

EPR of vanadyl ion in a natural mineral, apophyllite

GEETHA RAMAKRISHNAN, M B V L N SWAMY,
P SAMBASIVA RAO and S SUBRAMANIAN*

Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras
600036, India

MS received 28 November 1990; revised 5 April 1991

Abstract. Single crystal EPR spectra of a natural mineral, apophyllite, containing VO(II) ion as an impurity have been investigated. The EPR spectra of the mineral, as obtained, was complex in nature, but was simplified by annealing the crystals at 490 K. The EPR parameters of the VO(II) species in the annealed crystal, $g_{\parallel} = 1.924$ (2); $g_{\perp} = 1.983$ (2); $A_{\parallel} = 18.35$ (5); and $A_{\perp} = 7.24$ (5) mT, are very close to a typical VO(II) impurity. Theoretically calculated line positions, using second-order hyperfine terms in the spin Hamiltonian with an axially symmetric g and A tensor values, agreed very well with the experimental ones. The EPR analysis of the annealed crystal has further revealed that the most preferred location of the VO(II) impurity is a substitutional Ca(II) site. The calculated bonding parameters and admixture coefficients indicate a fair amount of covalent bonding in the complex.

Keywords. EPR; apophyllite; vanadyl; bonding parameters; annealing.

1. Introduction

Unaggregate and uncemented deposits of mineral and organic particles or fragments cover large portions of the earth's crust. The minerals are formed by various combinations of the basic elements oxygen, hydrogen, silicon, aluminium, potassium, calcium, iron etc., in regular crystalline arrangements. The clay minerals are produced by the recrystallization and recombination of the original rock-forming minerals in solution (Scott and Schouster 1968).

Vanadyl ion with $3d^1$ configuration allows paramagnetic resonance to be observed at ambient temperature; hence many studies have been reported (Kohin 1979). All the results reported for the vanadyl ion in the literature can be classified into two groups: fixed orientations if it is surrounded by water or sulphate ligands or random orientation as in most ionic lattices (Viswanath 1977). The EPR study of vanadyl ions in minerals have been reported for synthetic corundum, rutile, perclase, titanite (Vassilikov-Dova and Lehmann 1988a), blue zoisite (Tsang and Ghose 1971) etc. Previous studies in apophyllite, $KFCa_4Si_8O_{20} \cdot 8H_2O$ (Bershov and Marfunin 1965; Vassilikov and Lehmann 1988b), have indicated that the impurity exhibits two chemically distinct centres where V(IV) occupies the cation K^+ and Ca^{++} sites in the mineral. The authors also discussed the superhyperfine interactions due to F or

* For correspondence

OH (replacing F) ions. However, these studies have not removed all doubt about the impurity location (K or Ca) on the source of the mineral. In addition, the effect of annealing on the EPR spectra has not yet been studied. Hence, to gain further insight into the natural doping of impurities in apophyllite, we have procured several samples (source: Department of Geology, Indian Institute of Technology, Madras). The interesting observation of VO(II) paramagnetic impurity in apophyllite is discussed in the present paper.

2. Experimental

The mineral sample was quarried from Bihar mines. The external forms of the mineral displayed holohedral tetragonal symmetry. The crystals were clear and free from apparent solid or liquid inclusions. The morphology of the crystal was determined in an Enraf-Nonius CAD-4 X-ray diffractometer. The crystal showed perfect basal cleavage. Greenish semi-transparent crystals were found to have the following unit cell dimensions $a = b = 8.96 \text{ \AA}$; $c = 15.76 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$ and the space group for the crystal was $P_{4/nmc}$. The unit cell dimensions classify the mineral to be potassium calcium silicate fluoride hydrate or apophyllite with the chemical formula $\text{KF} \cdot \text{Ca}_4\text{Si}_8\text{O}_{20} \cdot 8\text{H}_2\text{O}$ (mineral index no. 19–82).

All the EPR spectra presented in this paper were recorded at room temperature on a Varian E-112 EPR spectrometer operating at X-band frequency of approximately 9.5 GHz with 100 kHz field modulation and phase sensitive detection to obtain the first derivative signal. DPPH was used as an internal field marker ($g = 2.0036$).

3. Structure of apophyllite

If three oxygen atoms of each SiO_4 are shared with other tetrahedra, six-membered ring sheets characteristic of mica or a puckered form found in gillespite or four- and eight-membered rings found in apophyllite are formed (Wells 1987). In apophyllite, successive sheets of tetrahedra are linked across the reflection planes $(001)_0$ and $(001)_{1/2}$ by calcium ions lying in these planes. A projection of the apophyllite lattice along the c -axis is given in figure 1. Two K–Ca layers, adjacent on two sides of the Si–O layers, are related by 45° , resulting in two types of Si–O rings. Two additional non-equivalent Ca positions and one K position emerge as a result. Each K–Ca layer can be superimposed in two ways differing by 90° . This does not produce any new positions for Ca but produces two for K. Thus there are four non-equivalent Ca and K positions in apophyllite. The seven-fold coordination around the calcium atom is similar to calcium in titanite (Zachariasen 1930). The potassium ion is surrounded by a symmetrical group of eight ‘water molecules’, the distance being 2.85 \AA . It is much more difficult to remove the water from apophyllite by heating. The dehydration curve is quite smooth, provided that the heating is very slow (Taylor and St. Naray-szabo 1931). The optical properties of the crystal are unaltered until the specimen becomes opaque at about 550 K (Cavinato 1927). Hence, in the present work, crystals were annealed at 490 K for approximately 24 hours (see below).

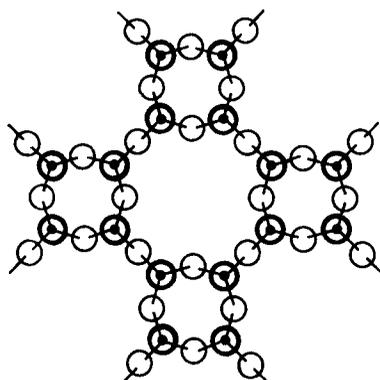


Figure 1. A projection of the apophyllite lattice about the c -axis. Small black circles represent Si atoms and the open circles oxygen atoms. Oxygen atoms lying above Si atoms are drawn more heavily. Ca and K atoms lie above and below the silicon-oxygen atoms along the c -axis. This figure is helpful in identifying the number of magnetically distinct sites, when the crystal was rotated about the three crystallographic axes.

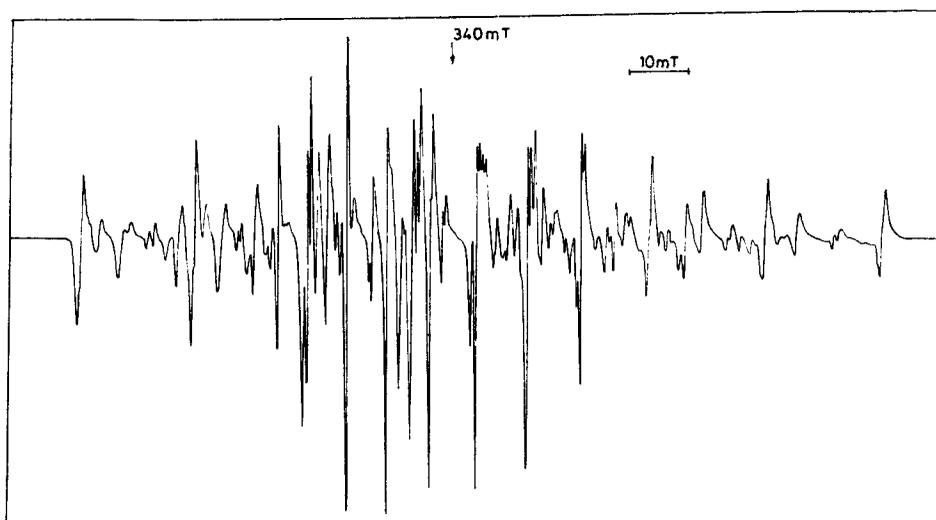


Figure 2. Room temperature X-band (frequency = 9.5 GHz) single crystal EPR spectrum of apophyllite at an arbitrary orientation in the ab plane of the crystal, as obtained from the source, i.e., before annealing the sample. The spectrum indicates different vanadium sites (substitutional and/or interstitial) in the lattice.

4. Results and discussion

4.1 EPR data

The EPR spectrum recorded for the mineral shown in figure 2 was of complicated nature but could be analysed. It is indicative of a large number of orientations of the impurity (both interstitial and substitutional sites) in the crystal. The crystal was annealed at 490 K. Even though no characteristic change occurred in the mineral, the spectra were simplified. The EPR spectrum taken for the annealed crystal is shown

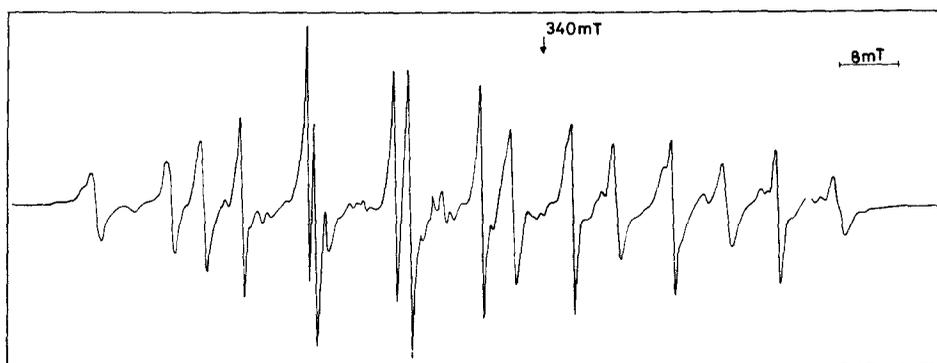


Figure 3. Room temperature X-band (frequency = 9.5 GHz) single crystal EPR spectrum of apophyllite at an arbitrary orientation in the ab plane of the crystal, which was annealed at 490 K for 24 hours.

in figure 3. The crystal rotations were carried out in the three mutually perpendicular planes (ab , bc and ac). The line positions of EPR spectra in the ab plane are shown in figure 4, which is indicative of four distinct sites. However, spectra obtained for rotations about the ac and bc planes of the crystal are identical, where only two distinct sites can be noticed. From these isofrequency plots, the g and A tensors have been calculated using the standard procedure (Schonland 1959) and the results are given in table 1, along with the EPR parameters of some known vanadyl systems. The A_{zz} value obtained for VO(II) in apophyllite is among the highest values observed so far.

g and the hyperfine tensors are found to be axially symmetric for the VO(II) complex. This was confirmed by a strictly axially symmetric powder spectrum of apophyllite (after annealing the crystal) taken at X-band frequencies. The spin-Hamiltonian parameters obtained from the powder spectrum agree very well with the values obtained from single-crystal data. When only first order perturbation is considered, the experimental line positions showed considerable deviation (Abragam and Bleaney 1970). Hence, the second-order perturbation equation (Bleaney 1952) for axial symmetry has been used to calculate the line positions and the agreement between theoretical and experimental values is very good.

From the crystal geometry, four equivalent sites are present for calcium, if one rotates the crystal around the c axis. Hence, four different sites are expected. The isofrequency plot (figure 4) in the ab plane of the mineral confirms the presence of four sites (marked by \circ , \bullet , \triangle , \blacktriangle) in the lattice. As these sites are related by a 90° rotation about the c axis, the EPR spectrum is also repetitive and superimposable for a 90° rotation about this axis. The spectra are also repetitive for every 45° rotation (from the crystal structure data, see figure 1) and this confirms that VO(II) enters the lattice in a substitutional site rather than an interstitial one. From the crystal structure, one expects to have two sites in the ac or bc planes of rotation, which is really observed.

Previous studies (Bershov and Marfunin 1965; Vassilikov-Dova and Lehmann 1988b) have indicated the possibility of VO(II) replacing the two cations, K and Ca. In the present case, annealing has stabilised the vanadyl ion replacing the calcium sites only (this is noticed from the powder spectrum recorded after annealing the

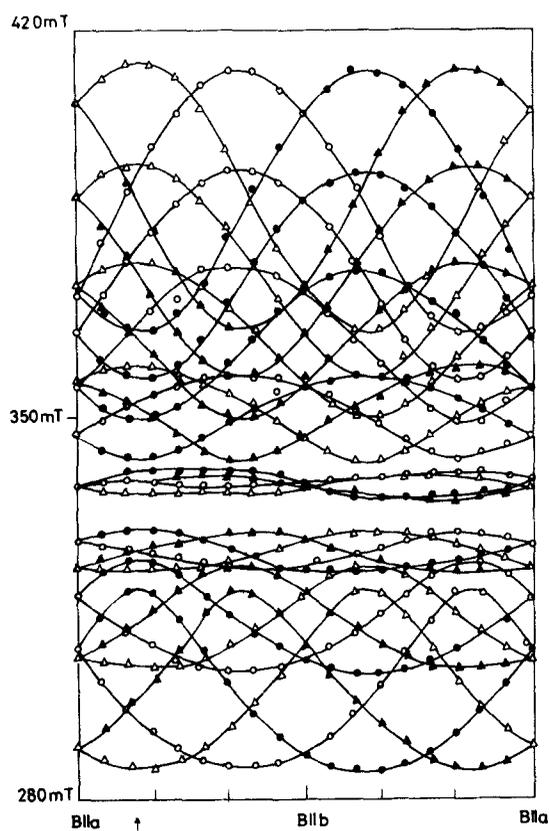


Figure 4. Angular variation of ^{51}V hyperfine lines for c axis rotation of the annealed crystal (frequency = 9.41 GHz) at room temperature. The symbols \circ , \bullet , \triangle , \blacktriangle , correspond to different sites. The spectra are similar when the applied magnetic field is parallel to either the a or b axis of the crystal.

Table 1. EPR parameters for vanadyl ion in a few lattices.

Host	g_{\parallel}	A_{\perp}	A_{\parallel} (mT)	A_{\perp} (mT)	Reference
$\text{Zn}_2(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	1.932	1.981	18.28	7.10	Borcherts and Kikuchi (1964)
GeO_2	1.929	1.976	17.55	6.82	Siegel (1964)
$\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	1.940	1.972	16.30	6.00	Golding (1962)
$(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$	1.945	1.985	17.30	6.38	DeArmond <i>et al</i> (1965)
$\text{Zn}(\text{AP})_2(\text{NO}_3)_2^*$	1.934	1.976	17.10	6.59	Prasad (1986)
Apophyllite	1.933	1.982	18.02	6.02	Vassilikou-Dova and Lehmann (1988)
Apophyllite (single crystal data)	1.934(2)	1.983(2)	18.34(5)	7.24(5)	Present work

*AP – antipyrine

sample). In addition to this, charge compensation considerations are also expected to favour the vanadyl replacing the calcium sites.

The isofrequency plot of the crystal in the *ab* plane (figure 4) does not show maxima/minima either along the *a* or the *b* axis of the crystal. Also, because the lines are broad, we could not separate g_{xx} and g_{yy} (hence A_{xx} and A_{yy}). One would expect g_{zz} and A_{zz} to be approximately along the V=O bond direction. Figure 4 indicates the A_{\max} occurring at $25 \pm 2^\circ$ (marked by an arrow \uparrow) from the *a* axis. From the crystal structure of apophyllite, the projection of Ca-OH₂ direction makes an angle of 27° with [100]. This confirms the assumption that VO(II) occupies a substitutional calcium site. In addition, we did not notice any extra lines due to the replacement of K by the vanadyl ion or fine structure due to superhyperfine interaction from F or OH (replacing F) ions. In our case, the absence of fluorine hyperfine interaction can be attributed to the replacement of the latter ions by OH during the crystal growth and the hyperfine due to OH, if any, should be of the order of the line widths (~ 0.8 mT) of the main hyperfine lines. Hence, we can say that our crystal has a higher hydroxyl content than the two crystals for which the EPR results were reported (Bershov and Marfunin 1965; Vassilikov-Dova and Lehmann 1988b).

4.2 Admixture coefficients

According to Seth *et al* (1983), the equations relating g , A and the admixture coefficients C_1 , C_2 and C_3 to P and κ are given by,

$$g_{\parallel} = 2(3C_1^2 - C_2^2 - 2C_3^2),$$

$$g_{\perp} = 4C_1(C_2 - C_3),$$

$$A_{\parallel} = P[g_{\parallel} - (\kappa + (15/7))(1 - 2C_3^2) - (3/7)(1 + C_1 C_2 C_3)],$$

$$A_{\perp} = P[(11/14)g_{\perp} - 2C_1 C_2(\kappa + (9/7))].$$

Here $P = g_e \beta_e g_N \beta_n \langle r^{-3} \rangle$ and κ is a dimensionless constant describing the core *s*-polarization. From the above equations, P and κ values are calculated for VO(II) in apophyllite and are given in table 2, along with the values of admixture coefficients. The calculated value of P in the present system (0.0122 cm^{-1}) is considerably reduced from the free ion value of 0.016 cm^{-1} (Freeman and Watson 1965) and indicates a fair amount (25%) of covalent bonding in the complex.

In conclusion, the EPR spectra of mineral apophyllite, which contains VO(II) as the paramagnetic impurity have been successfully analysed. The complex spectrum

Table 2. Orbital admixture coefficients and bonding parameters for vanadyl ion.

Host	C_1	C_2	C_3	κ	P (10^{-4} cm^{-1})	Reference
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	0.7060	0.7077	0.0266	0.88	121.0	Muralikrishna (1984)
$\text{Cd}(\text{Im})_2\text{SO}_4^\ddagger$	0.7059	0.7080	0.0202	0.86	118.9	Muralikrishna (1984)
$\text{Zn}(\text{AP})(\text{NO}_3)_2^\ddagger$	0.7007	0.7135	0.0085	0.83	116.0	Prasad (1986)
Apophyllite	0.7018	0.7124	0.0028	0.86	122.7	Present work

*Im - imidazole; \ddagger AP - antipyrine

was simplified by annealing the sample at 490 K, which resulted in a system, in which the impurity was found to occupy preferred sites corresponding to lowest energy configuration. Based on EPR and charge considerations, it is concluded that VO(II) substitutionally replaces Ca(II) and not K(I). Although there is no compelling need to expect an axial symmetric EPR spectrum, in many VO(II) systems, in spite of apparent low symmetry of surrounding ligands, axial spectra have been observed (Bansal *et al* 1989), as in the present case. It is presumed that some sort of relaxation or libration around the VO(II) moiety is responsible for the observed high symmetry of the system, down to 77 K. In our samples, almost all F^- ions have been replaced by OH ions, as inferred from the absence of F^- superhyperfine spectrum. As expected, the VO(II) impurity in the annealed mineral apophyllite falls in the category, in which the ion is preferentially oriented.

Acknowledgements

GR thanks the Indian Institute of Technology, Madras, for allowing her to do part-time research work and PSR thanks the Council of Scientific and Industrial Research for a fellowship.

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