

EPR of [Pb-Pb]³⁺ mixed valence pairs in amazonite-type microcline

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ABSTRACT

Using electron paramagnetic resonance (EPR) at 9.2 GHz between 5 and 295 K, [Pb-Pb]³⁺ pairs, unknown in natural minerals, were studied in single crystals of amazonite of different colors and localities. The EPR data indicated two nonequivalent Pb ions, A and B, at adjacent K positions in the microcline structure. The calculated Hamiltonian parameters for the [Pb_A-Pb_B]³⁺ dimeric center are $g_{11} = 1.80 \pm 0.03$, $g_{22} = 1.56 \pm 0.03$, $g_{33} = 1.36 \pm 0.03$, and $A_{11}^A = 790 \pm 10$, $A_{22}^A = 1575 \pm 10$, $A_{33}^A = 1730 \pm 10 \times 10^{-4}$ T, and $A_{11}^B = 695 \pm 10$, $A_{22}^B = 1270 \pm 10$, $A_{33}^B = 1530 \pm 10 \times 10^{-4}$ T. Estimated electron spin density coefficients c_s^2 and c_{pz}^2 of both Pb ions A and B are $^A c_s^2 = 0.04$, $^A c_{pz}^2 = 0.44$, $^B c_s^2 = 0.05$, and $^B c_{pz}^2 = 0.31$. Stable [Pb-Pb]³⁺ dimeric centers can be formed only in ordered feldspar and only if one of the Pb²⁺ ions is charge compensated by Al,Si exchange at adjacent T,m positions. If the second Pb²⁺ ion is also compensated, no stable [Pb-Pb]³⁺ centers can arise.

Heating at 543 K for 10 h caused Pb diffusion, and about 70% of Pb pairs were destroyed, whereas the color, EPR spectrum, and optical absorption (OA) band at 630 nm became unobservable. Subsequent irradiation can restore about 30% of the EPR spectrum, the OA band, and the blue color. Heating above 1073 K caused diffusion of the remaining Pb (about 30%), and the EPR spectrum, OA band, and color were destroyed irreversibly. The calculated activation energy for Pb diffusion for light blue, blue, and green amazonite in the temperature range 673–773 K is 12, 14.5, and 21 kcal/mol, respectively.

Irradiation-induced, stable [Pb-Pb]³⁺ pairs causing the typical blue-green color were found only in amazonite-type microcline. In other similarly colored potassium feldspar and sodium feldspar, such centers are not known. Therefore, the name “amazonite” should be limited to classical, ordered microcline of blue-green color with [Pb-Pb]³⁺ pairs as the chromophore.

INTRODUCTION

Amazonite is a variety of microcline with a characteristic blue to bluish green to green color of varying intensity. Since Breithaupt (1847), the name “amazonite” has been used only for triclinic potassium feldspar. According to Ratiev and Puliev (1964), Bugaetz (1967), and Shmakin (1968), the origin of the amazonite color is characteristic of maximum-ordered microcline. They suggested that this color can be produced with admixed elements (Fe, Pb, Rb, and others) only in potassium feldspars with a high degree of Al,Si order. Previously Breithaupt (1847) associated the color with the chromophore features of Cu. Since that time, the source of amazonite color has been the subject of many investigations and conflicting opinions, and several controversial hypotheses and models have been proposed.

Kapustin (1939) suggested that the intensity of color was proportional to the Pb content. According to Kuts (1964), both Rb and Pb are responsible for the color; Zhirov and Stishov (1965) noted that a measurable

amount of Pb is typical of amazonite and that the Pb concentration is up to three times higher in the colored than in the uncolored parts. Taylor et al. (1960) analyzed a large number of trace elements and claimed that none was responsible for the color. They suggested that structural defects and strain may cause the color. Foord and Martin (1979) attributed amazonite color to the charge-transfer $Pb^{2+} + Fe^{3+} \rightarrow Pb^{3+} + Fe^{2+}$.

Particularly in the Russian literature, “amazonitization” is often mentioned. This term was introduced by Zavaritskii (1943); in his opinion, the green color of amazonite is related to a late stage of the pegmatite process, i.e., it is of epigenetic origin. Likewise, Arnaudov et al. (1967) associated the color of amazonite with late metasomatic processes, which took place at an increased activity of Na and by introduction of Pb and Rb. Several authors noted that amazonitization occurs during metasomatism (Oftedal, 1957; Taylor et al., 1960; Kuts, 1964; Godovikov, 1975). According to Zhirov et al. (1959) and Zhirov and Stishov (1965), amazonitization is a process of Pb (also Rb and Tl) metasomatism: $K^{1+} + Si^{4+} \rightarrow Pb^{2+} + Al^{3+}$ or $2K^{1+} \rightarrow Pb^{2+}$. Plyusnin (1969) suggested that the color results from substitution of Pb^{2+} : $2K^{1+} + O^{2-}$

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→ Pb²⁺ + 2OH⁻. He noted that Pb content increases with increasing OH content and that intensively colored amazonite contains up to ten times more H₂O than white or yellowish microcline does. This process occurs when potassium feldspar is attacked by metasomatic solutions at temperatures exceeding 600 °C.

Oftedal (1957) examined the decoloration rate upon heating of a very intensely colored green amazonite from Tordal in Telemark, Norway, finding that the rate varied with temperature according to Arrhenius's law. The estimated activation energy of 30 kcal/mol is in the range of those for nonvolume diffusion of *M* cations (Smith, 1974, p. 152). He concluded that the color of amazonite is due to color centers (F⁻ ions replace O²⁻) and that these centers were introduced at temperatures below 300 °C, probably about 250 °C, that is, in already crystallized and considerably cooled feldspar. He correlated this with field observations where the amazonite color is connected with formation of cleavelandite veins in already existing microcline pegmatite.

Optical absorption (OA) studies lead also to controversial models for the cause of the amazonite color. Eliseev (1949) assigned the typical "amazonite" OA band, centered in the region of 600–650 nm, to Fe²⁺ and the decoloration and partial restoration of amazonite color after heating and irradiation, respectively, to the oxidation-reduction process Fe²⁺ ↔ Fe³⁺. Tarashchan et al. (1973) observed that in amazonite the intensity of the ultraviolet absorption band of Pb²⁺ increased after heating but decreased after subsequent irradiation and suggested a change of Pb²⁺ to Pb¹⁺. Hofmeister and Rossman (1983, 1985a, 1986) studied a large number of amazonite samples and other feldspars from different localities having Pb content between approximately 20 and 2000 ppm, and they attributed the amazonite color to electronic transition involving Pb³⁺ or Pb¹⁺ with association of a H₂O molecule with the precursor Pb site. They noted that the blue color of microcline results from a broad OA band in the region of 550–850 nm (centered at about 630 nm) and that the green color of orthoclase comes from the broad OA band in the region of 600–950 nm (centered at about 720 nm). A blue-green color arises when both absorptions are present. Blue samples have only the 630-nm band and are triclinic. Monoclinic samples contain only the 720-nm band and are green. Samples with both bands are less well ordered than the blue samples. Amazonites with <1000 ppm Pb are blue and denoted as B type; those with higher Pb content are green and denoted as T type. However, some feldspars with as much as 1000 ppm Pb are not colored (Foord and Martin, 1979; Hofmeister and Rossman, 1985a). In microcline from Ireland and Norway and in amazonite from Australia, Speit and Lehmann (1982) found O¹⁻/²⁰⁷Pb²⁺ centers, but they are not associated with amazonite color. Using OA measurements of systematically heated and irradiated amazonite single crystals, Platonov et al. (1984) and Vokhmentsev et al. (1989) attributed the amazonite absorption band at 630 nm to the formation of exchange-

linked Pb¹⁺-O-Fe³⁺ complexes causing a strong intensity increasing of the transition ⁶A₁ → ⁴T₁ in Fe³⁺ ions substituting Al at T_{1,0} positions. In microcline with well-ordered distribution of Al,Si over the four nonequivalent tetrahedral positions, nearly all Al atoms are located at T_{1,0} and nearly all Si atoms at T_{1,m}, T_{2,0}, and T_{2,m}.

Cech et al. (1971) investigated green orthoclase containing 1.19% PbO from pegmatites of metasomatic-metamorphic origin near Broken Hill, New South Wales, Australia, and proposed to extend the name "amazonite" to all similarly colored potassium feldspar between orthoclase and microcline and to other feldspars with similar color. On the basis of the similarity of the reflection spectra of sodium plagioclase and amazonite, Rudenko and Vokhmentsev (1969) suggested that the pale blue color of plagioclase has the same origin as that of amazonite. Hofmeister and Rossman (1985a, 1986) investigated green orthoclase from Broken Hill and pale blue albite and oligoclase. They concluded that the blue and green colors of potassium feldspar and sodium feldspar are produced by an electronic transition of Pb, as is the cause of the amazonite color. However, OA spectra of orthoclase and plagioclase showed very broad bands at about 730 and 630 nm, respectively, but the annealing temperatures of the bands were lower than that of the amazonite band at 630 nm.

The amazonite problem is still controversial, because all studies are based on two methods: (1) chemical analyses, and (2) absorption spectroscopy and their correlation. Method 1 cannot solve this problem. Correlations of Pb content and color give no information about the origin of color. For instance, Pb²⁺ shows OA in the UV region, so it cannot produce visible color. In the case of amazonite color with very broad OA bands (about 300 nm), method 2 gives no unambiguous interpretation. Therefore correlated OA and EPR measurements are needed.

EPR spectra of Pb¹⁺ in single crystals of amazonite from Keivy, Kola Peninsula, Russia, were observed first by Marfunin and Bershov (1970), but their interpretation was based only on the estimated *g* values for an ion in the p¹ state (Goovaerts et al., 1983; Heynderickx et al., 1986a, 1986b; Roberts and Eachus, 1972) and were attributed to even ^{204,206,208}Pb isotopes (nuclear spin *I* = 0, natural abundance 77.38%). Unambiguous identification of Pb by hyperfine structure (HFS) of the odd ²⁰⁷Pb isotopes (*I* = 1/2, natural abundance 22.62%) was not possible. In powder spectra of blue and green amazonites from Lake George, Colorado, New York Mountains, California, and Keivy, Russia, Hofmeister and Rossman (1985a) observed three EPR lines corresponding to the three *g* values detected in single crystals by Marfunin and Bershov (1970), and they interpreted low- and high-field signals as HFS of ²⁰⁷Pb. However, their Figure 6 clearly shows a classical powder spectrum of a paramagnetic center (electron spin, *S* = 1/2, nuclear spin *I* = 0) of orthorhombic symmetry without HFS, the same center of ^{even}Pb as described by Marfunin and Bershov (1970).

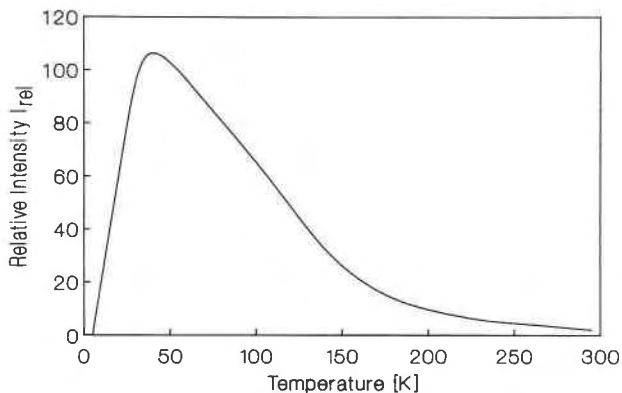


Fig. 1. Temperature dependence of the central line intensity of the [Pb-Pb]³⁺ center in amazonite at controlled measuring conditions, rotation $+c^*\parallel Z^0$, $+a\parallel X^0$, $\theta = 70^\circ$.

In the past two decades, much EPR data on simple crystal systems doped with pⁱ ions (Van Puymbroeck et al., 1981; Schoemaker et al., 1985; Heynderickx et al., 1986a, 1986b) including Pb¹⁺ (Roberts and Eachus, 1972; Goovaerts et al., 1982, 1983; Heynderickx et al., 1986a, 1987) were published. Because of the significant differences of *g* and *A* values, the large number of distinct Pb centers in alkali halides doped with Pb²⁺ can be identified unambiguously only by correlated EPR and OA measurements (Schoemaker and Kolopus, 1970; Frey et al., 1975; Goovaerts et al., 1982; Heynderickx et al., 1986a). For example, in KCl four types of Pb centers, four distinct Pb¹⁻ (Goovaerts et al., 1982), four distinct Pb¹⁺⁽¹⁾ (Heynderickx et al., 1986a), one Pb¹⁺ (Cl_i) (Goovaerts et al., 1983), and one Pb³⁺ (Schoemaker and Kolopus, 1970) center were detected. Using OA measurements Stott and Crawford (1971) found only isolated Pb¹⁺⁽⁰⁾ centers in NaCl. However, EPR studies demonstrated the existence of five distinct [Pb-Pb]³⁺ dimeric centers, but spectra of isolated Pb¹⁺ ions were not observed (Heynderickx et al., 1987). In more complex crystal systems and in natural minerals, [Pb-Pb]³⁺ centers are unknown.

In this paper EPR and OA studies of [Pb-Pb]³⁺ dimeric centers in systematically heated and irradiated single crystals of amazonite of different colors and from different localities were presented. The origin of amazonite color and the proposal to extend to the name "amazonite" to all similar colored feldspars are discussed.

SAMPLES

Forty-two single crystals of different colors and localities were investigated. According to the notation of Hofmeister and Rossman (1985a) the different amazonite samples can be denoted as type B (turquoise-like blue) and type T (malachite-like green), with Pb contents lower than 1000 and higher than 1000 (up to 2000 ppm), respectively. Type B amazonite samples were from Transbaikal, the pegmatite veins from Kukurt, East Pamir, Tadjikistan (light blue), and India (blue). Type T samples were from Ilmenyi (Ural) and Keivy (Kola Peninsula,

Russia). No phases other than sodium feldspar (white perthitic parts) and potassium feldspar (colored parts) were revealed by X-ray diffraction analyses of the amazonite samples. The five samples of green orthoclase were fragments from three megacrystals from the Hybin pegmatite of the Kola Peninsula.

The volumes of 47 single-crystal fragments cut for EPR experiments were approximately 1 mm³. The samples are {001} and {010} cleavage fragments exceptionally clear and free from flaws, cleaved from the colored parts of larger crystals. Thin sections of the crystals were inspected optically for orientation of the crystallographic axes.

EXPERIMENTAL DETAILS

EPR spectra of single crystals of amazonite were recorded with a commercial X-band spectrometer between 4.2 and 295 K, details of which were described by Petrov and Hafner (1988). The applied magnetic field *B* for each recorded spectrum was calibrated by simultaneous measurement of *B* using a B-H15 field controller. The single crystals were aligned on a goniometer in the cavity of the spectrometer. They were rotated at different temperatures within the cryostat in the orthogonal laboratory system X⁰, Y⁰, Z⁰. Their relation to the crystallographic axes has been reported earlier (Petrov et al., 1989a). Spectra were recorded every 10°, and every 1–5° over critical ranges. The spin Hamiltonian parameters and direction cosines were obtained by matrix diagonalization.

Polarized OA measurements were performed in a Cary 14-R spectrometer. The light was polarized along the indicatrix axis *Z*, i.e., E \parallel Z, the angle between *Z* and the crystallographic axis *b* being 18°.

Heat treatments of the samples were carried out in air between 473 and 1073 K for heating times between 0.17 and 85 h. In order to correlate loss of the EPR signals and the amazonite absorption band at about 630 nm (15873 cm⁻¹), systematic heating and irradiation experiments were carried out at the same conditions as those of Platonov et al. (1984), using type B and T amazonite crystals from each of the different localities. Between 473 and 973 K, heating occurred in steps of 50 K; the heating time at each temperature was 10 min.

To create the paramagnetic centers or to raise their concentration to saturation, the crystals were exposed to X-radiation up to about 2 × 10⁶ Gray.

RESULTS

A large number of resonance lines may be observed in the EPR spectrum of amazonite at 295 K. Analysis of their angular dependence shows that they are due to Fe³⁺ at T₁₀ sites in microcline, described first by Marfunin et al. (1967). Inspection of the spectra recorded at various temperatures between 5 and 295 K revealed that the [Pb-Pb]³⁺ centers could be studied at temperatures lower than 250 K and that the intensities of the lines were maximized at *T*_m = 40 K (Fig. 1). The spectrum of Pb-associated centers in amazonite exhibits a sharp line of high intensity and pairs of weaker satellites, with a relative

intensity ratio of 59.9:8.75:1.3 (Fig. 2). This spectrum may be due to interaction of an unpaired electron with two nonequivalent Pb ions, A and B. Pb⁰ and Pb²⁺, with electron configurations 6s²6p² and 6s², respectively, are diamagnetic. In chemical compounds Pb exists as Pb²⁺, and by capture of one electron the paramagnetic center Pb¹⁺ (6s²6p¹) is produced. If this electron is delocalized at two Pb²⁺ ions, a [Pb-Pb]³⁺ center arises. The most intense central EPR line is due to the interaction of the 6p¹ electron with ^{even}Pb_A-^{even}Pb_B isotopes (*I* = 0 of ^{even}Pb, natural abundance 77.4%). The two weaker doublets can be considered as HF components of the interaction with A and B nuclei in ²⁰⁷Pb_A-^{even}Pb_B and ^{even}Pb_A-²⁰⁷Pb_B pairs, respectively. Additionally, very weak doublets caused by ²⁰⁷Pb_A-²⁰⁷Pb_B (*I* = 1/2 of ²⁰⁷Pb, natural abundance 22.6%) were observed.

The individual peak-to-peak widths, ^{even}Δ*B*_{pp} of the central line, and HF components did not change within experimental error between 5 and 250 K. The ^{even}Δ*B*_{pp} of the central line is about 7 ± 0.5 × 10⁻⁴ T, the widths ²⁰⁷Δ*B*_{pp}^A and ²⁰⁷Δ*B*_{pp}^B being about 11.5 ± 0.5 and 15.3 ± 0.5 × 10⁻⁴ T, respectively, and ²⁰⁷Δ*B*_{pp}^B·²⁰⁷Δ*B*_{pp}^A ≈ 1.33.

X-ray diffraction patterns of B- and T-type amazonite yielded lattice parameters corresponding to low microcline with near-maximum triclinicity. Optically, the crystals from Keivy showed much finer crosshatched twin domains than crystals from Ilmenyi. Thus, unique determination of the *g* and *A* tensors in the triclinic single-crystal domains was not possible for the crystals studied. For both types of specimens, the orthogonal axis system *X*, *Y*, *Z* is referred to orientations that are averages of the set of crosshatched axes of the separate twin elements, so that the twinned system can be considered as effectively monoclinic. Therefore, the error in *g* values and direction cosines is ±0.03 and 3°. B- and T-type specimens show the same spectrum. The intensity of the [Pb-Pb]³⁺ spectrum in T-type amazonite is about two times higher than in B-type specimens.

The EPR spectrum for a system consisting of one electron with spin *S* = 1/2 and *n* nonequivalent nuclei of spin *I_i* = 1/2 (*i* = A, B and *n* = 2) may be described by the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{B} \mathbf{g} \mathbf{S} + \sum_i^n \mathbf{S} \mathbf{A}_i \mathbf{I}_i \quad (1)$$

where β is the Bohr magneton, *S* and *I* are the electron and nucleus spin operators, respectively, *g* and *A* are the spectroscopic splitting factor and HFS tensor, respectively, and *B* is the Zeeman field vector. Terms of the nuclear Zeeman energy and the nuclear quadrupole energy are omitted from Equation 1, since they are small.

The hyperfine interaction (HFI) between *S* and *I* in the second term of Equation 1 leads to a splitting of the electron levels. Figure 3 shows a schematic diagram of the energy-level splitting of the [Pb_A-Pb_B]³⁺ center, caused by the HFI. Each of the two electron levels at *M_s* = ±1/2 is split because of HFI with one or both nonequivalent nu-

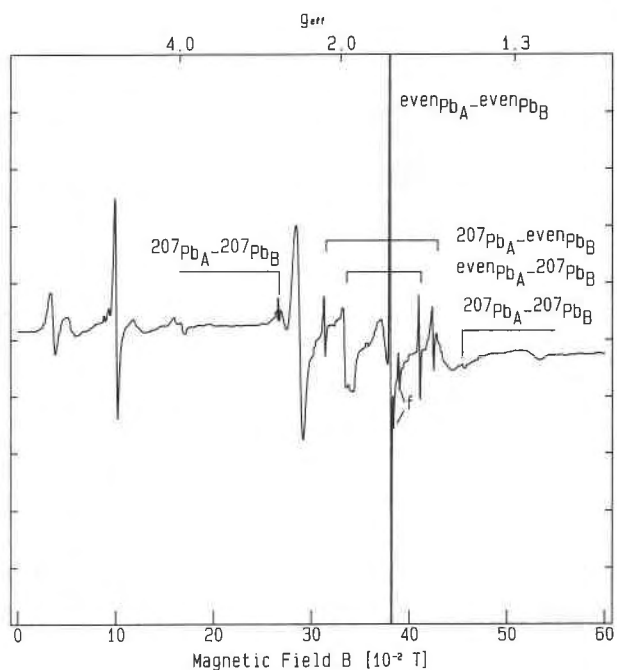


Fig. 2. EPR spectrum of [Pb-Pb]³⁺ center in amazonite, rotation +c*||Z⁰, +a||X⁰, Θ = 180°, ν = 9.2427 GHz, *T* = 40 K. The transition designation is the same as in Fig. 3, *f* = forbidden transition, additional wide lines are due to Fe³⁺ at T₁0 positions.

clei A or B into two sublevels, *m_i* = ±1/2, with splittings of *hA_A*/2 or *hA_B*/2, respectively. Furthermore, HFI with both nuclei A and B causes a splitting into four sublevels. In accordance with the selection rules (Δ*M_s* = ±1, Δ*m_i* = 0), in the first two cases, only two transitions are allowed, in the latter case four. In Figure 3, *M_s*, *m_i*^A, and *m_i*^B states are designated as 0, +, and -, according to their quantum numbers, 0, +1/2, and -1/2, respectively. The 6p¹ electron interacts with two adjacent Pb nuclei. The probability that both are nonmagnetic is 59.5%. The ^{even}Pb-²⁰⁷Pb combination for both nonequivalent nuclei A and B has a concentration of (8.75 × 2)%, and the ²⁰⁷Pb-²⁰⁷Pb combination a concentration of (1.3 × 4)%. In the case of electron interaction with two ^{even}Pb-^{even}Pb nuclei, the spectrum consists of one resonance line, in the case of one ^{even}Pb and another ²⁰⁷Pb the resonance spectrum contains two lines, and for the ²⁰⁷Pb-²⁰⁷Pb combination the spectrum contains four lines. The relative intensity of these lines is 59.9:8.75:1.3 (Fig. 3).

Eigenvalues of diagonalized *g* and *A* tensors and direction cosines of the [Pb_A-Pb_B]³⁺ center in amazonite are listed in Table 1. These *g* values are close to those of Pb¹⁺ in several investigated matrices (cf. references in Table 2) and are very similar to the *g* values determined by Marfunin and Bershov (1970) in amazonite, assigned to Pb¹⁺. Because of the absence of any symmetry elements in the position of the [Pb_A-Pb_B]³⁺ center, it is impossible to align crystals along any desirable direction within high precision; therefore, the error in calculated

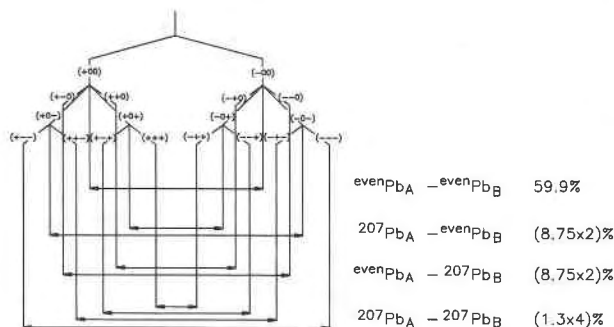


Fig. 3. Energy level splitting for the [Pb-Pb]³⁺ center, described by spin Hamiltonian Eq. 1 with $S = 1/2$, $I_A = 1/2$, $I_B = 1/2$; (M_s, m_l^p, m_s^p) states are designated in accordance with quantum numbers 0, $+1/2$, and $-1/2$ as 0, +, and - within parentheses. The allowed transitions and their intensities are given on the right.

values of Hamiltonian parameters is greater than might be expected from observed line widths. A stereographic projection of the eigenvectors \mathbf{g} and \mathbf{A} is given in Figure 4.

The annealing rate of the [Pb-Pb]³⁺ center was tracked in 50-K steps from 473 up to 973 K, for a constant heating time of 10 min by measuring the central $\text{evenPb}_{\text{evenPb}}$ signal at $g = 1.8$ in Figure 5. In Figure 6 the relative intensity of the signal for type B and T amazonite vs. temperature is plotted. By heating up to about 573 K, the signal intensity of type B is not changed; the signal intensity of type T does not change up to 623 K. Above 573 and 623 K for both types the annealing rate rises rapidly, and at 823 K only about 3% of the initial signal intensity remains. The development of the annealing curves for B- and T-type amazonite is similar, the intensity of the signal being approximately $I_{\text{rel}}^{\text{B}} \cdot I_{\text{rel}}^{\text{T}} = 1:2$. For crystals of type B and T, heat treated between 723 and 973 K at heating times between 0.17 and 85 h, 30% of the EPR signal and a light blue color only can be restored by subsequent irradiation with a dose $\geq 1 \times 10^6$ Gray. After crystals were heated above 1073 K for 10–30 min, signal and color were destroyed irreversibly. Subsequent irradiation up to about 2×10^6 Gray could not reproduce the EPR signal and color for both types of amazonite.

The signal behavior after heating and irradiation can be well correlated with the behavior of the amazonite OA band at 630 nm (15873 cm^{-1}) in Figure 7. OA band, color, and EPR signal of [Pb-Pb]³⁺ show a similar annealing rate curve between 473 and 973 K (Fig. 6). Heat treatments between 723 and 973 K caused a simultaneous reduction and destruction of the OA band and EPR signal and, therefore, a decrease in intensity of the color or a decoloration of the amazonite crystal, respectively. The intensities of the Fe^{3+} spectra remained unchanged (Fig. 5); thus it is unlikely that Fe^{3+} (e.g., as $\text{Fe}^{3+}\text{-O-Pb}^{1+}$) is involved in the production of color, as proposed by Platonov et al. (1984) and Vokhmentsev et al. (1989). Subsequent irradiation restores about 30% of the initial

TABLE 1. Eigenvalues and direction cosines of \mathbf{g} and \mathbf{A} (10^{-4} T) tensors for the [Pb_A-Pb_B]³⁺ center in B- and T-type amazonite

Eigenvalues	Direction cosines		
	X	Y	Z
$g_{11} = 1.80$	0.29	-0.07	0.96
$g_{22} = 1.56$	0.31	0.95	0.03
$g_{33} = 1.36$	0.91	-0.31	-0.29
$A_{11}^{\text{A}} = 790$	0.49	-0.06	0.87
$A_{22}^{\text{A}} = 1575$	0.14	0.99	0.01
$A_{33}^{\text{A}} = 1730$	0.86	-0.23	-0.50
$A_{11}^{\text{B}} = 695$	-0.02	-0.26	0.97
$A_{22}^{\text{B}} = 1270$	0.19	0.95	0.26
$A_{33}^{\text{B}} = 1530$	-0.98	0.19	-0.03

Note: $\mathbf{X} \parallel \mathbf{a}$; $\mathbf{Y} \parallel \mathbf{b}^*$; $\mathbf{Z} \perp \mathbf{a}, \parallel (010)$. Experimental error for direction cosines $\pm 3^\circ$, g values $+0.03$, A values $\pm 10 \times 10^{-4}$ T, cf. text.

EPR signal and OA band, and therefore approximately 30% of the color. Heat treatment above 1073 K causes an irreversible loss of the OA band, EPR signal, and color of amazonite.

DISCUSSION

Pseudoaxial symmetry model of the hyperfine tensor

The Hamiltonian parameters of the [Pb-Pb]³⁺ center from Table 1 demonstrate a quasi-orthorhombic or lower local crystal-field symmetry around the defect. Because of the sizeable spin-orbit interaction, the relation of the EPR parameters in a crystal field of low symmetry is very complex. The postulation of a pseudoaxial symmetry for diatomic molecules as used by Schoemaker (1973) for p^1 ions and Heynderickx et al. (1987) for [Pb-Pb]³⁺ dimers can simplify the problem.

For diatomic radicals, the unpaired electron is in the antibonding orbital, which is a linear combination of $6s$ and $6p_z$ orbitals:

$$\psi = c_s(6s_A + 6s_B) + c_{pz}(6p_{zA} - 6p_{zB}) \quad (2a)$$

and

$$c_s^2 + c_{pz}^2 = 1. \quad (2b)$$

Following Schoemaker (1973) and Heynderickx et al. (1987) the hyperfine parameters A_{\parallel} and A_{\perp} ($A_{11} = A_{\parallel}$, $A_{22} + A_{33}/2 \approx A_{\perp}$) and the deviation Δg_{\parallel} and Δg_{\perp} ($g_{11} = g_{\parallel}$, $g_{22} + g_{33}/2 \approx g_{\perp}$) of the g value from the free-electron values can be related to each other in a crystal-field model including the spin-orbit interaction to second-order

$$A_{\parallel} = (1 - 1/2 \Delta g_{\parallel}) A_o + (2 + 3/2 \Delta g_{\perp} - 2 \Delta g_{\parallel}) \rho_s + 3/2 \Delta g_{\parallel} \rho_l \quad (3a)$$

$$A_{\perp} = (1 - 1/2 \Delta g_{\parallel}) A_o - (1 + 3/4 \Delta g_{\perp} + 1/4 \Delta g_{\parallel}) \rho_s - (5/2 \Delta g_{\perp} - 5/2 \Delta g_{\parallel}) \rho_l \quad (3b)$$

where $A_o = A_{\parallel}^{\text{I}} + A_{\parallel}^{\text{II}}$ is the isotopic hyperfine interaction, which is the sum of the positive Fermi contact term $A_{\parallel}^{\text{I}} = 8\pi/3 \cdot \mu_l/I \cdot c_{pz}^2 |\psi_s(0)|^2$ and a negative term from exchange polarization $A_{\parallel}^{\text{II}} = \mu_l/I \cdot c_{pz}^2 \langle r^{-3} \rangle$, and $\rho = \rho_s + \rho_l$ is

TABLE 2. Hamiltonian parameters (A and ρ in 10^{-3} T) and calculated spin density coefficients c_s^2 and c_{pz}^2 of the 6s and 6p orbitals of Pb-associated centers in different matrices

Matrix	Center	$\Delta g_{ }$	Δg_{\perp}	$A_{ }$	A_{\perp}	A_c	ρ	c_s^2	c_{pz}^2	$c_s^2 + c_{pz}^2$	Ref.
CaF ₂	Pb ¹⁺	0.30	0.81	245.5	166.3	238.6	13.0	0.08	0.56	0.64	a
SrF ₂	Pb ¹⁺	0.29	0.83	222.7	193.2	240.9	4.7	0.08	0.20	0.28	a
BaF ₂	Pb ¹⁺	0.37	0.96	218.5	240.5	280.7	-3.3	0.10	0.14	0.24	a
KCl	Pb ¹⁺	0.37	0.67	163.5	256.8	265.1	-17.5	0.09	0.75	0.84	b
RbCl	Pb ¹⁺	0.39	0.72	167.1	263.5	277.7	-17.4	0.10	0.75	0.85	b
NaCl	(Pb-Pb) ³⁺	0.37	0.67	125.0	120.0	148.9	0.9	0.10	0.08	0.18	c
SrF ₂	(Pb-Pb) ³⁺	0.29	0.60	169.3	116.6	161.8	10.2	0.12	0.88	1.00	a
KAlSi ₃ O ₈ *	[$\begin{smallmatrix} \text{Pb}_A\text{-B} \\ \text{A-Pb}_B \end{smallmatrix}$] ³⁺	0.20	0.55	84.0	136.5	126.0	-10.3	0.04	0.44	0.84	d
		0.20	0.55	115.0	152.0	150.9	-7.3	0.05	0.31		

Note: The ρ , c_s^2 , and c_{pz}^2 values were calculated using the A values of the original works and the corrected A and ρ values of the free Pb ion, according to Morton and Preston (1978); a = Fockele et al. (1989), b = Heynderickx et al. (1986a), c = Heynderickx et al. (1987), d = this work.

* Pb_A, Pb_B, A, and B describe the nuclei ²⁰⁷Pb_A, ²⁰⁷Pb_B, ^{even}Pb_A, and ^{even}Pb_B, respectively (cf. Fig. 3).

the anisotropic hyperfine interaction, including dipole-dipole interaction between the magnetic moments of the electron and nuclei $\rho_s = \frac{2}{5}\mu_1/I \cdot c_{pz}^2 \langle r^{-3} \rangle_s$ and interaction between the orbital moment of the electron and the nuclear moments $\rho_l = \frac{2}{5}\mu_1/I \cdot c_{pz}^2 \langle r^{-3} \rangle_l$. For many of the atomic and molecular systems, it has been found that $\rho_s = 1.13 \rho_l$ (Schoemaker, 1973).

In numerous works (Fockele et al., 1989; Goovaert et al., 1982, 1983; Heynderickx et al., 1986a, 1987) the signs of $A_{||}$ and A_{\perp} are assigned according to an imposed constraint of constant ρ_s for the different Pb¹⁺ (6p¹) defects, ρ_s possessing the same sign as that of the magnetic moment of the Pb nucleus and calculated values having opposite signs. However, for the calculated electron density based on $A_{||}$ and A_{\perp} with opposite signs for Pb-associated centers in various matrices, only the c_{pz}^2 coefficient from Equation 2 (i.e., the part of the p-electron density) will be $c_{pz}^2 > 3$. The angular dependence of the [Pb_A-Pb_B]³⁺ spectra in amazonite shows clearly that all $A_{||}$ components have the same sign. The angular dependencies for p¹ ions in different matrices given in several papers (Fockele et al., 1989; Heynderickx et al., 1987) also show that the signs of the $A_{||}$ components are the same. Comparison of Hamiltonian parameters and the calculated c_s^2 , c_{pz}^2 , and ρ values for [Pb_A-Pb_B]³⁺ centers in amazonite, and Pb-associated centers in various matrices are given in Table 2. The c_s^2 , c_{pz}^2 , and ρ values were calculated using the data of the original works and the corrected A_c and ρ values of 81500 and ($\% \times 1626$) \approx 650 MHz, respectively, of the free Pb ion, according to Morton and Preston (1978). Isolated Pb¹⁺ ions and [Pb-Pb]³⁺ dimers in several matrices showed a similar s-electron density near $c_s^2 = 0.1$; the p-electron density is predominant and about $c_{pz}^2 = 0.7$ -0.8; the total electron density is close to 1.

The small total electron density at the Pb nucleus in CaF₂, SrF₂, and BaF₂ can be explained by a progressive increase in the distance between the Pb nuclei and ligands in the sequence Ca²⁺ \rightarrow Sr²⁺ \rightarrow Ba²⁺. Thus, the unpaired p¹ electron is shifted to the ligands, and the total electron density at the Pb ion becomes less. In NaCl five distinct [Pb-Pb]³⁺ centers are present simultaneously (Heynderickx et al., 1987). The eigenvalues of the g tensor of these

centers do not coincide with Na-Na direction. These centers are very complex and elongated; therefore, only a part of the electron density can be found at the Pb nuclei.

Model of the [Pb-Pb]³⁺ color center

The EPR data of the [Pb-Pb]³⁺ center in amazonite indicates that the Pb²⁺ substitution is the result of process 1, K¹⁺ + Si⁴⁺ \rightarrow Pb²⁺ + Al³⁺, as proposed by Zhiron et al. (1959) and Zhiron and Stishov (1965). Generally it is assumed that in metrically triclinic microcline ordered and disordered domains are formed. The formation of short-range disordered domains is due to Al-O-Al clustering (violation of the principle of Loewenstein, 1954) and construction of O¹⁻/²⁷Al centers (Petrov et al., 1989a). Such an Al excess (i.e., Al:Si > 1:3) is expected to be associated with structural defects in their local environment that give rise to a deficiency of positive charge. This substitution may be charge compensated by bivalent cations at K positions, i.e., Pb²⁺. EPR data of the [Pb-Pb]³⁺ center indicate two nonequivalent Pb_A and Pb_B ions at adjacent M positions. In quasi-disordered domains of ordered feldspar and quasi-ordered domains in disordered feldspar with large M cations (M = K, Ba), e.g., microcline, sanidine, and hyalophane, more than 70% of the O¹⁻/²⁷Al centers are a_i centers; the remainder are d_o centers (Petrov, 1993). The symbols a_i and d_o designate O¹⁻ centers at Al and D(O) positions between T₁₀ and T_{1m} and T₁ and T₂ tetrahedral positions, respectively (Petrov et al., 1989a).

Comparison of direction cosines and eigenvectors of the g and A tensors with those of the K-K direction in the microcline structure shows that the eigenvector with the largest value, A_{33}^{\wedge} , is approximately parallel to the K-K direction, that A_{33}^{\wedge} has a deviation of about 25°, and that the eigenvector with the largest deviation from the value of the free electron g_{33} deviates by about 18° from the K-K direction (Table 1, Fig. 4).

The line width ΔB_{pp} of HF doublets of the ²⁰⁷Pb_B nucleus is 1.3 times larger than those of the ²⁰⁷Pb_A nucleus. The ΔB_{pp} value is nearly independent of temperature between 5 and 250 K, within experimental error. This indicates that the lifetime of the excited state does not in-

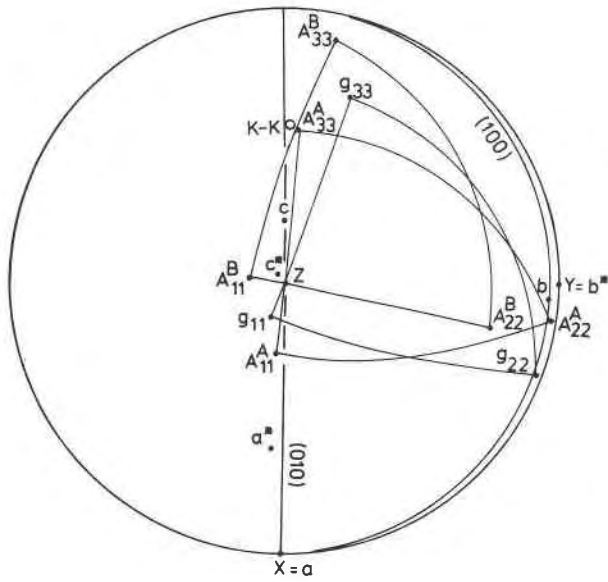


Fig. 4. Stereographic projection of the g and A eigenvectors of $[\text{Pb}_A\text{-Pb}_B]^{3+}$ center in amazonite.

fluence the line width ΔB_{pp} . The large line width of the $^{207}\text{Pb}_B$ HF doublet must be due to other phenomena, most probably to disorder in the Al,Si occupancy of adjacent tetrahedra (e.g., Petrov and Hafner, 1988; Petrov et al., 1989a, 1989b). This suggests that the Pb^{2+} ion B replaces the more disordered K site with adjacent Al at T_1O and T_1m positions. Thus, only the Pb_B ion is charge compensated by Al,Si exchange at adjacent T_1m positions. If the second Pb_A ion is also compensated, this section of the structure is charge neutral overall, and no stable $[\text{Pb-Pb}]^{3+}$ dimeric centers can arise by capture of one electron.

The HF spectrum of the $[\text{Pb-Pb}]^{3+}$ center could be observed only at temperatures lower than 250 K. At room temperature, the thermal exchange of the $6p^1$ electron between two Pb ions A and B apparently occurs so rapidly that, according to the Schrödinger uncertainty principle, only about 3% of the broadened central line can be seen in the EPR spectra. At 40 K, the calculated $6p^1$ electron density at the Pb_A atom is about 30% higher than those at the Pb_B atom (Table 2). In all 42 investigated crystals of different color and localities only centers at Pb-Pb pairs are present, but not at isolated Pb ions. In Pb^{2+} -doped KCl with a K-K distance of 4.6 Å, only isolated Pb^{1+} could be detected (Goovaerts et al., 1983; Heynderickx et al., 1986a). In NaCl doped with Pb^{2+} , only Pb^{1+} - Pb^{2+} dimers at adjacent Na positions (Na-Na distance 4 Å) could be detected (Heynderickx et al., 1987), but no isolated Pb^{1+} ions. The K-K distance in amazonite is very similar (3.9 Å) and, analogous to the alkali halides, only Pb-Pb dimers are expected.

Fockele et al. (1989) studied the OA properties of CaF_2 , SrF_2 , and BaF_2 using optical detection of electron spin resonance (ODESR) and optical detection of electron nuclear double resonance (ODENDOR). They demonstrated a direct association of the EPR spectrum of Pb^{1+} and the OA absorption band in the range of 630–660 nm and

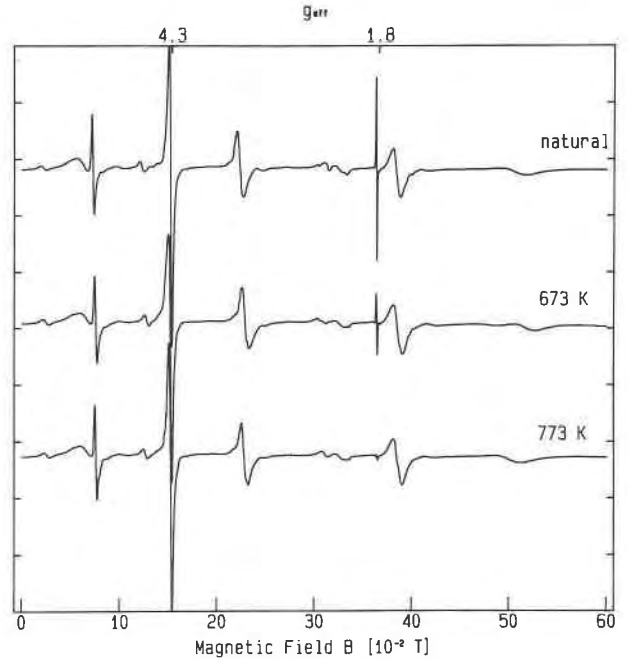


Fig. 5. EPR spectra of the $[\text{Pb-Pb}]^{3+}$ center in natural amazonite and T-type amazonite heat treated at various temperatures. Rotation $+\mathbf{b}^* \parallel \mathbf{Z}^0$, $+\mathbf{c}^* \parallel \mathbf{X}^0$, $\Theta = 125^\circ$, $\nu = 9.2394$ GHz, $T = 40$ K. The intensity of the ^{207}Pb - ^{207}Pb central line decreases with increasing temperature of annealing; the intensities of the five fine structure lines of Fe^{3+} remained unchanged.

noted that the optical properties of the $[\text{Pb-Pb}]^{3+}$ dimeric centers are similar to those of the Pb^{1+} center.

Using magnetic circular dichroism (MCD) tagged by EPR, Ahlers et al. (1985) investigated in Tl^{1+} -doped KCl, RbCl, and KBr the isoelectronic $6p^1$ centers Tl^0 and Tl^{1+} - Tl^0 , with visible OA in the same range. In KCl the OA band of Tl^0 is centered at 630 nm. The optical absorption and emission properties of the Tl^{1+} - Tl^0 center are also very similar to those of the Tl^0 defect. Therefore it was suggested that the unpaired electron, which is mainly in a $6p_z$ orbital along the line connecting the Tl^{1+} ion and the anion vacancy, hops (or tunnels) between two Tl^0 -like configurations. Motional averaging yields the experimental EPR eigenvalues of the g and A tensor components. The overlap of $6p$ and $6s$ electron wave functions of the Tl^0 and Tl^{1+} ions, respectively, is reflected in a tilting of the $6p$ orbital with respect to the $[100]$ axis of 12.1° in KCl and 13.6° in RbCl. In the OA data, there is no motional averaging, as shown by the strong similarity to the properties of the Tl^0 and Tl^{1+} - Tl^0 transitions. These observations are directly connected with the jump (or tunneling) frequency of the unpaired electron, which is fast compared with the EPR microwave frequency and slow compared with the optical frequencies.

The similar annealing behavior of the EPR spectra and OA of amazonite indicates that the band at 630 nm (15873 cm^{-1}) may be assigned to $[\text{Pb-Pb}]^{3+}$ centers. Heating at 543 K for ≥ 10 h caused Pb diffusion, and about 70% of the Pb pairs were destroyed. This caused loss of the EPR

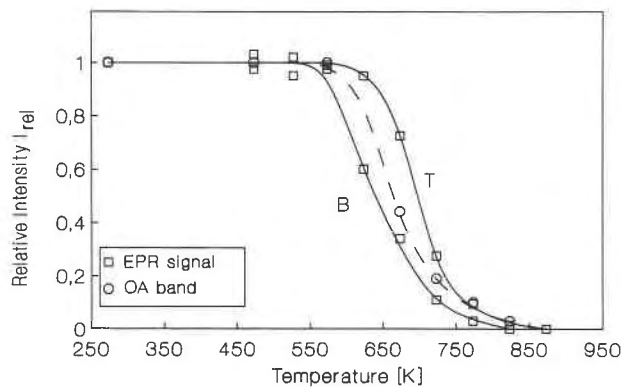


Fig. 6. Relative intensity of the central evenPb-evenPb line vs. temperature of annealing with constant heating time of 10 min. The EPR line intensities (error: $\pm 5\%$) of both types of amazonite B and T and the intensity of the OA band from Fig. 7 are normalized to 1.

signal, the OA band at 630 nm, and the amazonite color. The same effect appears during short heating times, between 0.17 and 10 h, for high temperatures (673–973 K). Heating above 1073 K causes diffusion of the remaining Pb (30%), and the EPR spectrum, OA band, and color are lost irreversibly.

The calculated activation energies for type B and T amazonite in the temperature range of 573–773 K are 12 (light blue), 14.5 (blue), and 21 kcal/mol (green). These values correspond to the activation energies for Pb diffusion in various matrices. The activation energy for Pb diffusion in the temperature range between 550 and 750 K in KBr is about 10.6, in KCl 12.9, and in AgBr 18 kcal/mol. The Pb self-diffusion in PbSe is 12.5, and in PbTe it is 13.8 kcal/mol (e.g., Haufler and Seyferth, 1966).

Hofmeister and Rossman (1985a) modeled the production of color in amazonite. They suggested that Pb³⁺ is the cause of the OA band at 630 nm rather than Pb¹⁺, and it is the cause therefore of the amazonite color, and that for samples with constant Pb content the intensity of color is linearly related to the content of structurally bound H₂O. The Pb:H₂O ratio in the color centers is 1:1, and much of the structural H₂O is coupled with Pb by the substitution Pb²⁺ + H₂O → K¹⁺. The authors supposed that γ irradiation disassociates H₂O molecules, forming H⁰ and OH⁰. The atomic H diffuses and the stationary component oxidizes a neighboring O atom, forming OH⁻ and an O¹⁻ hole center. The hole is delocalized at O¹⁻ and the adjacent Pb²⁺, producing Pb³⁺ and thus the color. On the other hand, the same mechanism was proposed for inhibiting of radiation-induced smoky coloration of feldspar by destruction of the O¹⁻ centers, e.g., by attaching H⁰-forming (Al,Si)-OH and releasing a hole (Hofmeister and Rossman, 1985b).

However, Pb³⁺ has electron configuration 6s¹, the g value should be very close to the value of the free electron $g_e = 2.0023$, and the HF interaction should be isotropic, or with a very small anisotropic part (e.g., Born et al., 1971, 1974). The strong anisotropic g and A values in Table 1 are typical of a p¹ ion. Furthermore, no H⁰ signals

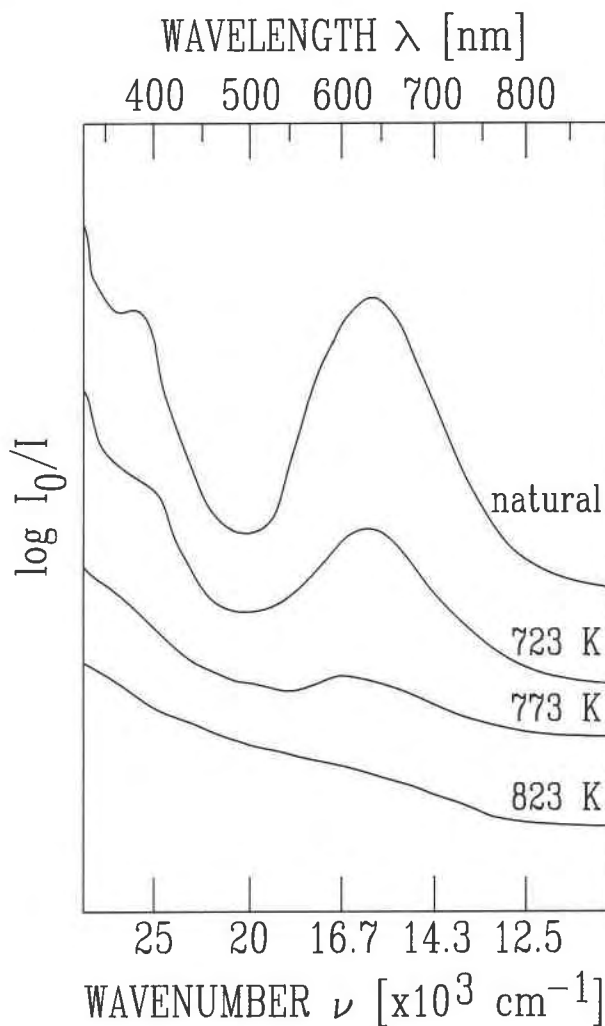


Fig. 7. Polarized OA spectra of natural and T-type amazonite heat treated at various temperatures. $E \parallel Z$, $Z \wedge b = 18^\circ$, $T = 295$ K. The spectrum labeled as natural was from a crystal heated at 573 K to destroy the O¹⁻ centers; the intensity of the amazonite band remained unchanged, cf. Fig. 6.

could be detected in EPR spectra of amazonite after irradiation at low temperature. After irradiation, spectra of atomic H ($I = 1/2$, 100% natural abundance of ¹H) with A values in the range of 1408–1460 MHz were observed in quartz (Weeks and Abraham, 1965; Petrov et al., 1990), beryl, enstatite, clinohumite (Bershov, 1970; Andersson, 1974; Edgar and Vance, 1977), and tourmaline (Bershov et al., 1968; cf. also Petrov, 1990). In beryl the formation of H⁰ centers can be strongly correlated with the dissociation of H₂O molecules in the channels. In EPR spectra of feldspar with CH₄ radicals at K sites, the formation of CH₃ after γ irradiation and the diffusion of the protons are clearly indicated. Two protons diffuse to a nearby Fe³⁺O₄ tetrahedral complex, creating Fe³⁺O₂(OH)₂. Consequently, the Fe³⁺ spectrum is additionally split ($A \approx 78$ MHz) because of HFI, with the two protons giving triplets with intensity ratios of the individual components of 1:2:1. However, in the spectra of [Pb-Pb]³⁺ centers in

amazonite and of O¹⁻/2²⁷Al and O¹⁻/[Si,M²⁺] centers in feldspars with radiation-induced smoky color, no additional HF splitting due to OH groups or spectra of H⁰ could be observed at low temperatures up to 5 K (Petrov, 1993). In Fe-rich ferriferrous orthoclase from Madagascar and adularia from the Hybin pegmatite with Fe₂O₃ contents of 1–3 wt% (FeO up to 0.25 wt%), after irradiation only O¹⁻/[Si,M²⁺] but no O¹⁻/2²⁷Al centers and no smoky color is formed. The deficiency of positive charges in the “forbidden” Al-O-Al fragments (violations of the principle of Loewenstein) may be compensated by the substitution of Fe²⁺ for K⁺, i.e., K¹⁺ + Si⁴⁺ → Fe²⁺ + Al³⁺, similar to the case of amazonite. Thus, no stable O¹⁻/2²⁷Al centers and, therefore, no smoky color can be induced by irradiation.

Moreover, structurally bonded H₂O is stable in the temperature range in which the OA band at 630 nm and the color of amazonite were lost. Chakraborty and Lehmann (1977) studied the IR absorption of OH in synthetic quartz and found that heating the crystals at 523 and 823 K for 120 and 24 h, respectively, does not destroy the OH band. In the IR spectrum of Eifel sanidine, Beran (1986) attributed the two OH bands at 3400 and 3050 cm⁻¹ (with NIR combination band of molecular H₂O at 5150 cm⁻¹) to two types of structurally bonded H₂O. Heating the crystal at 973 K for 3 d does not destroy both bands. Further heating up to 1173 K for 4 d reduces the intensity of both bands to one-half of their initial intensity. The bands are unobservable after heating at 1323 K for 3 d.

The [Pb-Pb]³⁺ dimeric complex seems to be one of the last products of the structural evolution of amazonite. Its formation is due to a complicated postcrystallization process, beginning with the metasomatic transformation of potassium feldspar. In this phase, the precursors of the complex were formed. The subsequent chemical evolution of the structure is caused by radiation-stimulated diffusion, deperthitization, ion exchange, and other processes. Vokhmentsev et al. (1989) reported an increasing content of radioactive elements (U, Th, Rb) in amazonite in relation to the paragenesis of amazonite with U and Th minerals. The maximum center concentration was detected in the oldest Precambrian pegmatite of Keivy (Kola Peninsula). It forms by constant exposure to natural radiation over time on the order of billions of years. This causes the high concentration and the thermal and radiation stability of the [Pb-Pb]³⁺ center in the structure.

The name “amazonite”

For more than a hundred years “amazonite” has been the name of blue to green, triclinic, ordered microcline. Several authors (Rudenko and Vokhmentsev, 1969; Cech et al., 1971; Hofmeister and Rossman, 1983, 1985a, 1986) proposed the extension of this name to all similarly colored feldspars. However, the results of this study imply that [Pb-Pb]³⁺ pairs cause the color and are characteristic of amazonite-type microcline.

The OA band at 630 nm and the blue-to-green color of amazonite is caused by [Pb-Pb]³⁺ color centers. In all

studied crystals of green orthoclase from the Hibyn pegmatite, no signals of [Pb-Pb]³⁺, ²⁰⁷Pb¹⁺, or even Pb¹⁺ could be detected. Hofmeister and Rossman (1985a, 1986) also could not detect EPR spectra of Pb-associated centers, neither in green orthoclase from Broken Hill nor in pale blue albite and oligoclase from different localities. The bands at about 730 and 630 nm in orthoclase and plagioclase, respectively, and the color were destroyed after heating at about 573 K (Hofmeister and Rossman, 1983, 1985a, 1986). However, the color and the OA band at 630 nm in amazonite were lost at 723–773 K. This indicates a different origin of color in orthoclase and plagioclase, apparently caused by distinct O¹⁻ centers. For instance, the blue topaz color is caused by a similar broad OA band centered at about 650 nm assigned to O¹⁻ centers (Petrov, 1977, 1983, 1993). In albite with a Pb content of about 20 ppm and in oligoclase with a Pb content of about 350 ppm, the possibility for formation of Pb-Pb pairs is very small. In B- and T-type amazonite, with about 700–1000 and about 1800–2000 ppm, respectively, the ratio of Pb content to the intensity of the [Pb-Pb]³⁺ EPR signal is about 1:2. The Pb ions are distributed among the K sites in the feldspar structure, and the probability of pair formation in feldspar with a Pb content of about 20–350 ppm is much smaller. But the primary assumption for center formation is a high degree of Al,Si order in the structure. Stable [Pb-Pb]³⁺ centers can be formed only in ordered feldspar and only if one of the Pb²⁺ ions is charge compensated by Al,Si exchange at adjacent tetrahedral positions. If the second Pb²⁺ ion is also compensated, the [Pb-Pb]³⁺ center is not stable. In the case of a relatively high degree of disorder of Al and Si over the four nonequivalent tetrahedral positions, the overall charge balance of the structure is preserved; thus no stable centers can be formed. For example, in orthoclase from Broken Hill with PbO of 11900 ppm (Cech et al., 1971), no [Pb-Pb]³⁺ centers could be detected (Hofmeister and Rossman, 1985a).

If by correlated EPR and OA measurements, amazonite-type [Pb-Pb]³⁺ centers can be detected in feldspars other than the classical ordered amazonite, the name “amazonite” loses its meaning.

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