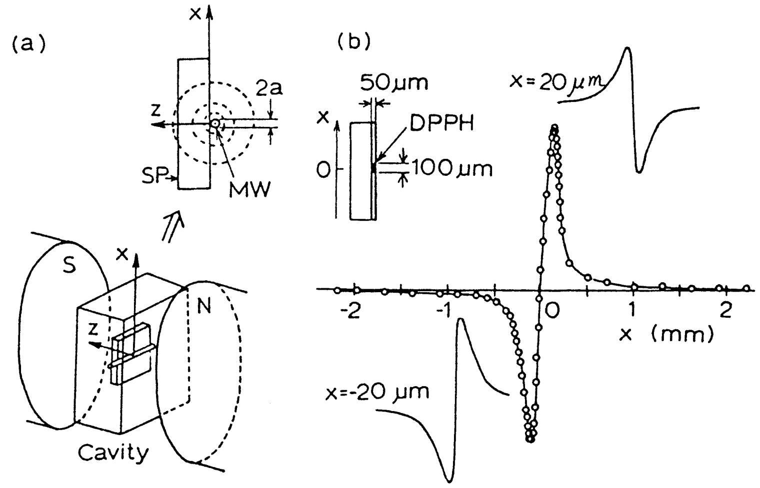


Fig. 5. (a) The direction of the magnetic field and of the modulation in the differential modulation method. The difference of the signal intensity is obtained. (b) Microdosimetry of alanine pellet X-rayed through a pin-hole (Miki & Ikeya: 1988).

2. *Scanning static magnetic field*

Additional field of a few tenth of mT at a pin-hole region shifts the resonance magnetic field. Mechanical or electronic scanning of the site of the pin-hole magnetic field gives the two dimensional ESR image. One way to obtain such an image is to scan the field site mechanically as described for the ESR microscope system which scan the modulation coil. Sample scanning may be also used as previously. However, more refined method is proposed to scan the local field electronically with a microfabricated wire arrays.

Figure 6(a) shows the schematic illustration of the wire arrays. The magnetic field at the wire spacing is enhanced or reduced by H, due to the two way current flow at i th and $(i+1)$th wire. A typical 1-D imaging sample holder that creates magnetic field locally above the wire array is indicated. Wire arrays for 2-D imaging is shown in Fig. 6(b). Similar current along x-direction produce field Hz between j th and $(j+1)$th wire. The intersection element at the square give the magnetic field of (H_1+H_2). If the uniform static magnetic field is kept constant so that $H+H_1+H_2$ is in resonance and H is in "off-resonance", ESR signal intensity at the square site is obtained. By switching "on" and "off" the current in the wire, two dimensional ESR imaging can be obtained. A test sample holder for one dimensional microwire arrays printed on quartz sample holder with the modern regist-masking method. The wire width is about 50 μm and the bottom end was connected.

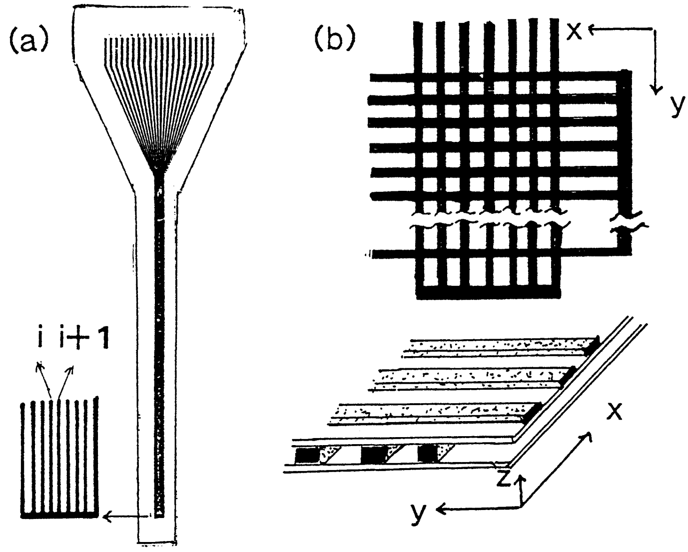


Fig. 6. (a) Microfabricated wire arrays for creation of the local static magnetic field. The sample holder with the expanded tip of the wire arrays. (b) Two dimensional wire array printed on quartz plate for 2D-image.

Figure 7(a) shows the ESR spectrum with the two way current in two adjuscent wires. The standard test sample of a triangle DPPH pattern is attached to the holder. The ESR signal intensity estimated from the height at the shifted field position give the pattern as inserted in the figure.

One dimensional arrays can give the spin concentration of the triangle as shown in Fig. 7(b). The concentration of the spins can be obtained with the resolution of the wire spacing. The disadvantage of this microwire array system is the heating of the thin wire by the high current flow.

The advantage of these methods is to detect the concentration of the specific radicals by tuning the magnetic field. The disadvantage is the detection of ESR

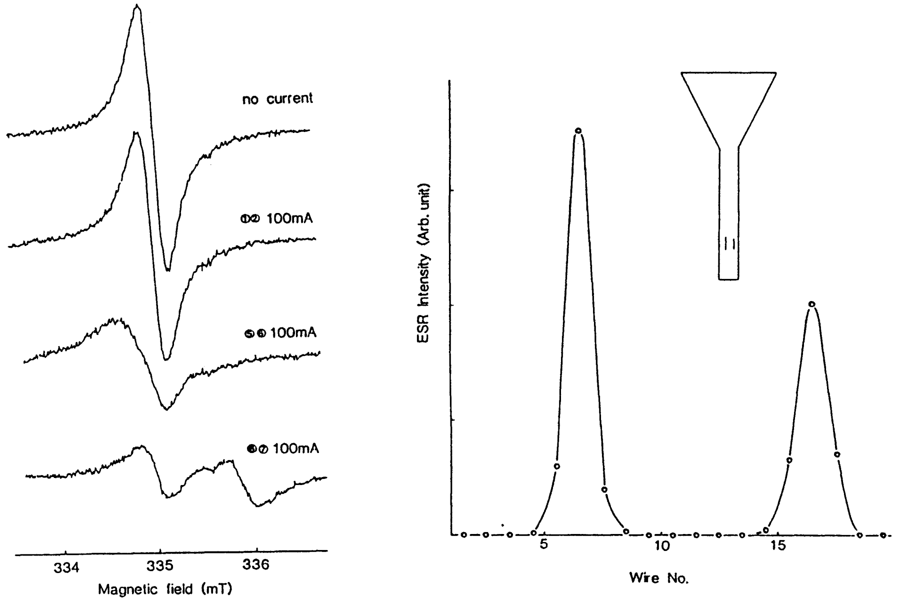


Fig. 7. (a) The ESR spectrum of the DPPH test sample. The signal intensity is shifted by the application of the voltage to the adjacent wire. (b) The intensity profile of the shifted ESR signal intensity as a function of the site for two point test pattern with DPPH.

image only at the surface, i.e. two dimensional imaging at the surface region rather than in the bulk since the pin-hole magnetic field intensity is the strongest at the surface but not so deep inside the sample.

MICROWAVE FOCUSED MICROSCOPY

1. A scanning ESR microscopy

Previous scanning ESR microscope employed the sample scanning at the localized pin-hole resonance field region or pin-hole modulation field. Present system employs the microwave magnetic field for resonance at a pin-hole localized region. The simplest one is the system shown in Fig. 8. The microwave cavity has a small hole from which the microwave magnetic field along x-direction is used for ESR measurement. The sample is scanned mechanically by the stepping motor.

Figure 9 shows a typical example of fossil crinoid recently measured in this laboratory (Furusawa & Ikeya: 1988). The concentration of Mn^{2+} and radiation-induced radicals in some minerals and fossils are imaged on the CRT. Modulation of 100 kHz is made by the wire above the slice of the sample in the arrangement.

The resolution of the microwave forcus scanning ESR microscope is not the size of the hole but the step length of the position scanning. If the microwave field intensity inside the hole region is calibrated with a small particle of DPPH, one can get the system function $r(z, x)$. The convolution integral with the distribution function of the spin concentration within the pin-hole region gives the microwave

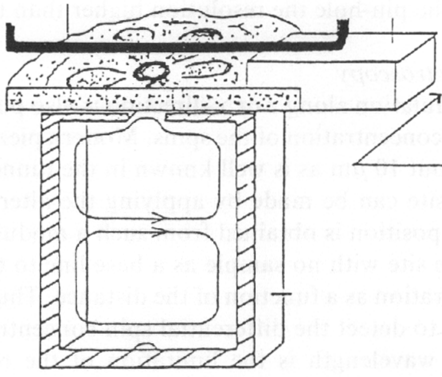
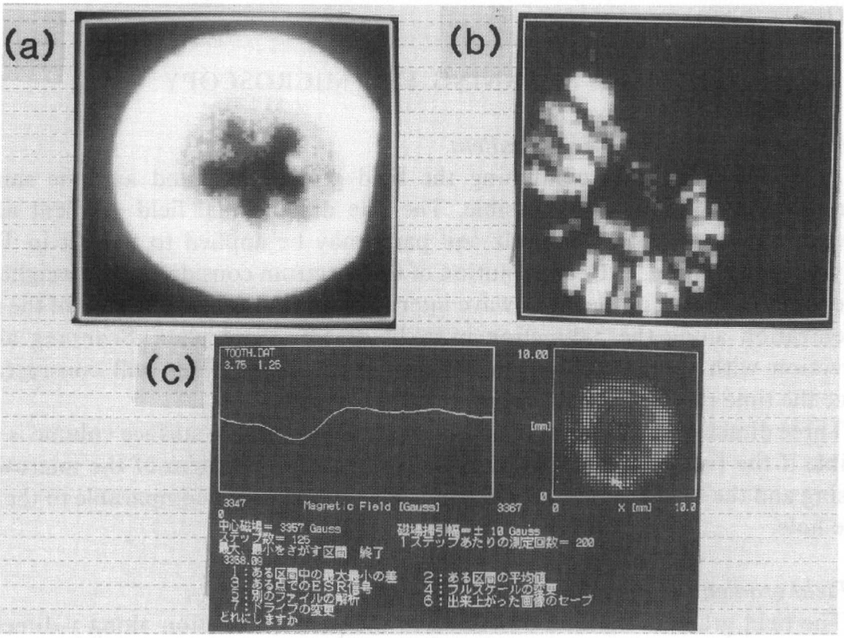


Fig. 8. ESR microscope for focused microwave field. The sample is scanned mechanically by a stepping motor (Furusawa and Ikeya: 1988).



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0
中心磁場= 3357 Gauss          磁場掃引幅= ± 10 Gauss
ステップ数= 125               1ステップあたりの測定回数= 200
最大、最小をさがす区間  終了
 3358.09
  1：ある区間中の最大最小の差     2：ある区間の平均値
  3：ある点でのESR信号           4：フルスケールの変更
  5：別のファイルの解析           6：出来上がった画像のセーブ
  7：ドライブの変更
どれにしますか
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Fig. 9. ESR microscopic imaging of a carbonate fossil (a) "crinoid", (b) ammonite and (c) the ESR spectrum of gamma rayed tooth and the image (Furusawa & Ikeya: 1988).

absorption.

$$g(z, x) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} r(z-z', x-x') f(x', z') \mathrm{d}x' \mathrm{d}z'.$$

The deconvolution of the ESR spectra by scanning *z* and *x* gives with a step much smaller than the size of the pin-hole the resolution higher than the size of the hole.

2. *Site modulation spectroscopy*

The sample site modulation along z or x-direction is also possible in this system to obtain the differential concentration of the spins. Modern piezoelectric transducer shifts the position to about 10 μm as is well known in the tunnelling spectroscopy. The modulation of the site can be made by applying the alternative voltage. The differential signal to the position is obtained from such a modulation spectroscopy. The integration from the site with no sample as a base line to the other side of the sample gives the concentration as a function of the distance. Thus, the site (position) modulation is a method to detect the differential spin concentration. The modulation amplitude not the wavelength is the limitation of the resolution. It is our misunderstanding to consider that the resolution is the length of the electromagnetic wave or the size of the spot of the electromagnetic wave. We have already shown that the resolution of 10 μm with the microwave of the wavelength 3 cm. The resolution of such a site modulation spectroscopy is the amplitude of the modulation (Ikeya, 1989).

OTHER SCANNING ESR MICROSCOPY

1. *Microwave focus and field gradient*

A hybrid techniques combining the field gradient method and the sample scanning microscope is also possible. The one dimensional field gradient along z-direction with the anti-Helmholz coil pairs may be applied to the slit in TE_{102} cavity as shown in Fig. 8. Deconvolution of the spectrum considering the weight due to the inhomogenuity of the microwave intensity will give the distribution of the spin concentration along the z-direction in a slit of TE_{102} end plate. Scanning along x-direction with stepping motor will give the 2D-image. This will considerably reduce the time required for the measurement.

Three dimensional (3D) imaging, although limited to the surface volume is also possible if the field gradient is along y-axis. The simple system of the microwave focusing and the field gradient give the image up to the depth comparable to the size of the hole.

2. *Field gradient and local modulation*

The field gradient method described in the previous section along y-direction with the cavity having a hole will give the depth profile of the spin concentration along y-axis. The scanning local modulation with a small modulation wire tip will determine the concentration in y-z plane. If the size of the hole is a few mm, the microscopic distribution of the spin concentration can be determined. Several other combination is possible in principle to establish ESR microscope.

SUMMARY

Our new scanning ESR microscope system is described. The conventional field gradient method used in 3-D NMR imaging and ESR imaging may be useful with the intense field gradient produced by the coil in the resonator cavity. If the cavity is of a special type, the field gradient by the coils close to the sample is intense enough to guarantee the resolution of μm or a few tenth of μm: the main obstacle is the low concentration of spins.

Scanning of local magnetic field or the local modulation field at a pin-hole region on the surface of the sample is new development made in our laboratory. Two dimensional surface image can be obtained by scanning the probe or the sample itself. Forcusing the microwave magnetic field in a small region is another procedure to obtain the local spin concentration. Scanning the sample or the localized microwave give the two dimensional image. The site (position) modulation is another way to get a high resolution.

Hybridization of several of these techniques is also possible to establish an ESR microscope. The potential use of ESR microscopes is enormous in clinic diagnosis, chemistry, biology, mineralogy, paleontology as well as in engineering such as ceramics and semiconductor technology. ESR microscope system attached to a portable ESR spectrometer in which permanent magnet of NdBFe (NEOMAX) and field sweep coils are used will be a convenient tool in a wide field.

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DISCUSSION

Q1. Are you going to apply your technique to medical problems?

Q2. Is it possible to increase the resolution? (Takaki, R.)

A1. Our major interest is earth science. But we will apply this ESR microscope to medical problems to demonstrate the usefulness.

A2. Yes. The actual resolution is neither the size of the local magnetic field nor that of the microwave spot. It is the step distance in the scanning or the site modulation amplitude that restricts the resolution. It is by no means the wavelength. For the details, see the proposal in my review article in Analy. Science 5, 5–8 (1989).

Note added in proof

Our portable ESR spectrometer using a permanent magnet circuit of NdBFe (Neomax) is 2.2 kg in weight. The microwave oscillator using a dopplar-radar Gunn diode for an automatic door system has reduced the cost considerably. An ESR microscope using this portable ESR is realized (IKEYA and FURUSAWA (1988) in the proceedings of International Symposium on ESR Dosimetry and Applications in München).