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EPR SPECTRA OF TRIVALENT IRON IN VESUVIANITE

Abstract. EPR spectra of Fe^{3+} ions in vesuvianite from several localities have been reported and described. The spectra appeared effective discriminant of low and high temperature vesuvianite. Upon thermal treatment of low vesuvianite its EPR spectrum is transformed into typical of high vesuvianite. Possible location of part of Fe^{3+} ions in $\text{B} = \text{Y}(1)$ sites on 4-fold axis was discussed.

Key-words: vesuvianite (low, high), EPR spectra, site population, Fe^{3+} ions.

INTRODUCTION

Allen and Burnham (1992) have distinguished two types of vesuvianite: the so-called low vesuvianite occurring in rodingites, rocks formed at lower temperatures ($\leq 300^\circ\text{C}$), and that occurring in calc-silicate rocks formed at relatively high temperatures ($400\text{--}800^\circ\text{C}$) and named high vesuvianites. The discrimination between high- and low vesuvianite was based on the ordering of its crystal structure.

The crystal structure and symmetry of vesuvianite has been determined by Coda et al. (1970), Rucklidge et al. (1975), Yoshiasa and Matsumoto (1986), Allen and Burnham (1992), Groat et al. (1992, 1993), Ohkawa et al. (1992, 1994) and others using X-ray and, more recently, also electron diffraction. In the vesuvianite crystal lattice there are two octahedral non-equivalent positions labelled $\text{A} = \text{Y}(2)$ and $\text{AlFe} = \text{Y}(3)$, a 5-coordinate square pyramide site $\text{B} = \text{Y}(1)$ and an 8-coordinate square anti-prism site $\text{C} = \text{X}(4)$ (see Groat et al. 1992) where transition metal ions can be distributed. The arrangement of cations in partly filled B and C sites lying on 4-fold axes was the main basis of discrimination by Allen and Burnham (1992) between high- and low vesuvianite. The former contains a long-range

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disordered structure of P4/nnc average symmetry while for latter ordered domains of lower than P4/nnc symmetry are characteristic.

The question of the localization of transition metal ions in the vesuvianite structure is still the subject of discussion. Most of experimental work concerned the site occupation of iron and used the Mössbauer and optical spectroscopy (Manning 1968, 1976; Manning, Tricker 1975; Cao, Zhu 1990) and only few reports on EPR studies of transition metal ions in vesuvianite can be found in the literature (Rager et al. 1984; Dyrek et al. 1992).

The distribution of iron between the vesuvianite lattice sites still remains ambiguous. The aim of this paper was to check what kind of information of the location of Fe³⁺ on different sites of vesuvianite crystal structure may be obtained by means of EPR spectroscopy.

EXPERIMENTAL

Investigated vesuvianite samples are listen in Table 1. They represent different geological origin and differ in total iron content and the Fe³⁺/Fe²⁺ ratio. All the samples come from the Mineralogical Museum of the Academy of Mining and Metallurgy in Cracow, Poland.

The chemical composition was determined by means of wet method (total iron content), Mössbauer spectroscopy (Fe³⁺/Fe²⁺ ratio) and semi-quantitative spectral analysis (determination of subordinate elements). The results of analysis and colour of the samples are given in Table 1. The blue colour of vesuvianite from

TABLE 1

Vesuvianite samples

Specimen locality	Colour	Fe ₂ O ₃ (total wt.%)	Fe ²⁺ (% of total Fe content)*	Some subordinate elements (wt.%)		
				1.0—0.1	0.1—0.01	0.01
RODINGITE—LIKE ROCKS						
Piz Longhing, Switzerland	creamy-white	1.80	n.d.	B	Mn, Ti	V, Ni, Cu
Ala, Italy	green	4.50	—	Mn	Ti, Cu, B	V, Cr, Ni
Hindubagh, Pakistan	green	5.09	—	B	Ti, Mn	Co, Ni, Cu
Transvaal, S. Africa	green	3.20	7	Cr	Be, Ti, Mn, Cu, B	V, Ni
METAMORPHIC CALC-SILICATE ROCKS						
Monzoni, Italy	brown	5.10	15	Mn, B	Be, Ti, Cu	V
Canzoccoli, Italy	brown	4.46	14	Mn, B	Ti	V, Ni, Cu
Cziklova, Rumania	yellow	2.80	13	Mn	Ti, B	V, Ni, Cu
Telemark, Norway	blue	1.34	12	Mn, Cu	Be,Ti, B	V, Ni

* According to Mössbauer investigations.

n.d. = not detectable.

Telemark is due to copper content. The colour of remaining samples, in which low amounts of Mn and Ti and only traces of some other transition elements have been detected, is mainly determined by total concentration of iron and Fe³⁺/Fe²⁺ ratio (Manning, Tricker 1975). In green, low-Ti vesuvianite, iron is present almost exclusively as trivalent, while the yellow and brown specimens contain also significant quantities of divalent Fe.

EPR spectra of powder samples were recorded at 77 and 290 K using an ESR 220 spectrometer operating at X-band with 100 kHz modulation. DPPH was used as g factor standard and NMR MJ-111 teslameter was used for magnetic field calibration. The effective g values were determined directly from the spectra, from resonance formula $g_{eff} = hv/\beta B$. Relative amplitude (peak-to-peak high ratio) of the component signals in a complex EPR spectrum was used to distinguish, qualitatively, different types of spectra. Simulation of EPR spectra was performed using a subroutine published by Nettar and Villafranca (1985).

Mössbauer investigations were performed in the Institute of Nuclear Physics in Cracow.

RESULTS AND DISCUSSION

The EPR spectra of eight investigated vesuvianite samples are shown in Figs 1 and 3. The collation of the spectra revealed two distinct groups labelled hereafter as group I and group II.

The group I contains the samples from Piz Longhin, Ala, Hindubagh and Transvaal in which iron exists almost exclusively in the trivalent state (see also Manning, Tricker 1975). The spectra of this group are relatively simple and are characterized by only two components around $g_{eff} = 6$ and $g_{eff} = 2$, the amplitude of the low field line being much greater (Fig. 1). Such spectra are characteristic of Fe³⁺ in axial symmetry and can be described in terms of spin Hamiltonian \hat{H} with $S = 5/2$ and high spin configuration of ferric ion:

$$\hat{H} = g\beta BS + D \left[S_z^2 - 1/3S(S + 1) \right] + E \left(S_x^2 - S_y^2 \right) \tag{1}$$

when $E = 0$ and $D \gg g\beta B$ (Castner et al., 1960). I such a case the crystal field splits the ground ⁶S state of Fe³⁺ into three Kramers doublets, and providing that separation between them is greater than ca. 1.0 cm⁻¹, the lowest lying $| \pm 1/2 \rangle$ doublet, that alone is populated, gives rise to a signal with two components of $g_{eff} = 6$ and $g_{eff} = 2$ (Menil et al. 1979).

In the vesuvianite crystal lattice sites of the appropriate symmetry that could give rise to the observed signal, if occupied by Fe³⁺ ions, are those located along the fourfold axis, i.e., sites B of the square pyramid symmetry and square anti-prism sites C. Mössbauer data (Kraczka, private communication) indicate, that amount of iron in position C (with unusual for Fe³⁺ 8-fold coordination) is

below limit of detection while occupations of sites B can be considered. The location of Fe^{3+} in B sites seems to be probable also on the basis of stoichiometric arguments (vide infra). The localization of the trivalent iron in lattice positions B was proposed by Rucklidge et al. (1975) and Ohkawa et al. (1992) on the basis of X-ray and optical spectra. However, other authors prefer to locate trivalent iron in the AlFe octahedra (Manning, Tricker 1975; Yoshiasa, Matsumoto 1986).

Assuming the CMASH formula $\text{Ca}_{19}\text{MgAl}_{12}\text{Si}_{18}\text{O}_{70}(\text{OH})_8$ of vesuvianite (Allen, Burnham 1992), in which magnesium was completely replaced by iron in B positions, stoichiometric calculations show that the maximal iron content in sites B corresponds to 2.8% Fe_2O_3 . From the all investigated samples belonging to the group I only that from Piz Longhin has the total iron content below this upper limit (1.80% Fe_2O_3). Therefore, only in the case of that sample, the site B could host all trivalent iron. Taking into account the distinctly axial character of the iron EPR signal and sufficient capacity of the site B, we tent to locate trivalent iron of Piz Longhin vesuvianite in this position. On the contrary, for the remaining samples from group I, stoichiometric arguments reveal that at least two different sites for iron location are necessary.

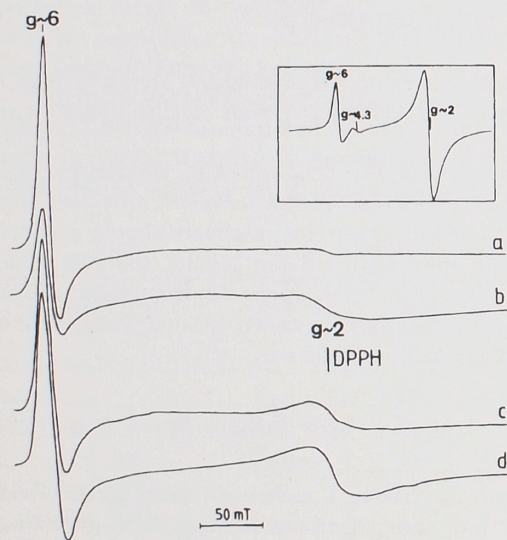


Fig. 1. EPR spectra of low-temperature vesuvianite. In inset EPR spectrum of 1d sample after heating for 20 hrs at 800°C is presented. In parentheses total iron content as Fe_2O_3 wt.% is given
a — Piz Longhin, Switzerland (1.80); b — Ala, Italy (4.50); c — Hindubagh, Pakistan (5.09); d — Transvaal, S. Africa (3.20)

Indeed, measurements at different temperatures have shown that in the case of Piz Longhin sample both components have the same relaxation characteristics. Moreover, for $D \geq 1 \text{ cm}^{-1}$ the theoretical ratio of amplitudes of both components at $g = 6$ and $g = 2$, obtained via simulation amounts to 43 which is closed to the value derived from the experimental spectrum equal to 46.

Comparison of amplitudes ratio of the lines at $g\sim 6$ and $g\sim 2$ of Fe^{3+} signals of low iron Piz Longhin sample with remaining samples belonging to the group I (Fig. 1) shows that in the case of iron rich vesuvianite a considerable increase of absorption in the region of $g\sim 2$ occurs. Registration of spectra at 77 K revealed for those samples that amplitude of the signal at $g\sim 6$ increased while that of the signal

at $g\sim 2$ decreased and broadened (Fig. 2). The ratio of amplitudes of both components is lower in this case that obtained from simulation. It indicates the presence of an additional signal overlapping with the Fe^{3+} axial spectrum. This signal may correspond to Fe^{3+} in octahedral/tetrahedral coordination provided that zero field splitting (ZFS) is small (Evmiridis 1986), or to antiferromagnetically coupled $\text{Fe}^{3+}\text{--O--Fe}^{2+}$, or $\text{Fe}^{3+}\text{--O--Fe}^{3+}$ clusters found by Narducci et al. (1989) in iron containing glasses. Such clusters are often encountered in glass extra-framework positions. Broadening of the signal around $g\sim 2$ at 77 K (Fig. 2) suggests the antiferro/ferromagnetic nature of the interactions between the iron centres responsible for this signal. However, the unambiguous attribution of the broad line at $g\sim 2$ to the possible iron location sites in the vesuvianite lattice is not straightforward at present, and this is the subject of further investigations.

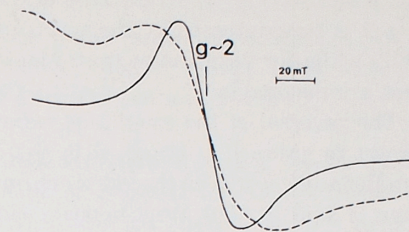


Fig. 2. EPR signal of vesuvianite from Ala ($g\sim 2$ region) registered at room temperature (solid line) and 77 K (dashed line). Similar temperature dependence is observed for vesuvianite from Hindubagh and Transvaal

Summarizing, we can state that the presence of dominant axial signal with two components at $g\sim 6$ and $g\sim 2$ and, in the case of samples of higher Fe content, also additional weaker broad line at $g\sim 2$, are characteristic features of vesuvianite belonging to the group I, i.e., to the so-called low vesuvianite.

To the second group of the more complicated spectra belong vesuvianite samples from Monzoni, Canzoccoli, Cziklova and Telemark, containing in addition to trivalent iron also appreciable amount of divalent Fe, as revealed by Mössbauer spectroscopy (Table 1). In addition to the already discussed signal at $g_{\text{eff}} = 6$ and $g_{\text{eff}} = 2$ the bands at $g_{\text{eff}} \sim 4.3$ and dominant broad line at $g\sim 2$ were

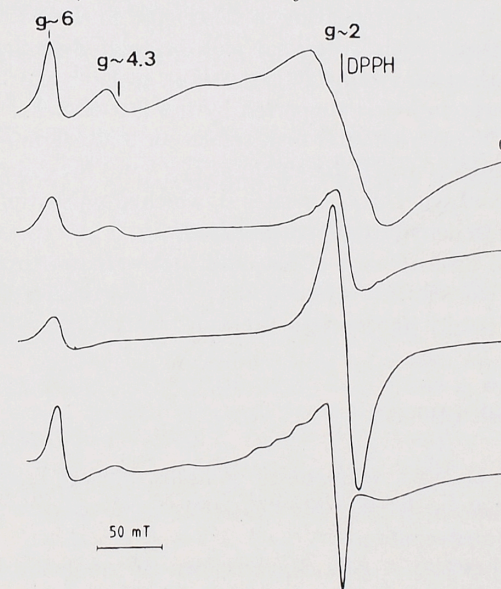


Fig. 3. EPR spectra of high-temperature vesuvianite. In parentheses total iron content as Fe_2O_3 wt.% is given
a — Monzoni, Italy (5.10); b — Canzoccoli, Italy (4.46); c — Cziklova, Rumania (2.80); d — Telemark, Norway (1.34)

also observed (Fig. 3). In the case of the sample from Telemark (Fig. 3d) the signal at $g \sim 2$ is superimposed by the spectrum of Cu^{2+} located in B position (Dyrek et al. 1992) while for vesuvianite from Monzoni and Canzoccoli the traces of Mn^{2+} EPR lines are detectable.

The reversal of the amplitude ratio of lines at $g_{\text{eff}} = 6$ and that of $g_{\text{eff}} = 2$, in respect to group I, is observed in the case of all samples. The former line is now significantly lower than the latter one, in contrast to the case of the group I vesuvianite (Figs. 1 and 3). The peak-to-peak width of the line at $g \sim 2$ exhibits remarkable variability depending on the kind of vesuvianite and is broadened when measured at liquid nitrogen temperature (77 K). The width of that line seems to be somehow correlated with the intensity of new appearing signal at $g \sim 4.3$. The mutual relation between these both signals was also revealed by heating experiment. Upon thermal treatment of the sample from Transvaal (belonging to the group I) at 800°C for 20 h, dramatic changes in the EPR spectrum was observed (inset in Fig. 1). The signal at $g \sim 4.3$ appeared and the amplitude of the signal at $g \sim 2$ significantly increased so that the amplitude ratio of the lines at $g \sim 6$ and $g \sim 2$ reversed. Therefore, the spectrum became typical of group II vesuvianite.

The signal at $g_{\text{eff}} \sim 4.3$ corresponds to isolated Fe^{3+} in cubic coordination of strong rhombic distortion with the ratio of zero field splitting parameters of the spin Hamiltonian (Eq.1) $E/D \sim 1/3$ (Menil et al. 1979). Appearing of this signal in the EPR spectrum of thermally treated vesuvianite from Transvaal may be related to the oxidation of Fe^{2+} , occupying sites of rhombic symmetry (e.g. AlFe), to Fe^{3+} which make them visible in EPR. Such interpretation is supported by the fact that Fe^{2+} quadrupol disappears in the Mössbauer spectrum after heat treatment of the Transvaal sample (Kraczka, private communication). To the signal at $g_{\text{eff}} \sim 4.3$ may also contribute Fe^{3+} in sites of previously axial symmetry (e.g. sites B) which after heating could undergo rhombic distortion due to dehydroxylation processes.

The EPR spectra appear effective discriminant of low and high temperature vesuvianite. Moreover, the heating experiment revealed that transformation of low to high vesuvianite can be induced by appropriate thermal treatment.

CONCLUSION

Comparison of the EPR spectra of eight vesuvianite samples coming from various localities revealed that they can be divided into two groups corresponding to low (group I) and high (group II) vesuvianite.

The strong $g \sim 6$ line and the weaker one at $g \sim 2$, characteristic of the group I vesuvianite, are components of an axial signal attributed to Fe^{3+} ions occupying sites B on 4-fold axis of vesuvianite. In the case of group II, the line at $g \sim 2$ dominates the spectrum and additionally a weak signal at $g \sim 4.3$ appears. The latter signal is characteristic of Fe^{3+} ions in rhombically distorted octahedral symmetry, e.g., Fe^{3+} ions in $\text{AlFe} = \text{Y}(3)$ sites. The antiferro/ferromagnetically coupled Fe ions were also found but their location in the vesuvianite structure

is not yet clear.

It was shown that upon heating of the low temperature vesuvianite it can be transformed into high temperature vesuvianite. Similar effects were observed recently by means of IR spectroscopy (Żabiński, Paluszkiwicz 1994).

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WIDMA EPR Fe^{3+} W WEZUWIANIE

Streszczenie

Zarejestrowano i opisano widma jonów Fe^{3+} w próbkach wezuwianu pochodzących z kilku miejsc występowania tego minerału (Tab. 1). Widma te są wyraźnie odmienne dla wysoko- i niskotemperaturowej modyfikacji strukturalnej wezuwianu (Rys. 1—3). Po wygrzaniu wezuwianu niskotemperaturowego jego widmo stało się typowe dla odmiany wysokotemperaturowej (Rys. 1). Podano argumenty przemawiające za występowaniem części jonów Fe^{3+} na tzw. pozycji sieciowej B = Y(1) leżącej na czterokrotnej osi symetrii.