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THE DISTRIBUTION OF URANIUM, RARE EARTHS, AND COLOR CENTERS IN A CRYSTAL OF NATURAL ZIRCON

P. E. Fielding, *Department of Physical and Inorganic Chemistry, University of New England, Armidale, N.S.W. 2351, Avstralia.*

Abstract

The uranium content and its distribution in a zoned crystal of zircon (hyacinth) is determined by the Lexan print technique. Flourescence photography and spectroscopy establishes the distribution of praseodymium. The relationship between these impurities and the color centers responsible for the characteristic red coloration is examined. It is concluded that the centers are Nb^{4+} ions produced by the radiation induced reduction of Nb^{5+} ions which occupy certain Zr^{4+} sites. The presence of a defect with a characteristic absorption band at 3400 cm^{-1} is required before the reduction can proceed in a natural crystal.

Introduction

Zircon is an important accessory constituent of many igneous and metamorphic rocks. It is also known to occur in substantial amounts in detrital deposits derived from both of these primary sources. Consequently many investigators have studied zircon in order to derive information on the geochemical conditions—igneous and metamorphic—prevailing at the time of growth (Deer, *et al.*, 1962).

Normal zircon belongs to the tetragonal crystal system and quite commonly contains rare earths and uranium in concentrations of the order of 6×10^3 ppm and 2×10^2 ppm respectively. Much higher concentrations are however usually associated with the isotropic metamict form (Berman, *et al.*, 1953).

The distribution of rare earths in zircon grains were studied by examining the fluorescence emission when excited by ultra-violet radiation and the intensity patterns used to infer their petrogenic significance (Foster, 1948). Age determinations of zircons are based mainly on the fission-fragment-track method (Fleischer, *et al.*, 1964), or on the measurement of the uranium-lead and lead-lead ratios (Aldrich, *et al.*, 1957).

Radiation damage effects ascribed to the presence of uranium provide the basis of several indirect methods. Included in the latter category is the thermoluminescence technique based on the thermal destruction of color centers (McDougall, 1968) and an X-ray diffraction method (Fairbairn and Hurley, 1953) in which the changes in certain interplanar spacings are related to the amount of radiation damage suffered by the lattice which in turn can be related to the age of the zircon. Inhomogeneous distribution of uranium in zircon has been shown by several investigations (Weigel, 1938) (Buttlar and Houtermans, 1951) to give rise to errors when the latter indirect dating method is used. Color centers in zircon seem to be associated with the presence of uranium (Weigel, 1938) and in some samples they occur in bands parallel to certain crystal faces. Recent publications claim to have identified these centers (Matumura and Koga, 1962; Chirkin, *et al.*, 1963), but the relationship of the latter to the distribution of uranium and rare earths is uncertain, this should be understood if this mineral is used in age determinations and petrological investigations.

The present report deals with this aspect. The results were obtained from a study of oriented sections prepared from a zircon crystal weighing 16 g, density 4.62 g/cm^3. This sample (Hyacinth) exhibited particularly well-developed growth zoning in shades of red and was recovered together with others weighing up to 50 g from the alluvium derived from a pegmatite in the New England Batholith. The age of this intrusion is late Permian ($250–225 \times 10^6$ years) and is based on potassium-argon measurements (Cooper, *et al.*, 1963) made on biotite separated from whole rock specimens of adamellite or granite and on hornblende from andesite.

Experimental Procedures

A preliminary examination showed that the red coloration was distributed as parallel bands extending through the crystal. The crystal was oriented on a jig so that 1 mm sections normal to these bands could be sawn off with a 0.3 mm thick diamond blade. The resulting wafers were transferred to a grinding-polishing jig, the final polish being given on a tin lap using Linde A aluminum oxide powder. Such sections gave straight extinction under a polarizing microscope with the *C* axis normal to the boundary between the red-banded and adjacent clear sections Figure 1 shows this in detail. The yellow fluorescence was excited using an Osram HBO-100 high pressure mercury lamp, quartz optics and a water-cooled Corning CS-7-50 filter (14 percent transmission at 3650 Å). The 3650 Å mercury emission was focused onto the specimen mounted on the stage of a metallurgical microscope and the fluorescing object was photographed through glass objectives on

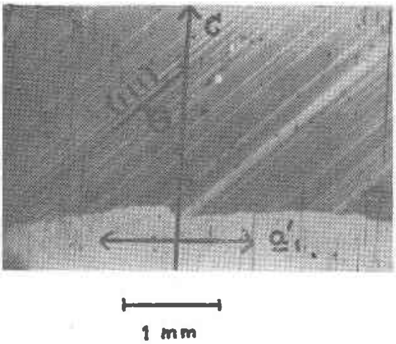

FIG. 1. Section in transmission showing bands containing color centers, for for *C*, *a'*, and *θ* see text.

Kodak Pan-F film. Exposure times of 1 to 10 minutes were sufficient. Great difficulty was experienced in preparing a print from the various negatives as the intensity of the emission from the clear section was much higher than that from the red section.

The fluorescence emission spectrum of a specimen taken from the clear section of this crystal was recorded using a Spex 0.75 m grating monochromator, an E.M.I. 9558C photomultiplier as detector, a 500 watt medium-pressure mercury lamp equipped with the same optical system and filter as above, the sample was cooled to 77°K in a cryostat and the excitation modulated at 720 Hz. This spectrum was compared with those obtained using flux grown zircons containing various rare earths.

The fission-track-registration in Lexan plastic print technique developed by Kleeman and Lovering (1967) was used to determine the uranium content and distribution in the prepared sections. They were mounted in contact with Lexan plastic discs in an aluminium holder together with sections of a standard glass also in contact with Lexan discs. The holder and contents were irradiated in the 3×10^{12} neutrons cm^{-2} sec.^{-1} thermal neutron facility of HIFAR at the A.A.E.C., Lucas Heights Research Establishment for times varying between 1 to 9 hours. The γ-ray dose rate in this section of HIFAR is about 4.8 mR per day. The Lexan discs were then etched in 7N NaOH at 70°C for 8 minutes and the fission tracks counted under ×400 magnification using dark field illumination.

Optical absorption spectra in the visible region were recorded with a Unicam SP 800 spectrophotometer or on a single beam microspectrophotometer (Fielding and MacKay, 1964) if high resolution were required. A Unicam SP 200 was used to record the infrared absorption spectra; alternatively a Grubb Parsons prism-grating instrument provided higher resolution and wavelength accuracy when required.

EXPERIMENTAL RESULTS

The prepared sections must either be normal to the (111), (110) or to the $(\bar{1}11)$, $(\bar{1}10)$ faces as they give straight extinction and the angle (θ) (see Fig. 1) between the c axis and the coloured bands is 48.3° compared with 47.83° calculated from unit cell data. The usual mineralogical axes a_1 and a_2 are at 45° to the unit cell axes which are labelled a_1' and a_2' in this paper. It is convenient to let the a_1' axis be normal to the (110) face and a_2' normal to $(\bar{1}10)$, also the color centers are assigned to bands parallel to the (111) face. This distinction between the (111) and $(\bar{1}11)$ faces is important as sets of bands parallel to both of these faces have not been observed by the author in any one single crystal specimen. Zircon crystals grown from a flux melt are tetragonal prisms of the first order doubly terminated by a pyramid and they show a similar tendency to segregate impurities into bands parallel to only one of these faces. These observations are interpreted as indicating that there are preferred growth sites under the (111) face. In general the boundary between the red (111) bands and the clear section containing the (110) planes is at 90° to the C axis whereas it is usually 45° in the case of crystals grown in this laboratory using cooling rates of 3°C per hour. If the growth velocities normal to these faces are $v_{(111)}$ and $v_{(110)}$ then the ratios $v_{(111)}/v_{(110)}=1/1.4$ and 1/0.5 satisfactorily account for the inclination of the boundary in the case of the zoned and flux grown crystals respectively. Inspection of

TABLE 1. FLUORESCENCE SPECTRUM OF THE NATURAL CRYSTAL AND ALSO OF FLUX GROWN ZIRCON CONTAINING PRASAEODYMIUM

Wavenumber (cm^{-1})	Relative Intensity	Wavenumber (cm^{-1})	Relative intensity
17544	0.03	20986	0.36
17528	0.08	20977	0.22
17494	0.13	20786	0.56
17421	0.05	20738	1.00
17412	0.520	20627	0.22
17379	0.18	20576	0.28
17367	0.09	20538	0.56
17319	0.17	20458	0.47
17262	0.91		
17247	0.17		
17205	1.00		
17085	0.07		

the boundary under higher magnification (Fig. 1) shows that the growth velocities were continually changing and that there is no obvious relationship between these and the composition of the hydrothermal solution at the time of formation of the zones now containing the color centers.

The intensity and spectral distribution of the fluorescence of this crystal was exactly the same as that of flux grown material containing praseodymium (see Table 1). An electron spin resonance investigation (G. Troup, Monash University, private communication) indicated a relatively large concentration of erbium, but it failed to detect the praseodymium. Qualitative emission and mass spectral analyses were then kindly provided by Dr. S. R. Taylor (Table 2) and they show that the heavier rare earths are enriched in relation to the lighter ones, this distribution is in agreement with that expected for xenotime type min-

TABLE 2. QUALITATIVE ANALYSES OF SPECIMENS TAKEN FROM ADJACENT CLEAR AND COLORED SECTIONS OF THE NATURAL CRYSTAL

A: *Elements determined by emission spectroscopy.*
1. Same concentration in both sections: Si, Mg, Ga, Cu, Be, Ti, Y, Co, Ni, Ca, V, Se, Ba, Sr, La and Mo.
2. Concentration higher in the clear section: Fe, Al and Mn.

B: *Elements determined mass spectrographically.*
1. Same concentration both sections: Nb, Hf, Sn, and Cd.
2. Heavy earths and enriched with respect to the lighter ones.

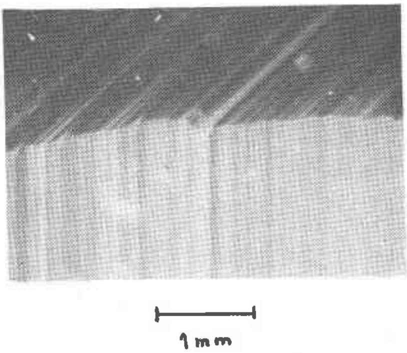

FIG. 2. Same section as in Fig. 1, fluorescing under ultra-violet excitation.

erals. The failure to observe the erbium fluorescence could be due to quenching interactions between rare earth ions (Idia and van Uitert, 1962), this point and the emission spectra of zircon containing various rare earths will be discussed elsewhere. Figure 2 shows a typical microphotograph of a section fluorescing under ultraviolet excitation. The intensity of the rare earth fluorescence is highest in the clear (110) region and the variation in the concentration of praseodymium across this region is apparent. Strongly fluorescing bands in the (110) region are continuous with similar bands in the (111) region and a comparison of Figures 1 and 2 shows that the color centered bands are associated with a relatively low praseodymium concentration. When the color centers

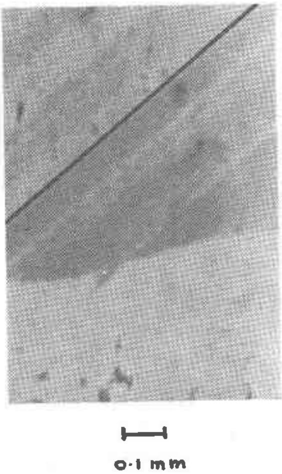

FIG. 3. Zoned section in transmission, corresponding bands in Figs 3 and 4 are marked ———————.

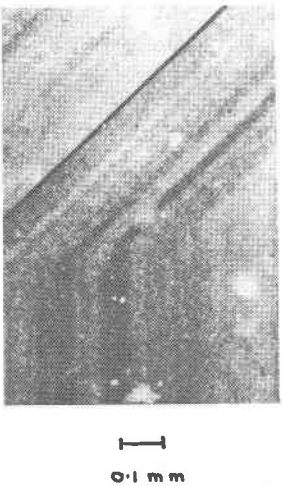

Fig. 4. Lexan print showing uranium distribution in section appearing in Fig. 3. Light regions correspond to those of relatively high uranium concentration. Dark field illumination.

are destroyed by heating in air at 600°C for two hours then the fluorescence distribution is unchanged, but the contrast between the various bands in the (111) region is increased showing that the colored sections were scattering the fluorescence emission to some extent.

The uranium concentration was 7.4 ppm in those (111), (110) bands that fluoresced brightly and it appeared to be uniform within any one band (see Fig. 5). A concentration of 2.7 ppm was associated with less brightly fluorescent bands, these relationships are shown in Figures 1, 2,

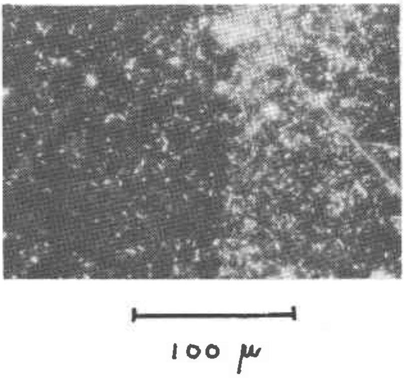

Fig. 5. Fission track distribution in (110) and (111) bands. Lexan print, dark field illumination.

3 and 4. Where one of the heat treated samples were re-irradiated in HIFAR (Figs. 6 and 7) the color centers were regenerated. However, this was not the case if strongly fluorescing zircons containing less than 0.5 ppm of uranium were irradiated. These experiments show that the presence of uranium is required for the formation of color centers.

The effect of growth rate variations can be seen when the uranium distribution in these sections is compared with that in a flux grown crystal doped with uranium. In the latter case all the uranium is segregated into the regions immediately under the pyramidal terminations of the crystal and the boundary previously mentioned is at 45° to the *C* axis. The conditions favouring uniform distribution remain to be determined.

Absorption spectra covering the spectral region from 4000 cm^{-1} to 1400 cm^{-1} are reproduced in Figure 6, the difference between the clear (110) and the colored (111) regions is quite marked. Lietz (1937) has classified the band at about 2000 cm^{-1} (A) which gives rise to the characteristic red coloration as belonging to an "*a*-center," and the only other band that appears to be associated with this is a doublet near 3400 cm^{-1} (D). Absorption maxima in the region of 15000 cm^{-1}–16000 cm^{-1} (B) and 6000 cm^{-1}–8000 cm^{-1} (C) are considered as belonging to transitions characteristic of impurities such as uranium, iron and the rare earths. In a red (111) section strong absorption bands are located at 1596 cm^{-1} (G), 3423 cm^{-1} and 3387 cm^{-1} (D) and might be identified with the fundamental vibrations of the free water molecule at 1595 cm^{-1}, 3652 cm^{-1} and 3756 cm^{-1} (Herzberg, 1945) thereby associating a color center with the presence of a water molecule or a proton bonded to the lattice to form OH^- groups. The infrared spectrum of a clear (110) section 8.2 mm thick was recorded without detecting the 3400 cm^{-1} doublet (D) indicating that the concentration of this absorbing species is less than one tenth of that in the (111) section, but the absorption at 1596 cm^{-1} is as intense as in a (111) section. The series of spectra in Figure 7 show that the 3400 cm^{-1} doublet (D) is destroyed by heating in an oxidizing atmosphere at 900°C, the band at 1596 cm^{-1} (G) remains unchanged. These observations lead to the conclusion that water is absent from either section and that the 3400 cm^{-1} doublet (F) is characteristic of some defect found only in the (111) growth planes.

Re-irradiation in HIFAR after heating to 900°C only regenerates the color centers showing that they are not directly associated with the defects responsible for these transitions, but they must be present in the original crystal if the centers are to develop in nature. These defects could be a substitutional or interstitial impurity or a vacancy in the lattice that is annealed out by heat treatment. Calculations based on optical constants and the γ-ray dose rate in HIFAR show that the orig-

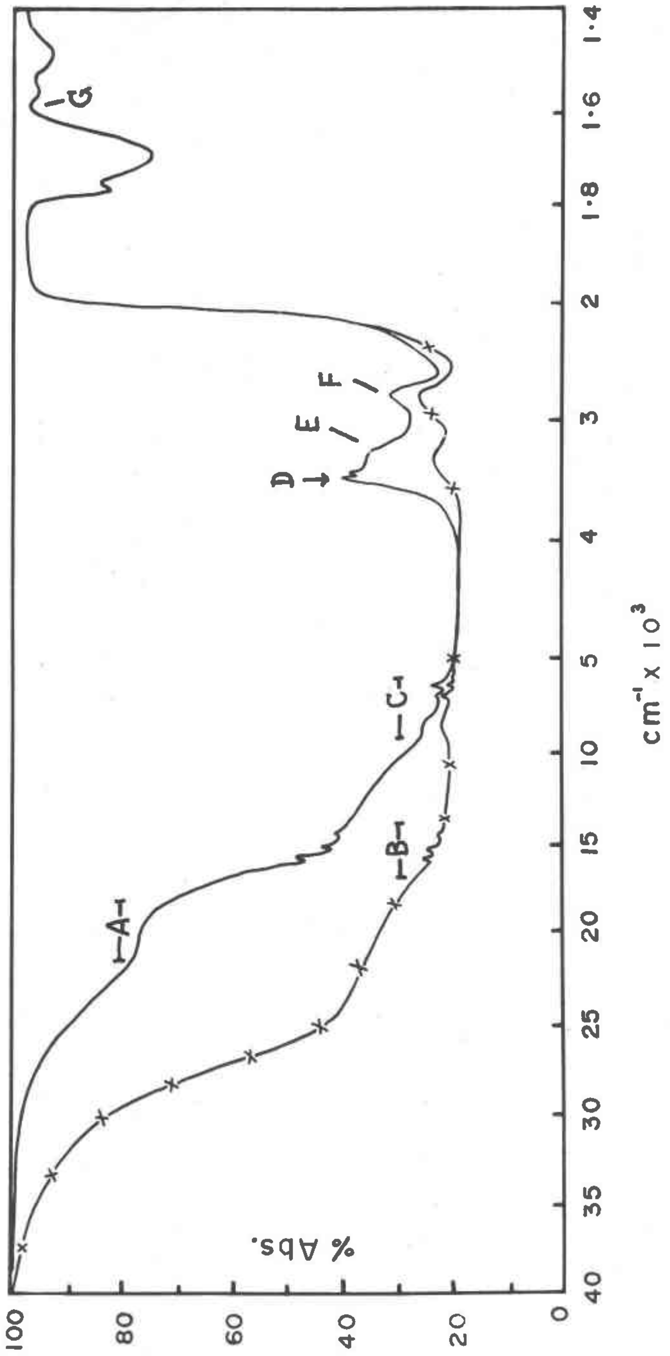

FIG. 6. Absorption spectra of a zoned section. Crosses: clear (110) region; solid line: red (111) region.

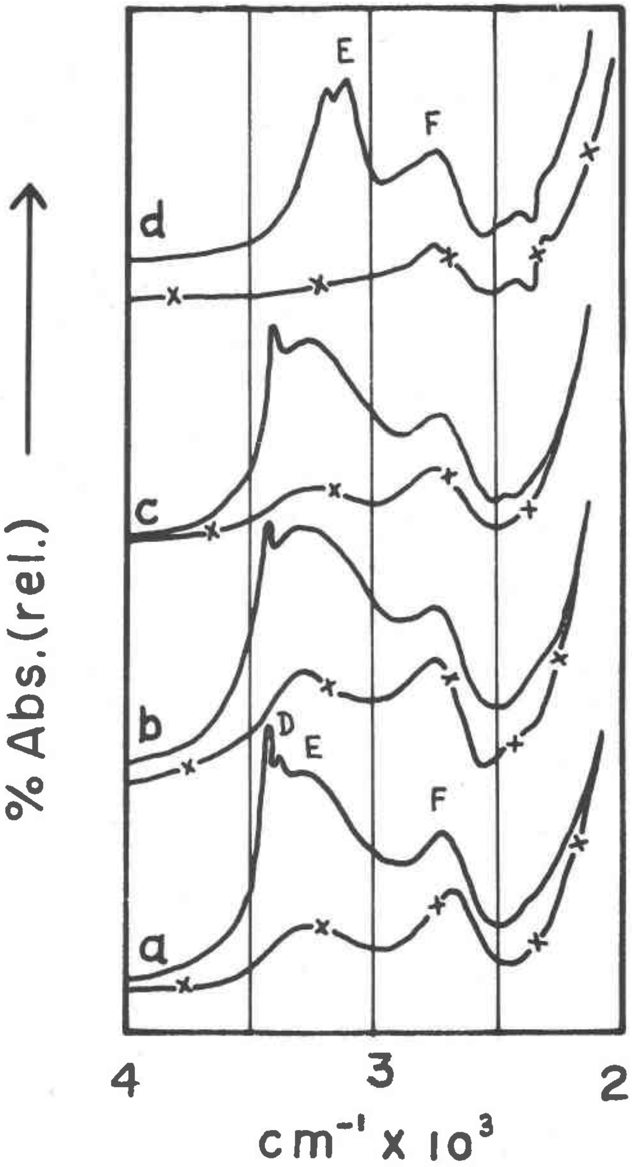

FIG. 7. Effect of heat treatment and irradiation on the infrared spectra of a zoned section. (a) Untreated crystal, (b) heated 2 hrs in air at 600°C, (c) heat treated crystal re-irradiated in HIFAR for 1 hr, (d) irradiated crystal heated 16 hrs in air at 900°C. Crosses: clear (110) region, solid line red (111) region.

inal concentration of color centers in the specimen was produced by natural radiation equivalent to a γ-ray dose of about 0.15 mR. Bronder and Matossi (1938) claim that bands at 1594 cm^{-1}, 2755 cm^{-1}, 3095 cm^{-1}, and 3175 cm^{-1} are either overtones or combinations, these are identified with the present bands at 1596 cm^{-1} (G), 2750 cm^{-1} (F), 3150 cm^{-1} and 3220 cm^{-1} (E) respectively. If a large number of natural zircons are studied then it is noticed that the bands at 3150 cm^{-1} and 3220 cm^{-1} (E) are sometimes absent and this is taken to show that the 2750 cm^{-1} (F) and 1596 cm^{-1} (G) transitions are the only bands in the above series characteristic of pure zircon.

Discussion

Matumura and Koga (1962) have identified the "*a*-center" in zircon with Zr^{2+} produced by the radiation-induced reduction of Zr^{4+}. This conclusion was based on ESR data taken at room temperature and is therefore open to question. The ESR spectrum at 77°K of Nb^{4+} substituted in a Zr^{4+} site was reported by Chirkin *et al.* (1963) and they point out that their conclusions are not to be identified with those of the Japanese, implying that Nb^{4+} did not result from a radiation induced reduction of Nb^{5+}. However, these workers did not describe their specimens and it is thought that both groups were studying the same center. This is made more probable in view of recent studies on radiation-induced Nb^{4+} centers in various glasses (Bray *et al.*, 1968) and the color centers in the (111) region are tentatively identified with Nb^{4+} substituted in Zr^{4+} lattice sites. This mechanism requires that during growth Nb^{5+} preferentially occupy Zr^{4+} sites located under the (111) growth faces and that the colored (111) region is enriched in niobium with respect to the clear (110) region. The projections of the unit cell shown in Figure 8 show that there are Zr^{4+} sites 1.0 Å under the (111) faces and 2.2 Å under the $(\bar{1}11)$ faces. Similar situations were described by Barry *et al.* (1965) in their study of the color centers in amethyst, selective occupancy of certain Si^{4+} sites by Fe^{3+} having occurred during growth. Taylor's analyses have shown that the concentrations of twenty trace elements including niobium are the same in both sections, the only exceptions were higher concentrations of iron, aluminium and manganese in the clear (110) region. This would require that the Nb^{5+} in the (111) region be associated with some defect capable of providing the electrons that contribute to the radiation-induced reduction process. Similar defects are presumably not found in the (110) region and it is proposed that this defect be tentatively identified with the absorption doublet at 3400 cm^{-1}. The conditions prevailing in the crystal after heat treatment and annealing procedures will not be discussed as it is expected that ionic diffusion

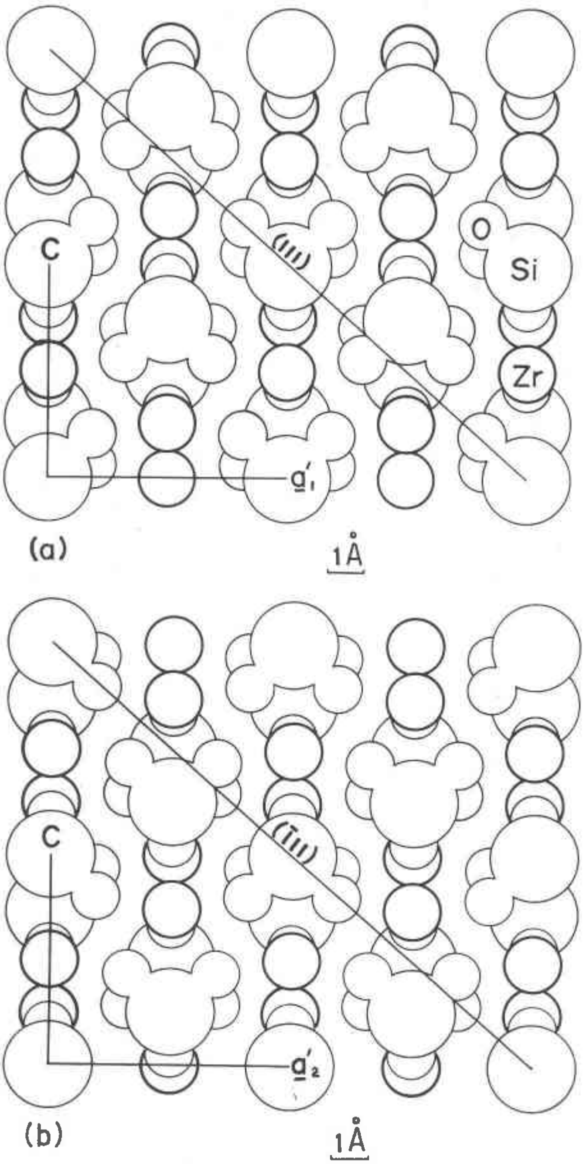

Fig. 8. Projection of the zircon structure onto the ($\bar{1}10$) and (110) planes respectively

at high temperatures will result in extensive rearrangements within the lattice. A calculation of the age of this zircon, based on a uranium concentration of 7 ppm, a radiation dose of 0.15 mR and assuming reasonable values for the thorium and potassium concentrations gave values of the order of 10^4–10^5 years. This is taken to indicate that the calculated dose is much too small and that factors such as the inhomogeneous distribution of uranium and thorium and the bleaching of the color centers during geological time under constant or varying temperature conditions are responsible for this discrepancy.

Further experimental work is in progress in order to understand what nuclear processes, charge compensation mechanisms, and growth conditions result in a (111) band enriched in uranium being followed by one containing the color centers and a low concentration of uranium together with some defect necessary for color center formation.

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