

# An Electrolytically Generated, Localized Hole Center in Quartz

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In natural smoky quartz and neutron-irradiated, initially colorless quartz a new hole center was formed electrolytically at temperatures near 1100 K in addition to the well-known smoky quartz center. Unlike the latter its electron paramagnetic resonance spectra can already be measured at room temperature due to firm localization of the hole on one oxygen. It is characterized by fairly small hyperfine splittings due to Al impurity and significant deviations of all three principal  $g$  factors from that of a free electron. A tentative model for the structure of this center is proposed.

An activation energy of 215 kJ/mol was determined for this electrolytic coloration from the temperature dependence of the electrolysis currents.

## Introduction

Paramagnetic defects (“color centers”) in insulating or semiconducting materials are usually created by high-energy (X- or  $\gamma$ -ray) radiation thus also imitating the action of natural radioactivity in many natural minerals which exhibit a characteristic color but are completely colorless as pure substances. Smoky quartz is the most thoroughly studied example of such a mineral with a hole on one of the oxygens adjacent to an Al impurity [1–4]. Since complementary electron and hole centers are simultaneously formed in this photochemical process, assignment of optical absorption bands to one of them is always a problem that is still largely unsolved in most cases since even correlation of the band intensity with the concentration of a certain center (measured, e.g. by electron paramagnetic resonance (EPR)) is not conclusive in cases where only one kind each of these centers is formed in equal concentrations and where they thus also decay simultaneously in equal amounts. For the smoky quartz center in particular it was shown by optically detected EPR that only a part of the absorption in the visible range is evidently due to this center [5].

An attractive alternative method for formation of such paramagnetic defects is the electrolytic injection of either electrons or holes. Only one kind of defects

(i.e. electron or hole centers) is normally formed in this way since the charge neutrality is achieved by migration (and ultimately removal) of mobile ions.

Creation of smoky quartz centers was shown to occur in quartz via electrolysis at temperatures between 1013 and 1293 K [6, 7], but at least one additional kind of hole centers was simultaneously formed. In contrast to those of the smoky quartz center its EPR spectra could already be detected at room temperature, but were not investigated in detail [8]. Analogous electrolysis experiments with the feldspar variety sanidine proved that an optical absorption very similar to that of smoky quartz is also due to a hole center of a closely related structure [9].

## Experimental

Electrolysis experiments were performed in air at temperatures between 1013 and 1123 K between platinum electrodes, a flat cathode and an anode with three tips to facilitate injection of holes. The quartz samples typically had sizes of  $(8 \times 8 \times 8) \text{ mm}^3$ , and electric fields in the range of 2.5 kV/cm were applied along the  $c$ -axis.

EPR measurements were performed at Q-band (room temperature and 77 K) and at X-band (15 K) using commercial instruments of Bruker Analytische Messtechnik, Karlsruhe for rotations about three mutually perpendicular axes parallel to the crystal  $c$ ,  $a$  and  $b$  ( $=c \times a$ ) axes. Spectra were recorded at  $5^\circ$

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intervals. Piceine was used as a standard for determination of the microwave frequencies [10], and the magnetic fields were measured using an NMR gaussmeter. For determination of the  $g$  and  $A$  matrices only results of Q-band measurements were used since those at X-band were considerably complicated by quadrupole effects resulting in intense forbidden transitions.

## Results and Discussion

### Electrolysis Experiments

If the electric field was already applied before a constant temperature around 1100 K was reached, the current dropped from an initial value of about 100  $\mu\text{A}$  at this temperature to about half this value within one hour. If it was applied after the constant temperature was reached it dropped from considerably higher values to about 100  $\mu\text{A}$  within a few minutes and then decreased more gradually. This decrease with time is largely analogous to that calculated for the model of the "exhausted source" [11]. 1023 K was the lowest electrolysis temperature for which a (slight) coloration was observed whereas after electrolysis at 1123 K a smoky coloration of similar intensity as that produced by ionizing radiation was formed. At 1073 and 1123 K, migration velocities of the color cloud between 4 and 5 mm/h were observed if the experiments were stopped before it had reached the cathode, but these results were not accurate enough for determination of the activation energy. In one experiment the temperature was lowered from 1123 to 1083 and 1013 K after half an hour. From the currents at these temperatures an activation energy of 215 kJ/mol was calculated; the possible error is estimated to be around 10%. This value is considerably higher than those reported for electrodiffusion of  $\text{M}^+$  cations: 70 to 130 kJ/mol for  $\text{M} = \text{Li}$  or  $\text{Na}$  and between 145 and 180 kJ/mol for  $\text{M} = \text{H}$  [12]. The main part of this energy is attributed to dissociation of  $\text{Al}-\text{M}^+$  complexes and only a small fraction to migration along the  $\text{Si}-\text{O}-\text{Si}$  chains. Since the temperatures required for electrolytic coloration are at least 300 K higher than those for exchange of these monovalent cations against each other, ionization of the  $\text{AlO}_{4/2}^-$  groups must be the highest energy barrier in this case. This activation energy is in reasonable agreement with the energies of the thermoluminescence emission associated with thermal destruction of smoky quartz centers formed by ionizing radiation: The emission maxima of

16 100 and 21 500  $\text{cm}^{-1}$  [13] correspond to 193 and 257 kJ/mol. The latter process is usually assumed to occur via excitation of electrons into the conduction band and their recombination with hole centers, i.e. the reverse of this ionization. As a result of the Franck-Condon principle systematically lower energies should be observed in the thermoluminescence emission. Therefore the emission at 16 100  $\text{cm}^{-1}$  is in better agreement with the value of the activation energy. In any case, the reasons for observation of two emission maxima are still not understood.

### EPR Data

Already at room temperature sharp EPR signals with a well-resolved hyperfine splitting are observed after electrolysis. Whereas at X-band these hyperfine patterns are very complex, at Q-band clear sextets were observed at many orientations. An example is shown in Figure 1. Splitting into up to six magnetically non-equivalent sets and their collapse into a single sextet for the magnetic field along the  $c$  axis clearly show that a single center of triclinic point symmetry is present. Complete collapse of the hyperfine splitting for certain orientations (as for the second component in Fig. 1) shows that the hyperfine splitting nearly vanishes. From the spectra obtained for rotations around  $c$ ,  $a$ , and  $b$  ( $=a \times c$ ) axes the  $g$  factors were determined and are shown in the rotational diagram in Figure 2. A similar rotational diagram was also obtained for the hyperfine splitting constants. Principal axes transformations of these data resulted in the

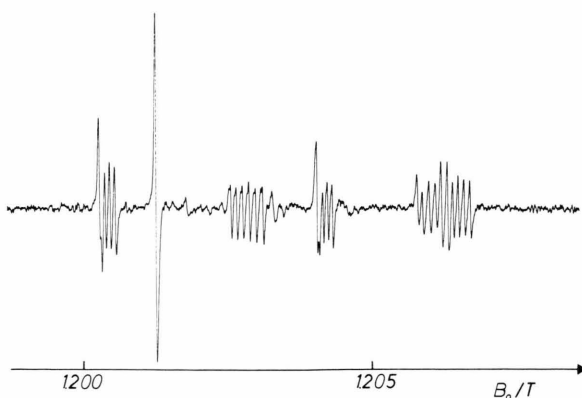


Fig. 1. EPR spectrum at 34.1 GHz and 295 K of an electrolyzed smoky quartz sample for the magnetic field perpendicular to  $b$  and  $30^\circ$  from  $c$ .

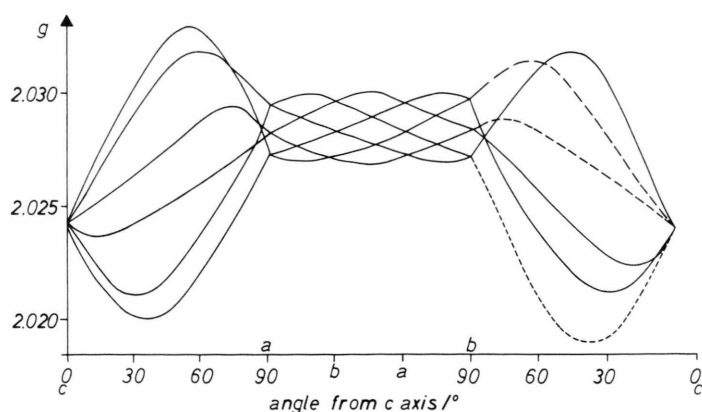


Fig. 2. Angular variations of the  $g$  factors (centers of hyperfine sextets) for rotations around the  $b$ ,  $c$  and  $a$  axes (from left to right). For rotation around the twofold  $a$  axis the full curves occur for rotation from 90 to 0° and the dashed ones for rotation from 90 to 180° ( $= -c$ ).

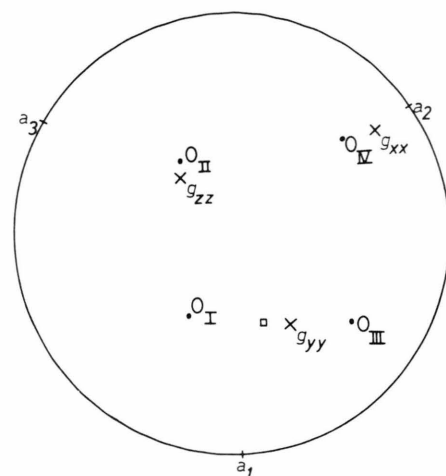


Fig. 3. Stereographic projection showing the correlation of the principal axes directions of the  $g$  matrix with structural directions of the pure quartz lattice: ● Si–O directions; Si–O<sub>I</sub> and Si–O<sub>II</sub> are the two longer bonds. □ O<sub>I</sub>–O<sub>III</sub> direction.

Table 1. Spin-Hamiltonian parameters for the localized hole center in electrolyzed quartz.

$l$	Principal values		Principal directions for $g_{ii}$	
	$A_{ii}$ /MHz	$g_{ii}$	$\vartheta/^\circ$ <sup>a</sup>	$\varphi/^\circ$ <sup>a</sup>
$x$	−2.32	2.0291	78.7	237.2
$y$	−4.18	2.0338	52.5	−30.5
$z$	−0.16	2.0188	39.7	141.5

Limits of error:

$\pm 0.15$  MHz for  $A_{ii}$ ;  $\pm 0.0002$  for  $g_{ii}$  and  $\pm 1.0^\circ$ .

<sup>a</sup>  $\vartheta$  and  $\varphi$  resp. are the tilting angles from the  $c$  and  $a$  axis resp. in the  $a$ – $c$  plane.

principal values listed in Table 1. The corresponding principal axes directions are only reported for the  $g$  matrix since significantly higher limits of error were obtained for the principal axes directions of the hyperfine tensor as a result of limited resolution and distortions of the regular sextet patterns like in the first and fourth component in Figure 1.

Since the hyperfine splitting can only be due to an Al impurity, the basic structure of this center is a hole on an oxygen adjacent to an Al impurity. Thus, like in a larger number of centers observed in the natural quartz variety citrine [13, 14], an as yet unidentified additional defect must cause a structural modification of the basic smoky quartz center as well as the firm localization of the hole. In the absence of additional

information about the nature of this defect (e.g. from additional hyperfine structure in case of a second impurity like in the hole center on an oxygen adjacent to Al and P in certain rose-colored natural quartzes [15]) no definite model for its structure can be established. A number of conclusions can, however, be drawn from results for other centers of known structure and from results of theoretical work.

#### A Tentative Model for its Structure

Considering first the  $^{27}\text{Al}$  hyperfine splitting, it is evidently much smaller than in the smoky quartz center [3, 4] as the basic center of this type without modification by an additional defect in the neighborhood. Decomposition of the principal values into their isotropic ( $A_{\text{iso}}$ ), dipolar ( $B$ ) and rhombic ( $C$ ) components for these as well as the Al...O<sup>−</sup>–P [15] and three localized centers observed in the natural quartz variety citrine [14] in Table 2 shows that for all centers with localized holes the isotropic part is much smaller than in the smoky quartz center. Their signs (determined from the fact that the dipolar part must always be positive) are variable, and the large negative value for the smoky quartz center was attributed to unpaired spin density of inner  $s$  electrons of Al due to core polarization [16]. It is a result of the inclination of the  $2p_z$  lobe of the unpaired electron relative to the Al...O<sup>−</sup> direction, whereas with increasing overlap

Table 2. Isotropic, dipolar and rhombic components of the  $^{27}\text{Al}$  hyperfine splitting for hole centers in quartz.

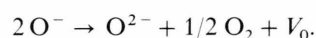
Center	$A_{\text{iso}}/\text{MHz}$	$B/\text{MHz}$	$C/\text{MHz}$	Source
Smoky quartz	-16.12	1.03	0.10	[4]
Al-O $^{\text{--}}$ -P	+ 4.18	0.79	0.59	[15]
Citrine #C	+ 3.6	0.3	0	[14]
Citrine #D	- 3.1	0.75	0.15	[14]
Citrine #E	- 2.2	1.0	0.85	[14]
This center	- 2.22	1.03	0.93	this work

of this lobe with the Al positive values should result from Fermi contact interaction [17]. Depending on the relative contributions of these opposing mechanisms, negative or positive isotropic parts may result, as observed for the localized hole centers listed in Table 2. Although both effects increase with diminishing Al...O $^{\text{--}}$  distance, it cannot be determined from such data even if the orientation of the half-filled 2p lobe is precisely known since the dependencies of both mechanisms on the angle of inclination are unknown. It can, however, be concluded from the almost perfect cancellation in the new center that this lobe must be significantly inclined to the Al...O $^{\text{--}}$  direction. In accordance with this conclusion  $A_{zz}$  was found to be close to the Si-O $_I$  direction and  $A_{yy}$  close to Si-O $_{IV}$ , i.e. they are inclined to the directions of both  $g_{zz}$  and  $g_{yy}$ .

The size of the dipolar part is in the upper range of those for the other centers listed in Table 2. It may indicate a relatively short Al...O $^{\text{--}}$  distance, but calculations based on a purely electrostatic model [18] do generally not lead to very consistent results. A twice as large value was recently observed for one of two Al adjacent to an (also localized) hole in the mineral brazilianite [19], where due to sixfold coordination of the Al these distances should be significantly larger than in quartz.

The directions of all three 2p lobes of the O $^{\text{--}}$  follow from the orientations of the principal  $g$  factors in Table 1. Obviously, two of them are close to Si-O bond directions, and normally the direction of  $g_{zz}$  indicates the direction of the half-filled p lobe. However, in this case  $g_{zz}$  is significantly larger than the value for the free electron, the deviation is about half as large as for the largest value  $g_{yy}$ . Nearly the same relative deviation was also observed for the Al...O $^{\text{--}}$ -P center in quartz [15] (with a smaller overall anisotropy of the  $g$  matrix). This absence of a principal value close to that of the free electron is usually

attributed to rapid fluctuation of the unpaired electron between different configurations. A significant axial elongation with the 2p $_z$  level at lowest energy and the unpaired electron in one of the (at least nearly) degenerate 2p $_x$ , 2p $_y$  levels may cause such a situation. In view of the similarities to the Al...O $^{\text{--}}$ -P center, where the hole is formed adjacent to the effectively positive charge of P $^{5+}$ , the removal of monovalent cations during electrolysis and absence of additional hyperfine structure, it is tempting to assume the presence of an oxygen vacancy adjacent to Al. Such vacancies  $V_0$  may be initially present or formed during electrolysis by thermal destruction of hole centers according to



Presence of this vacancy would be a plausible explanation for the postulated axial elongation and for alignment of the (filled) 2p $_z$  level close to the Si-O $_{II}$  direction. In any case, the unpaired electron should be more stable on the oxygens with longer bond distance in the SiO $_{4/2}$  units (i.e. O $_I$  and O $_{II}$ ), and localization of the hole in the 2p $_z$  level leads to the postulated inclination relative to the Al...O $^{\text{--}}$  direction. Thus this model appears to be consistent with all known properties of this center. The question, however, remains whether such a center is really stable enough at the temperature of electrolysis to be quenched to room temperature. One may also assume that an oxygen vacancy may tend to capture an electron to form a center of the  $E'$  type [20]. However, all centers of this type reported so far always involve an additional monovalent cation impurity and thus have a more complex structure than possible after removal of these impurities.

### Concluding Remarks

The model proposed for this center is still speculative. If the vacancies are formed during electrolysis, the relative concentration of centers formed from them should (at least initially) increase with temperature of electrolysis. We plan to investigate this temperature dependence. EPR measurements at 77 K showed that, like in the previous electrolysis experiments [6, 7], smoky quartz was formed in much higher concentrations (ratio about 1000:1). It is likely that in these previous experiments the same localized hole

center was observed since an almost isotropic  $g$  factor of 2.02 was reported (for X-band measurements with smaller Zeeman splitting than in our Q-band measurements [8]).

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