The anomalous optical absorption spectrum of low zircon

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SUMMARY. Further lines of the anomalous optical absorption spectrum in low metamict zircon have been observed in the infra-red. Low-temperature polarization studies have enabled a clear distinction to be made between lines due to the anomalous spectrum and those due to the normal spectrum of U^{4+} in zircon. Magnetic circular dichroism measurements showed, for the anomalous spectrum, only contributions due to the mixing of the energy levels by the magnetic field; thus the A spectrum results from singlet $\rightarrow$ singlet transitions. The anomalous spectrum appears to derive from U^{4+} incorporated in polycrystalline zirconia.

THE optical absorption spectra of natural zircons have been studied for many years by Anderson, who also discussed the subject in his recent book (Anderson, 1971). Anderson has attributed the visible spectrum of natural zircon to uranium impurities (Anderson and Payne, 1939; Anderson, 1962, 1963, 1971). Detailed polarization studies of synthetic U^{4+}-doped zircon at low temperatures have been made by Richman et al. (1967) and, in the visible section of the spectrum, the spectrum of the synthetic material agrees largely with the natural zircon spectra (Anderson and Payne, 1939), though the spectra of the natural zircons are broadened by radiation damage arising from the decay of radioactive impurities.

The anomalous (A) optical absorption spectrum in low zircon was first observed, in the visible region, by Anderson and Payne (1939) and a recent study showed the appearance of the A spectrum to be correlated with X-ray evidence of randomly oriented small particles of cubic or tetragonal ZrO_2 in a radiation-damaged zircon lattice (Vance and Anderson, 1972a, b). The aim of the present work was to study the A spectrum at low temperatures, thus minimizing thermal broadening of the lines, to detect any possible lines in the infra-red, and to draw some conclusions about the origin of the A spectrum.

Experimental. X-ray and density measurements were made as described previously (Vance and Anderson, 1972a, b). Optical absorption spectra were measured over the range 350–2500 nm using a Cary 17 spectrophotometer; the resolution of this instrument was adequate as the widths of the A spectrum lines were at least five times greater than the spectral bandwidth of the instrument. A cold-gas flow tube enabled spectra to be recorded at any temperature between 15 and 290 °K. Infra-red measurements to 50 μm were made with a Perkin-Elmer spectrometer with the specimen maintained between 40 and 300 °K. Measurements of magnetic circular dichroism, in the range

350 to 810 nm, were made with a Cary 61 spectropolarimeter in conjunction with an Oxford Instruments superconducting solenoid. The solenoid provided steady magnetic fields of up to 7·7 tesla,[1] and the specimen could be held between 5 and 80 °K. Alternating-current Stark effect measurements were made using phase-sensitive detection, over the 400 to 700 nm range, with the sample at liquid nitrogen temperature.

Two green low zircons showing both the A spectrum and an X-ray pattern of polycrystalline ZrO_2 were studied. One was a polished parallel-sided plate cut from a Ceylon stone of density 3·94±0·04 g cm^{-3} (Stone Y of Vance and Anderson, 1972a) and the other, of density 3·99±0·03 g cm^{-3}, was of unknown origin. Two cuboids of a few mm^3 were cut from this latter stone; the c-axis was located by optical methods only, as no Laue spots were observed on back-reflection X-ray photographs (see Vance and Anderson, 1972b).

Heat treatments were carried out in air. Pieces of the low zircon of unknown origin were analysed for U and Th by the Radiochemistry Division, A.A.E.C.R.E. The U and Th contents of the zircon were determined as 5600 and 450 ppm respectively, in good agreement with values for the low Ceylon zircon (Vance and Anderson, 1972b).

Results. The A spectrum, being unpolarized (Anderson, 1962), was in the main easily distinguished from the normal (N) spectrum due to U^{4+} in zircon, which is completely polarized (Richman et al., 1967) apart possibly from the line at 1660 nm (6030 cm^{-1}). However, in radiation-damaged samples that have not been annealed at high temperatures, as in the present case, the σ polarized line at 653·5 nm overlaps in wavelength with the π polarized line at 652·5 nm and the σ line at 589 nm overlaps with the π polarized line at 588·5 nm, hence possible A spectrum lines at c. 653 and 589 nm could remain unobserved. This point will be dealt with below and it will be shown that any such A spectrum lines are weak. Spectra indicating the A lines (arrowed) and the σ polarized N lines are shown in figs. 1 and 2.

Lines of the A spectrum were observed in the infra-red, though none were observed beyond 1500 nm. In the visible, the spectra were essentially as described by Anderson and Payne (1939) except that the line at 686·5 nm was a singlet, not a doublet consisting of N-spectrum lines at 686·5 and 691 nm. No line at 686·5 nm was detected in the N spectra of any of nine natural zircons (Vance and Mackey, 1974) and no such line is evident in the results of Richman et al. (1967). Also, the σ polarized line at 691 nm can be completely suppressed by cooling below c. 20 °K (see also Richman et al., 1967).

Unpolarized measurements in the infra-red on the plate cut from the Ceylon zircon showed two weak diffuse peaks near 3 μm, together with strong absorption beyond 5 μm. Since there appear to be no observable N spectrum lines between 2·5 μm and the lattice absorption cutoff at 5 μm (Vance et al., in preparation; see also Dawson et al., 1971) and because the widths, in terms of energy, of the peaks near 3 μm were roughly the same as those of the A spectrum, it seemed that the peaks near 3 μm were perhaps part of the A spectrum. However, the profiles of the peaks near 3 μm were temperature-independent between 40 and 300 °K, whereas the A spectrum lines

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[1] 1 tesla (symbol T) = 10^4 gauss.

in the visible and near infra-red decreased markedly in intensity on heating over the same temperature range. Hence, the diffuse peaks near 3 μm would not seem to be part of the A spectrum and could be due to OH' ions or hydrogen-bonded water (Dawson *et al.*, 1971). The observed lines of the A spectrum are set out in Table I.
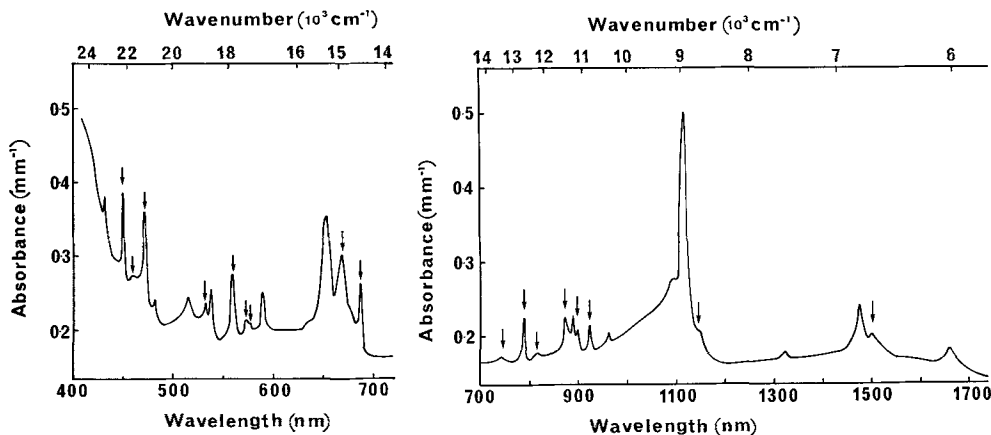
FIGS. 1 and 2: FIG. 1 (left). Visible region of σ spectrum of low zircon, recorded at 15 °K. Lines of A spectrum arrowed. FIG. 2 (right). Infra-red region of σ spectrum of low zircon, recorded at 15 °K. Lines of A spectrum arrowed.

TABLE I. *Lines of the A spectrum and approximate relative intensities*

λ	$I*$	λ	$I*$	λ	$I*$	λ	$I*$
450 nm	25	572 nm	6	745 nm	5	899 nm	8
459	1	576	3	789	30	923	15
472	30	669	100	814	5	1145	15†
532	3	686·5	30	872	30	1500	30
559	25						

* Proportional to the area under a plot of absorbance v. wavelength. The strongest line, at 669 nm, is given an intensity of 100.
† Very approximate, due to incomplete resolution from another line.

One sample cut from the low zircon of unknown origin was annealed for 3 days at 850 °C but this treatment failed to sharpen the A spectrum, though the N spectrum was very slightly enhanced. Annealing for 1 hour at 1150 °C considerably reduced the intensity of the A spectrum and produced a corresponding decrease in the proportion of ZrO_2 (now clearly recognizable by X-ray diffraction as tetragonal—see Vance and Anderson, 1972a). The N spectrum was considerably strengthened. The specimen was rather opaque after this treatment and annealing at 1450 °C for 1 hour produced a high degree of opacity and near-complete breakdown to monoclinic ZrO_2 ($+SiO_2$), as determined by X-ray work.

Magnetic circular dichroism measurements were made on the second sample cut

from the low zircon of unknown origin. In preliminary experiments at room temperature (in the absence of a magnetic field) the specimen was placed in series with an optically active liquid and the c-axis located by measuring the total circular dichroism; when the c-axis was parallel to the light beam, the measured circular dichroism was the same with and without the specimen in series with the liquid. This result showed that the sample did not appreciably degrade the circular nature of the polarization of the light beam. With the sample thinned to 0·3 mm, and annealed 2 hours at 800 °C in an attempt to relieve strains due to cutting and polishing, misalignments of up to 10° did not introduce serious errors. The magnetic circular dichroism (MCD), measured in 7·7 T at 5 and 50 °K, is shown in fig. 3. These data were obtained with a 20 μm slit. The resolution was 1·1 nm at 800 nm, reducing monotonically to 0·2 nm at 400 nm; under these conditions, the MCD spectrum would be almost fully resolved. No temperature dependence was observed and the MCD was linear in field strength. For the A spectrum, the MCD signals were purely B-type (see Stephens, 1970) and thus arose from mixing of the energy levels of the A spectrum by the magnetic field.
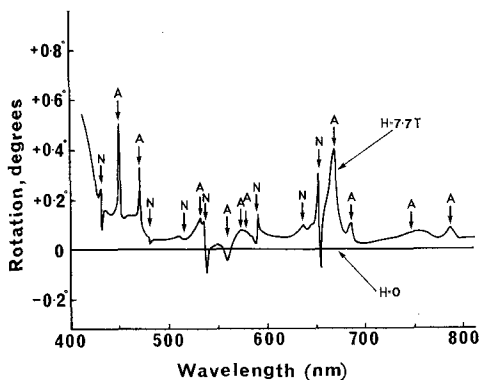

FIG. 3. Magnetic circular dichroism spectrum of low zircon in visible and near-visible regions of spectrum, recorded at 5K using a field of 7·7 T. A and N lines indicated. Magnetic field parallel to the c-axis.

Apart from the N spectrum line at 515 nm, which gave only weak B-type MCD, the strong lines of the N spectrum gave predominantly A-type (see Stephens, 1970) MCD with a small admixture of B-type MCD. The MCD of the N spectrum agreed qualitatively with results obtained in this laboratory on well-annealed zircon and will be discussed elsewhere (Vance *et al.*, in preparation). The 589 and 653·5 nm lines gave mainly A-type MCD, suggesting that they arise mainly from the N spectrum. Also, for the two different samples of low zircon studied, the intensities of the 589 and 653·5 nm lines did not correlate with the intensities of the other A spectrum lines. Again, this suggests that these lines are mainly due to the N spectrum.

No Stark effect was detected in the plate cut from the low Ceylon zircon, using an alternating electric field of 100 kV. cm^{-1}.

Discussion. Below c 1000 °C, the monoclinic form of ZrO_2 is stable rather than the cubic or tetragonal allotropes. Yttrium is a common impurity in zircon (Deer *et al.*, 1962); Yt_2O_3 stabilizes the cubic form of ZrO_2 at low temperatures. Electron-microprobe analyses on a piece of the low zircon of unknown origin, however, failed to detect any yttrium, the limit of detection being 370 ppm by wt. CaO and V_2O_3 also stabilize the cubic form of ZrO_2 but microprobe analysis did not detect these elements either, the detection limits being 600 and 500 ppm by wt respectively. Admittedly other oxides can be employed to stabilize zirconia. However, the observation of tetragonal rather than cubic ZrO_2 in A spectrum stones heated to c. 1100 °C would

not be favoured by an impurity-stabilizing mechanism. Thus it would seem that the volume change in the low-zircon → ZrO_2 (+SiO_2) transformation on heating to c. 900 °C (Anderson, 1962, 1963; Vance and Anderson, 1972a, b) is the critical factor determining which ZrO_2 phase appears, being smaller if the cubic or tetragonal form of ZrO_2 is involved, rather than the monoclinic form (see also Vance and Anderson, 1972b). The transformation itself must presumably originate from the relaxation of radiation-damage induced lattice strains on heating, but the details are not understood at present.

Since heating an A spectrum stone above c. 1100 °C enhances the N spectrum at the expense of the A spectrum it seems reasonable to suppose that uranium is responsible for both spectra (Anderson, 1962). That the widths of the lines of the N and A spectra were comparable is also evidence for uranium being responsible for both spectra.

The absence of both A and C-type (see Stephens, 1970) MCD for the A spectrum cannot be explained in terms of the random orientations of the ZrO_2 precipitate particles; for a crystal giving A or C-type MCD, rotation of the crystal by 180° about an axis perpendicular to the light beam will not change the sign of A or C-type MCD (see also Stephens, 1970; Dearman, 1973). Therefore all the transitions giving rise to the A spectrum are singlet → singlet. Hence the ions giving rise to the A spectrum cannot be of the odd-electron type and the point symmetry of the ions must be orthorhombic or lower.

As mentioned above, the ZrO_2 precipitates can be shown by X-ray diffraction to be tetragonal in low zircons heated to c. 1100 °C. However, for a tetragonal distortion of the CaF_2 structure the point symmetry would be still expected to be higher than orthorhombic. Local charge compensation would be a mechanism for low point symmetry and, from this point of view, U^{2+} would be more reasonable than U^{4+} as the origin of the A spectrum; Hargreaves (1971) has attributed some absorption lines in U-doped CaF_2 to the presence of U^{2+}. However, the present observations that the A spectrum is apparently confined between 450 and 1500 nm, with no lines detected in the near ultraviolet or between 1500 nm and the lattice cutoff at c. 5 μm, would be more consistent with U^{4+} being the cause of the A spectrum. Anderson (1962) has also mentioned the qualitative symmetry between the A and the N spectra; there seems little doubt from the work of Richman et al. (1967) and magneto-optical studies in progress in this laboratory that the N spectrum derives from U^{4+}.

If the A spectrum is caused by U^{4+}, a mechanism for the low point symmetry is required. Since the A spectrum is the same in a naturally occurring stone as in a laboratory-heated low zircon (Anderson, 1962, 1963), radiation damage, after the formation of the ZrO_2 precipitates, cannot be invoked. However, distortions could arise from the misfit strains between the precipitates and the skeleton zircon lattice.

REFERENCES

ANDERSON (B. W.), 1962. *Gemmologist*, **31**, 19–36.
—— 1963. *Journ. Gemm.* **9**, 1–6.
—— 1971. *Gem Testing*, London (Butterworths), pp. 240–8.
—— and PAYNE (C. J.), 1939. *Gemmologist* **9**, 1–5.
DAWSON (P.), HARGREAVE (M. M.), and WILKINSON (G. R.), 1971. *Journ. Phys. C.; Solid St. Phys.* **4**, 240–56.
DEARMAN (H. H.), 1973. *Journ. Chem. Phys.* **58**, 2135–44.
DEER (W. A.), HOWIE (R. A.), and ZUSSMAN (J.), 1962. *Rock-Forming Minerals*, **1**, London (Longmans Green), pp. 59–68.
HARGREAVES (W. A.), 1971. *Phys. Rev.* **B2**, 2273–84.
HOLLAND (H. D.) and GOTTFRIED (D.), 1955. *Acta Cryst.* **8**, 291–302.
RICHMAN (I.), KISLIUK (P.), and WONG (E. Y.), 1967. *Phys. Rev.* **155**, 262–7.
STEPHENS (P. J.), 1970. *Journ. Chem. Phys.* **52**, 3489–516.
VANCE (E. R.) and ANDERSON (B. W.), 1972a. *Min. Mag.* **38**, 605–13.
—— 1972b. *Ibid.* 721–4.
—— and MACKEY (D. J.), 1974. *Journ. Phys. C: Solid State Phys.* **7**, 1898–1908.