Canadian Mineralogist
Vol. 27, pp. 219-224 (1989)

EPR INVESTIGATION OF CARBONACEOUS NATURAL QUARTZ SINGLE CRYSTALS

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ABSTRACT

As part of an investigation of whether carbon can substitute for silicon in minerals, electron paramagnetic resonance studies were carried out on natural crystals of α-quartz from carbonaceous surroundings, *i.e.*, a carbonized log found in Utah. For these, as obtained, the room-temperature results at 9.6 GHz indicate the presence of the well-known oxygen vacancy (E_1') silicon center and an isotropic broad line with *g*-factor 2.0028(1) attributed to coal-like macro-regions in the crystals. No signals from $[AlO_4]^0$ or other aluminum hole centers usually found in α-quartz were observable, even at low temperatures (35 K) and after X-irradiation. Thus the dark color is not that of smoky quartz, but is due to macroscopic coal-like impurities. A weak Mn^{2+} spectrum could be observed at 24 GHz but not at 9.6 GHz. In concurrent measurements of Herkimer "diamonds" (New York state), doubly terminated quartz crystals containing black "anthraxolite" inclusions, the same type of broad line was found. The latter line was also seen in the black materials removed from these crystals, but not in inclusion-free crystals. Thus we have found coal-like materials containing free radicals to exist in intimate association with crystalline quartz. However, no oxygenic carbon centers, with C substituted for Si in the crystal, were identified.

Keywords: carbonaceous, coal, defects, EPR, paramagnetic resonance, quartz, silicon dioxide.

SOMMAIRE

Notre étude fait partie d'un projet visant à déterminer si le carbone peut remplacer le silicium dans les minéraux. Des cristaux de quartz-α prélevés d'un milieu carboné (un tronc d'arbre carbonisé du Utah) ont éte étudiés par résonance électronique paramagnétique. À leur état naturel, les cristaux produisent un signal à 9.6 GHz, témoin d'une lacune dans le site de l'oxygène (E_1') associé à un site Si, et d'une bande floue ayant un facteur *g* de 2.0028(1), que nous attribuons à des inclusions de matériau charbonneux. Aucun signal provenant de $[AlO_4]^0$ ou autre centre d'aluminium n'a été observé, même à très basse température et suite à une irradiation X. La couleur sombre n'indiquerait donc pas un quartz fumé, mais plutôt la présence d'impuretés macroscopiques charbonneuses. Un faible spectre du Mn^{2+} est relevé a 24 GHz, mais non à 9.6 GHz. Dans une suite de "diamants" de Herkimer (état de New York), cristaux de quartz doublement terminés contenant des inclusions noires d' "anthraxolite", aussi bien que dans l'anthraxolite elle-même, la même bande floue est présente; elle est absente dans le quartz sans inclusion. Ainsi nous avons trouvé du matériau charbonneux contenant des radicaux libres en association intime avec le quartz cristallin. Nos données ne révèlent aucune évidence de centres à liaisons carbone–oxygène dans lesquels le C pourrait substituer au Si.

(Traduit par la Rédaction)

Mots-clés: carbone, charbon, lacunes, résonance électronique paramagnétique, quartz, dioxyde de silicium.

INTRODUCTION

We undertook the current investigation partly in the hope of finding a paramagnetic center involving carbon occurring substitutionally for silicon in crystalline quartz. Certainly the question of whether carbon ever enters silicate structures substitutionally is of considerable interest. The substantially smaller ionic radius of C^{4+}(0.16 Å) compared to that of Si^{4+} (0.42 Å) and Ge^{4+} (0.53 Å) (Weast 1972) suggests that it may not do so, at least in fourfold coordination. As far as we know, no evidence for carbon as a substitutional impurity in quartz has been reported in the literature. Our recent *ab initio* self-consistent-field molecular-orbital calculations on carbon tetroxide clusters (McEachern *et al.* 1988) indicate that in fact it is unfavorable for tetracoordinate carbon to replace silicon in the quartz structure. We have recently synthesized and characterized a stable molecular species containing carbon linked (almost) tetrahedrally to four oxygen atoms, with an average C–O bond length of 1.39 Å, compared to a Si–O length of 1.61 Å in quartz (Latimer *et al.* 1989).

Some of the impurities that have been found to substitute for Si in α-quartz are Al, Fe, Ge, P and Ti. This topic is covered in a recent review article (Weil 1984). Pure, defect-free quartz is colorless, so that the color of quartz crystals can give information about the defects and impurities. Recently, we obtained some unusual crystals of black quartz from Utah, which we initially considered to be smoky quartz. The brown-to-black color of the latter is known to be associated with electron hopping on AlO_4 tetrahedra in the quartz structure (Meyer *et al.* 1984); this type of center is denoted by $[AlO_4]^0$. In a few cases (*e.g.*, Boyle 1953), a black or grey color has been attributed to disseminated carbon. Occurrence of black quartz crystals in coal has been reported (Leskevich 1959). Electron paramagnetic resonance (EPR) spectroscopy is an ideal tool to search for carbonaceous unpaired-electron species in crystalline quartz. It has been used to elucidate the nature of the free radicals in different types of coals (Retcofsky *et al.* 1981) and to make a rough estimation of the age of petrified wood (Ikeya 1982).

In this report, we present EPR results obtained for the black quartz crystals from Utah. The symmetry and structural features of α-quartz relevant to EPR have been discussed in some detail in a previous paper dealing with the $[AlO_4]^0$ center (Nuttall & Weil 1981).

During the course of the above study, we became aware that Herkimer "diamonds", beautifully formed doubly-terminated quartz crystals from the Herkimer region of northern New York state, commonly contain black "anthraxolite" inclusions (Dunn & Fisher 1954). Accordingly, we broadened our investigation to include specimens of these.

EXPERIMENTAL

The unique black quartz crystals used in the present study were discovered (1981) by Mr. F. Fornelius in the San Rafael Swell Country of Emery County, Utah. The area is rich in petrified wood and fossilized dinosaur bones. The crystals were found within a partly buried black fossil log. All of the surrounding logs are brown in color, the crystal-bearing log being the only black one in the area. The crystas were surrounded by a hard tar-like covering. This mantle material, when removed, revealed the crystals. However, some of these crystals were found on the surface of the "wood", and others as loose crystals within it. Generally the crystals are black in some parts (primarily near and at the crystal caps) and clear and colorless in other places, and tend to show well-developed faces. Two typical Utah black quartz (UBQ) crystals are shown in Figure 1.

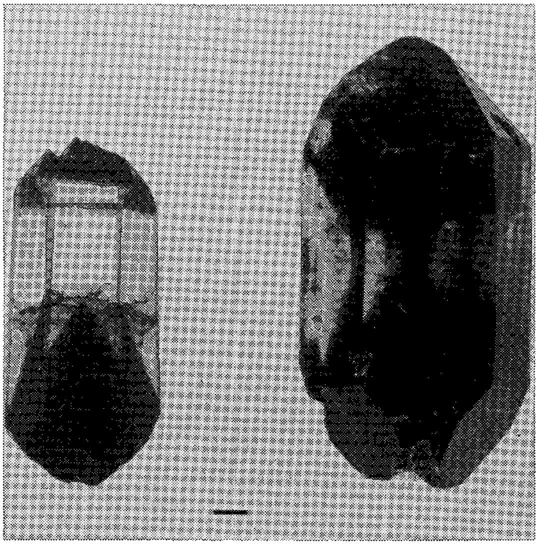

FIG. 1. Two typical crystals of black quartz, as found at the Utah location. Bar scale 1 mm.

Chemical analysis of the mantle material from Utah disclosed a composition of 80(5)% C, 8(1)% H, minute quantities of N and Si, 1% of ash and the balance presumably mostly of oxygen, with less than 5 ppm Mn. A neutron-activation analysis of the UBQ crystal indicates 1.4 ppm of U, 0.4 ppm As, and trace quantities of assorted rare-earths and precious metals. Radiocarbon dating of the mantle material revealed it to be older than 33,000 years.

The other group of quartz crystals studied, "diamonds" from Herkimer in New York, contain inclusions of the black material called anthraxolite. Such crystals are fairly common. The chemical analysis done on "black chunks" removed from the Herkimer crystals revealed 38% Si, 12(1)% C, 3% Fe, 2% H, 0.54% Mg, 10 ppm Ca, 8.5 ppm Mn, and some traces of N; the balance may be oxygen. They contain 16.9% by weight of compounds volatile at 773 K.

The EPR measurements were carried out primarily at room temperature (RT) using either a Bruker B–ER 418S spectrometer operating at 9–10 GHz frequency (X band) or modified Varian V4500 spectrometers operating at frequencies of 10 or 24 GHz (K band), both working with field modulation at 100 kHz and using phase-sensitive detectors. The microwave frequencies were measured with an EIP model 548A microwave frequency counter. The field positions were calibrated using a Bruker NMR Gaussmeter ER035M, and corrections for the relative positions of the sample and the NMR probe were by using DPPH as a standard. A few spectra were taken at low temperatures (LT), *ca.* 35 K, on a Varian V4500–10 EPR spectrometer operating at 9.9 GHz. The details of the cryogenic facility are described by Perlson & Weil (1975). One Utah crystal and several Herkimer crystals were X-irradiated at RT for 40 minutes using a Machlett AEG–50–S tube with tungsten target, at 50 kV and 50 mA, through a beryllium window (approximately 2 cm away), as was one sample of the mantle material. One Herkimer crystal was γ-irradiated (^{60}Co, *ca.* 400 krad) at RT.

RESULTS

A typical EPR spectrum of a UBQ crystal at RT, taken with $\hat{B}//\hat{c}$ $(=\hat{Z})$, is shown in Figure 2. Here B is the applied external magnetic field, and $\hat{c}$ is the crystal optic axis (superscript ^ indicates a unit vector). Figure 2 clearly shows a broad line and a single sharp line, plus much weaker lines at 341.185, 341.247, 341.342, 341.410, 342.115 and 342.420 mT (ν = 9.58089 GHz). The broad line has a g-factor of 2.0028(1) and a width of 0.75 mT, defined as the distance between the two extrema of the first derivative. The sharp line has a g factor of 2.00060(1) and a width of 0.030 mT. Crystal rotations with $\hat{B}$ in the XZ and XY planes ($\hat{X}$ is along a two-fold axis; see Nuttall & Weil 1981) disclosed that whereas the broad line is isotropic, the narrow line is not and shows site splittings on rotation. From the rotation data, the sharp line was unequivocally identified (from its g and ^{29}Si hyperfine values) as arising from the E_1' centre (Silsbee 1961). The other weak lines were found to be anisotropic.

When we cooled the UBQ crystal to *ca.* 35 K in the Varian spectrometer, we observed the same X-band EPR spectrum as at RT. No new lines were seen. As temperature was changed from RT to LT, the width of the broad line decreased from 0.75 to 0.61 mT, whereas the width of the E_1' line appeared to increase very slightly, from 0.030 to 0.036 mT. The areas of the absorptions follow the Boltzmann temperature dependence.

One Utah crystal was X-irradiated at RT for 40 minutes. Irradiation caused no change in the widths and g-factors of either the broad or the E_1' line at RT, whereas the relative intensity of the latter center increased (approximately 2.5 times) compared to the intensity of the former one. The crystal was then cooled to *ca.* 35 K in the X-band Varian spectrometer. To our surprise, no signal from $[AlO_4]^0$ or any other aluminum-based hole centers (Nuttall & Weil 1981) was observable. This is unusual in crystals of natural quartz. No lines from Ge^{3+} centers (Weil 1984) were seen either. The spectra do exhibit some additional features at LT, including two relatively strong anisotropic lines (approximately one-fourth the intensity of E_1' line) of nearly equal intensity, at 362.129 and 362.358 mT ($\nu = 10.1409$ GHz, $\hat{B}//\hat{c}$). We also noticed a single anisotropic weak line when $\hat{B}$ is parallel to $\hat{c}$ at 362.857 mT ($\nu = 10.1410$ GHz) with a width of 0.024 mT. We could not detect any nuclear hyperfine lines (such as from ^{29}Si or ^{13}C) for these above-mentioned additional features (excepting E_1'). The same crystal was subsequently heated in air at *ca.* 520 K for about 12 hours. The spectrum then recorded at LT showed very little change in the intensity of the E_1' line in comparison to its intensity measured before the X-ray treatment, but the above-mentioned lines disappeared.

The broad line is still observable in UBQ (at RT and LT) after the crystal had been heated to *ca.* 720 K for nearly 15 hours in air, whereas the E_1' line almost disappeared. Experience has shown that virtually all paramagnetic centers (except transition-metal ions such as Fe^{3+}) disappear when quartz is heated to this temperature. After X-raying the crystal at RT for nearly 45 minutes, the E_1' line reappeared with almost the same intensity as before bleaching. We did not notice any change in either the intensity or the linewidth of the broad line during this process.

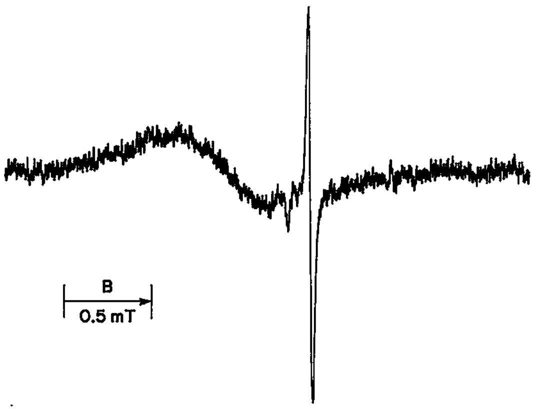

FIG. 2. A typical 9.6 GHz EPR first-derivative spectrum of a UBQ crystal at room temperature when $\hat{B}//\hat{c}$.

The RT EPR spectrum of UBQ at 24.3 GHz differs somewhat from that at 9.6 GHz described above. We again found the isotropic broad line (width 0.72 mT) and the E_1' line. In addition to these, we noted a sextet centered near the broad line. We assigned these six lines to Mn^{2+} (nuclear spin = 5/2) in the UBQ crystal. These six Mn^{2+} lines are isotropic, with a g-factor of 2.0011(1) with ^{55}Mn hyperfine splitting of 9.42 mT. This splitting is reasonable for Mn^{2+} bonded to oxygen in sixfold coordination (Simanek & Mueller 1970). The absence of all but the central fine-structure sextet suggests high static disorder for the occurrence of the (presumed) MnO_6 clusters. We tried to remove surface impurities in the UBQ crystal by warming it gently in various solvents (CS_2, conc. HNO_3, conc. H_2SO_4, conc. HCl). This treatment did not remove the Mn^{2+} signal.

The black mantle material also gives a broad line at RT, with characteristics identical to those observed in UBQ. An ENDOR study, at 9.59 GHz and *ca.* 100 K, of this material (in air) showed a strong single line at 14.5 MHz, plus some additional very weak features just above this RF frequency. Thus the EPR width appears to be caused by unresolved proton hyperfine structure. The 24 GHz EPR spectra of the mantle material reveal the presence of the isotropic broad line and the Mn^{2+} lines, plus some additional weak features. The g factor and ^{55}Mn hyperfine value are the same in the UBQ crystals and the surrounding mantle material. The additional features simultaneously present in the UBQ crystals and in the mantle material were not identified.

The mantle material was subjected to the following treatments: a) exposure to X rays at RT for 40 minutes, b) then heating in air for nearly 15 hours at *ca.* 720 K, and c) then exposure to X rays again at RT. The spectra were recorded after each treatment. There was no noticeable change either in the *g*-factor or linewidth of the broad line during the above experiments. No new lines were found.

Treatment of the mantle material at RT with conc. H_2SO_4(aq), conc. HNO_3(aq), conc. HCl (aq) and CS_2 showed it to be almost completely soluble in these solvents. The black-colored solutions thus obtained gave symmetrical broad EPR signals with identical *g*-factors (2.0028), but with decreased linewidths, compared to the width obtained from the solid mantle material. The broad line is still present (both at RT and at LT) in the UBQ crystals even after treating the crystals with these different solvents; the color of both the crystal and the solvent remained unchanged.

Our experiments to find carbon as a substitutional impurity for silicon in quartz were extended with studies of Herkimer "diamond" quartz crystals. The RT EPR spectra of these (four) crystals, containing small visible black inclusions, gave a broad line with a *g* factor of 2.0022(1) and a width of 0.42 mT, at both frequencies of measurement (9.4 and 24 GHz). We found the same broad line, at 9.4 GHz, in "black chunks" removed from the Herkimer crystals, with a *g* factor of 2.0026(1) and a width of 0.53 mT. At 24 GHz, we noticed some weak additional features (not Mn^{2+} lines), in addition to the isotropic broad line. Some of these Herkimer crystals were subjected to 45 minutes of X-irradiation. We did not find any $[AlO_4]^0$ centers (Nuttall & Weil 1981) in the LT EPR spectra of these crystals, but some do show lines due to Ge as an impurity (Weil 1984).

A Herkimer quartz crystal containing no visible black inclusions gave no EPR lines. Specifically, the broad line is absent. The crystal was then X-irradiated at RT, whereupon the RT EPR spectrum showed weak lines due to Ge and the LT EPR spectrum showed $[AlO_4]^0$, in addition to the Ge centers. Unlike the UBQ crystals, none of the Herkimer quartz crystals (with and without black inclusions) showed the E_1' spectrum.

DISCUSSION AND SUMMARY

A few oxygenic carbon-containing free radicals are known, but not in crystalline quartz. No carbon tetroxide free radical species seems to have been reported in any material. However, CO_3^- and CO_2^- radicals were observed after grinding quartz sand in a CO_2 atmosphere (Ebert & Hennig 1974) and presumably are surface species. Other known carbon–oxygen radicals potentially relevant to our study are CO_3^-, CO_3^{3-} (Serway & Marshall 1967), CO_2^- (Marshall *et al.* 1964), HCO_3^{2-} (Cass *et al.* 1974) (all the above observed in calcite), CO^+ on a H-type zeolite (Vedrine & Naccache 1973), and carbon–oxygen divacancy radicals present in irradiated silicon (Lee *et al.* 1977). All the above-mentioned carbon–oxygen radicals were measured with EPR at 77 K.

As was mentioned in the results section, we observed four weaker lines in UBQ at fields below the strong broad line and two more weaker lines above the broad line. We tried to measure angular dependences for these six lines at X band, but unfortunately the lines were too weak (and the strong lines interfered) to do this quantitatively. We can say that the range of *g* factors for the lower-field four lines is roughly 2.0057 to 2.0075, whereas for the other two lines it is 1.9987 to 2.0022. None of the above radicals cited in the literature can be responsible for these six lines, since the range of *g* factors for these carbon radicals (except perhaps CO^+) is incompatible with our results.

We can conclude that the color of the black quartz crystals investigated herein is due to macroscopic organic impurities present in the crystal, and not due to substitutional "point" impurities in the quartz structure. It has been suggested from the low-temperature EPR spectra of coal ash, which do not contain a broad line at $g = 2$, that the latter in coal arises from organic matter (Retcofsky *et al.* 1981). Since the width of the broad line in BQ remains the same both at 9.6 and 24.3 GHz, we conclude that the breadth is caused by unresolved hyperfine lines, presumably from protons, and not by overlap of different *g*-factor spectra (hyperfine values are independent of frequency). The width of the broad lines in coals usually depends on the percentage of carbon present. For coals with carbon contents ranging from 55 to 90%, the corresponding linewidths vary from 0.52 to 0.86 mT (Retcofsky *et al.* 1981). Our mantle material has a carbon composition of 80% and a linewidth of 0.75 mT, in good agreement with the above general trend.

As was mentioned in the results section, Herkimer quartz crystals with black inclusions do give the broad line, whereas crystals without these do not. Thus it is indeed the black "anthraxolite" particles that give rise to the free radical EPR signal.

The absence of the six Mn^{2+} lines in our X-band spectra of the UBQ and mantle material, and their presence at K band, may be due to greater line-broadening at the lower frequency (caused by the relatively greater anisotropy effects of the fine-structure terms in the spin Hamiltonian). Such effects were observed (Lehmann 1987) for Mn^{2+} in $AlPO_4$. Manganese in coals (Retcofsky *et al.* 1981), in minerals in oil sands (Malhotra & Buckmaster 1985) and in petrified wood from Bristol, England (Ikeya 1982) has been reported, and at least in some instances occurs in $CaCO_3$ inclusions (Malhotra & Graham 1985).

In summary, we have discovered that coal-like materials containing free radicals can be intimately associated with quartz crystals. Our attempt by EPR to identify carbon atoms occurring substitutionally for silicon in these samples of α-quartz, in which the opportunity for carbon substitution appeared to be high, gave negative results. This finding is consistent with our theoretical predictions.

ACKNOWLEDGEMENTS

This work was carried out under the auspices of the Natural Sciences and Engineering Research Council of Canada. We are most grateful to Mr. F. Fornelius (Centerville, Utah), Mr. & Mrs. C. Groman (Bethlehem, Pennsylvania), Ms J. Kaylor (Redpath Museum, McGill University, Montreal, Quebec), Mr. & Mrs. R. Mercer (Palmerton, Pennsylvania) and Mr. N. Rochester (Morris Museum, Morristown, New Jersey) for providing us with the crystals investigated. Thanks are due to Saskatchewan Research Council for the neutron activation analysis and radiocarbon dating, to our Department of Chemistry Analytical Lab and especially to Dr. L. W. Bader for the chemical analysis, and to Bruker Analytische Messtechnik (Rheinstetten, FRG) for providing the ENDOR spectra. We thank Prof. R. J. Kirkpatrick and an unknown referee for their helpful comments.

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Received April 15, 1988, revised manuscript accepted September 21, 1988.