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Magnetic Resonance in Irradiated Zircon

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Electron spin resonance has been observed in coloured zircon. The pattern is anisotropic with respect to the field orientation, and can be fitted with electronic spin $S=1$, $g=2.018$ and $|D|=10\times10^{-4}\,\mathrm{cm}^{-1}$. As a model for this magnetic centre, Zr^{2+} adjacent to an oxygen vacancy has been proposed. In zircon heated to 700°C in air, a very broad resonance absorption was found. The magnetization measurements have been carried out, and the results show that it has ferromagnetic properties.

Zircon, a natural crystal of zirconium orthosilicate ($ZrSiO_4$), occurs in colourless, brown, red and blue forms, but the last colour is not a natural product but obtained by heating stone of a different colour[1] under reducing conditions. The brown to red colouration can be regenerated by irradiation[2]. The experiments by Lietz[3] give a general explanation for this behavior. Irradiation (UV or radium) gives rise to the spectrum denoted by 1 in Fig. 1. Heating to 100 to 200°C changes this spectrum to 2. With further heating, the absorption fall uniformly over the whole range investigated, as showen by the curve 3. Lietz splits up the absorption curve into three separate maxima. In his paper, the curve producing the maximum "*a*", has been ascribed to the *F*-centres of the zircon, and the maximum "*b*" to the *F'*-centres. But this consideration seems to be without adequate physical foundation.

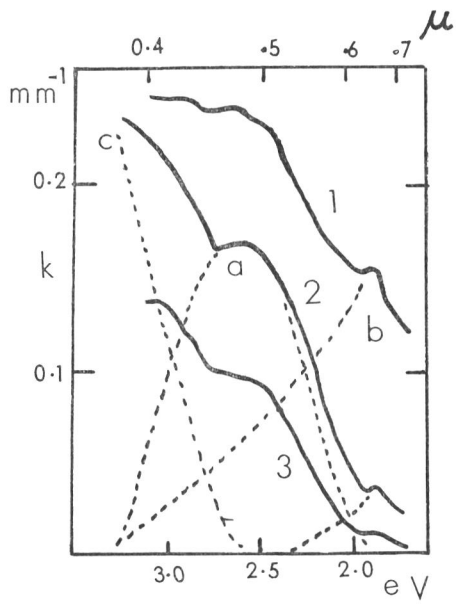


Fig. 1. The absorption bands produced in a colourless zircon by irradiating and heating (after Lietz).

We have measured the electron spin resonance of coloured zircon with gamma irradiation and thermal bleaching. A part of spectra obtained is shown in Fig. 2. The

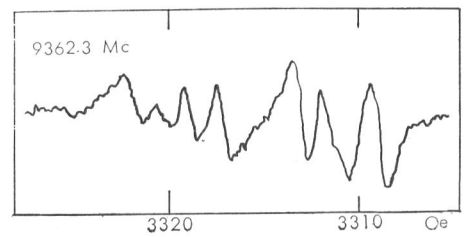
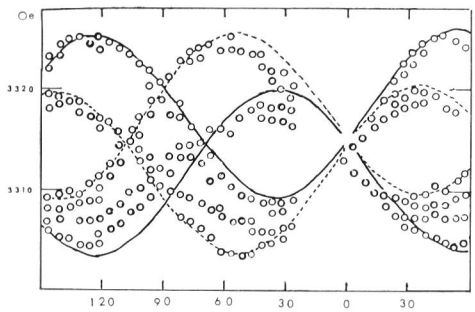


Fig. 2. Observed spin resonance spectrum of a coloured zircon.

resonance signal intensity shows little change with heating the crystal at 100°C for 2 hr., and decreased to about a half with heating at about 200°C for 2 hr. Therefore this magnetic centre is thought to correspond to the "*a*"-centre. The initial concentration of the centre was estimated to be about $5\times10^{18}/\mathrm{cm}^3$ from its signal intensity.

The spectra consist of several lines which are anisotropic with respect to the magnetic field orientation. When the magnetic field is nearly in the *bc*-plane of crystal, the observed angular variation of the line positions are shown in Fig. 3. When the field is parallel to the *c*-axis, only a single line is observed.

These results have been analysed by making the following assumptions: (1) the magnetic centres have the electronic spin $S=1$, (2) they are in a crystalline field of axial sym-



Angle between c-axis and magnetic field in degree

Fig. 3. Angular variation of the observed line positions (circles) when the magnetic field is rotated in the bc-plane. The full and dotted lines show the calculated values with the angles between the c-axis of the crystal and z-axes in the spin Hamiltonian taken as $+54°$ and $-54°$ respectively.

metry, (3) there are two nonequivalent centres whose symmetry axes make angles of approximately $+54°$ and $-54°$ with the c-axis respectively. The spin Hamiltonian is expressed in the following form,

$$\mathscr{H}=g_{\parallel}\beta \boldsymbol{H}_z\boldsymbol{S}_z+g_{\perp}\beta(\boldsymbol{H}_x\boldsymbol{S}_x+\boldsymbol{H}_y\boldsymbol{S}_y)+\boldsymbol{D}(\boldsymbol{S}_z^2-1/3\cdot\boldsymbol{S}(\boldsymbol{S}+1)),$$

with parameters $g_{\parallel}\approx g_{\perp}\approx 2.018$ and $|\boldsymbol{D}|=10\times 10^{-4}\,\mathrm{cm}^{-1}$.

As a model for this centre, we would like to propose Zr^{2+} adjacent to an oxygen vacancy[4]. The behavior of Zr^{2+} ($4d^2$, $^3\boldsymbol{F}_2$) under the influence of crystalline field has not been investigated, but it is thought to be similar to the case of V^{3+}($3d^2$, $^3\boldsymbol{F}_2$). Abragam and Pryce[5] have derived approximate formulas for the energy level of V^{3+} in an axial field.

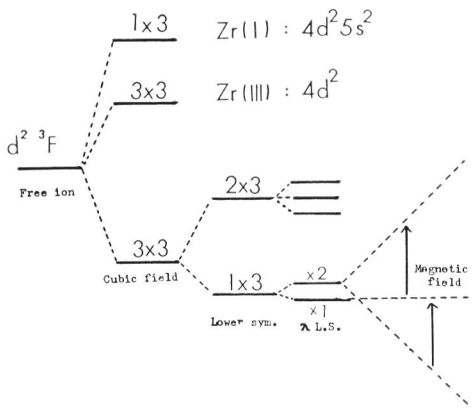


Fig. 4. Energy level diagram of d^2 in an axial field.

According to their results, as shown in Fig. 4, in these ions with two magnetic electrons ($S=1$), the sevenfold orbital level is split into an upper singlet and two triplets. The basic triplet is split into a lower singlet and an upper doublet. Under the spin-orbit coupling, these spin triplets are split with a singlet lying lowest, a doublet slightly higher, and the remaining levels some hundreds of cm^{-1} higher. The separation between the singlet and the doublet is small, and only these three electronic levels contribute to paramagnetic resonance phenomena. They can be regarded as associated with an effective spin $S=1$.

In zircon, as shown in Figs. 5 and 6, Zr^{4+} is in nearly cubic field surrounded by eight nearly equally distant oxygen ions[6]. By irradiation, a zirconium cation adjacent to an oxygen vacancy may become Zr^{2+} in an axial

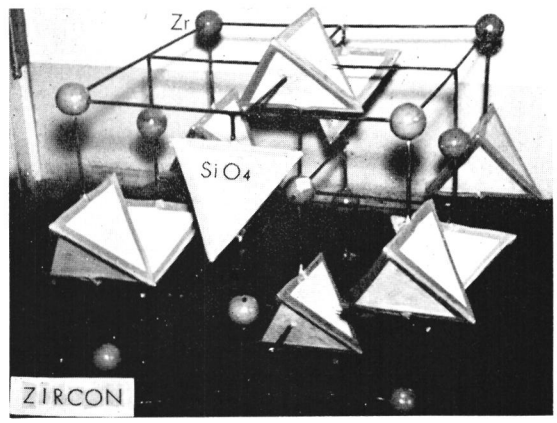


Fig. 5. Structure of zircon. The (SiO_4) ions are indicated by tetrahedra.

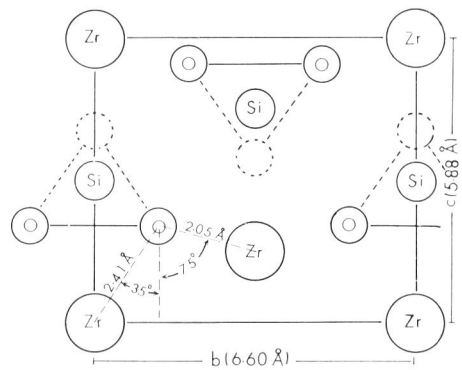


Fig. 6. Structure of zircon on the bc-plane showing the relative position of Zr and adjacent O atom. The dotted circles represent O atom above or below the plane.

field, and at the same time some displacement will occur resulting the symmetry axis in the direction at an angle of about 54″ with the c-axis.

If we assume that there are four types of magnetic unit, each with electronic spin $S=1/2$, and the same principal g-values but with symmetry of different orientations, then the values of parameters are obtained as $g_x=2.019$, $g_y=2.012$ and $g_z=2.025$, and one of the principal axes is nearly in the bc-plane at about an angle of 54° with the c-axis.

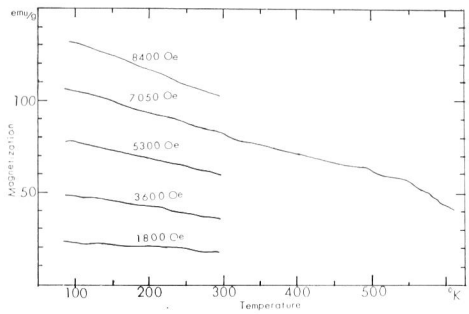


Fig. 7. Magnetization-temperature characteristics of the powder of baked zircon.

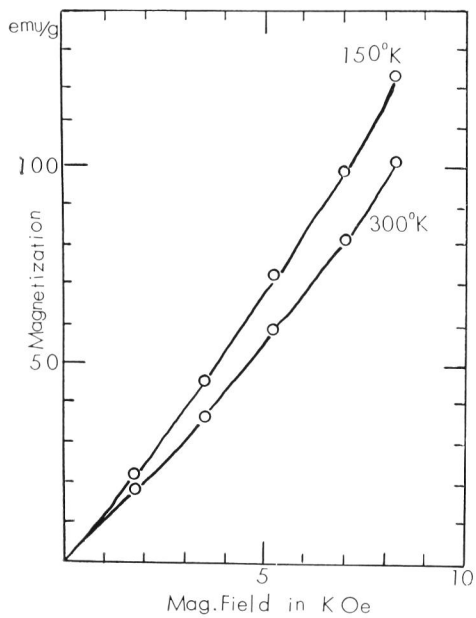


Fig. 8. Magnetization-field characteristics of the powder of baked zircon.

Some crystals show in addition weak spectra in both high and low sides of magnetic field. The analysis has not been performed yet.

When zircon is heated to about 700°C in air, the colour becomes dirty reddish brown. In this specimen, a resonance absorption with very broad width (over a thousand Oe) was observed. Though the measurements are still in progress, the observed magnetization characteristics of the powder of this baked zircon are shown in Figs. 7 and 8. From these results, this specimen seems to be ferromagnetic or ferrimagnetic.

Acknowledgements

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