

Four-valent vanadium in vanadinite

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ABSTRACT

V⁴⁺ was detected in grayish vanadinite Pb₅(VO₄)₃Cl from Keban, Turkey, by electron paramagnetic resonance at room temperature. The EPR data ($g_{zz} = 1.9025$, $g_{xx} = 1.9870$, $g_{yy} = 1.9681$, $A_{zz} = 175.9$, $A_{xx} = 106.8$, and $A_{yy} = 66.8$ with A_{ii} in 10^{-4} cm⁻¹) determined on single crystals indicate formation of a short V–O bond from V–O(I) of the regular VO₄³⁻ groups. The high concentration of V⁴⁺ and its incomplete destruction at higher temperatures favor low oxygen fugacity during crystal growth rather than ionizing radiation as the cause of the four-valent state. The grayish color most likely is due to the combined effect of absorption by this ion and radiation defects present in lower concentration, because V⁴⁺ in distorted tetrahedral coordination alone should cause a blue or green color.

INTRODUCTION

The apatite family of minerals with the general formula M₃²⁺(XO₄)₃Y is very variable in chemical composition: M = Ca or Pb; X = P, As, or V; and Y = OH, F, or Cl in the pure end-members of natural specimens. Still greater compositional variations have been realized in synthetic compounds. The solubility of impurities in all three positions M, X, and Y also appears to be quite pronounced. Because of volatility of MY₂ at higher temperatures, a deficiency of both M and Y (where Y = Cl or F) is possible as well as exchange of 2 Y with a divalent anion like O²⁻ or CO₃²⁻. Such local charge imbalances due to vacancies or aliovalent impurities favor formation of radiation defects ("color centers"). Indeed a number of investigations (largely performed on synthetic samples) have revealed formation of such radiation defects, in most cases at or near the Y positions (Swank, 1964; Piper et al., 1965; Shcherbakova et al., 1968; Prener et al., 1969; Gilinskaya et al., 1970; Prener, 1971; Knottnerus and den Hartog, 1975; den Hartog and Benning, 1977; Dugas et al., 1978).

Very little effort has so far been devoted to the investigation of paramagnetic defects in the lead apatites pyromorphite, vanadinite, and mimetite. To our knowledge there has been only one investigation of red vanadinite (from Morocco), in which the optical absorption spectra were assigned to ligand field bands of Cu²⁺ (near-infrared and visible) and a charge-transfer transition of VO₄³⁻ (near UV) (Nagara et al., 1986). However, the postulated presence of Cu²⁺ in vanadinite from this locality is not confirmed by EPR investigations (Vassilikou-Dova and Lehmann, unpublished results). Thus the origin of the common red color of vanadinites is still unknown, but seems to be associated with presence of radiation defects.

Commonly the type of impurity responsible for formation of a certain radiation defect is revealed by determination of its structure by EPR. However, certain elements (like Pb and V in vanadinite) have a pronounced tendency to change their valence state with exposure to high-energy radiation. Although in these cases a charge unbalance in the neighborhood of these stoichiometric constituents is most likely the cause of this change of valence, it is not so easy to detect the nature of this charge imbalance. The same uncertainty about the mechanism of charge compensation also exists if part of the vanadium is initially incorporated in a lower valence state. As will be shown, such a complication is indeed found in this vanadinite.

EXPERIMENTAL DETAILS

Short, prismatic, 50-mg, grayish crystals of vanadinite Pb₅(VO₄)₃Cl from Keban, Turkey, were investigated. Most EPR measurements were performed at X band on a Bruker 200 D spectrometer. Additional spectra were recorded at Q band down to 77 K on a Bruker 420 Q spectrometer. Piceine was used as a standard for determination of *g* factors and spin concentrations (Schmitz et al., 1979). Spectra were recorded, in most cases at 5° intervals, for rotations around the crystallographic **a**, **c**, and **b** (= **a** × **c**) axes.

RESULTS

At room temperature, the vanadinite yields octets with linewidths (distances between maxima and minima of the first derivative) of at least 1.2 mT. Figure 1 shows an example for the magnetic field parallel to the *c* axis. A concentration of spins of 0.26% per lattice site of V was determined using piceine as standard (Schmitz et al.,

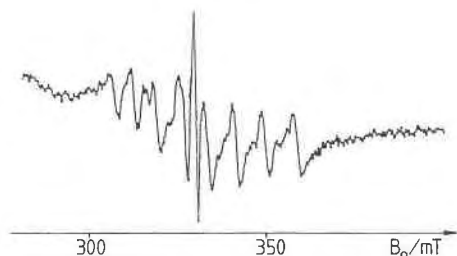


Fig. 1. EPR spectrum of vanadinite from Keban, Turkey, at 9.3 GHz and 300 K for $B_0 \parallel c$. The intense single line near the center of the octet due to V⁴⁺ stems from piccine as standard. The small signals near the last two members of the octet originate from a small concentration of Pb²⁺, whereas the extra signal between the second and the third member is due to an as yet unidentified paramagnetic species.

1979). This low concentration and the small size of the crystal (45 mg) in combination with the large linewidths cause the rather low signal/noise ratio. The angular variation of the two outermost components of these octets for rotations about the mutually perpendicular **a**, **b**, and **c** axes (Fig. 2) yields the spin-Hamiltonian parameters in Table 1. The coincidence of the **c** axis with a principal value (in this case the minimum) of the octet splitting—together with the site splitting into up to three magnetically nonequivalent sets away from this axis—clearly indicates that the site symmetry of the paramagnetic defect is monoclinic, with $C_s (=m)$ being the only possibility in the vanadinite space group, $P6_3/m$ (Trotter and Barnes, 1958).

At Q band the linewidths are at least 1.6 mT and do not decrease with cooling to 77 K. Heating of the crystals to 770 K for 1 h results in partial destruction of these EPR signals. The crystals always crack with heating, and a new very broad signal with $H_{pp} = 95$ mT appears. The same broad signal, of unknown origin, also appears after crushing the crystals to a fine powder.

DISCUSSION

The characteristic octet pattern and the spin-Hamiltonian data in Table 1 clearly indicate that the paramagnetic species is a V⁴⁺ ion with one unpaired electron. For this ion, an octet hyperfine splitting results from $I = 7/2$ of the ⁵¹V nucleus with 100% abundance. The high value of A_{zz} indicates formation of a VO²⁺ molecular ion with a rather short V–O bond. The most likely site of this ion is the regular lattice site of V⁵⁺, which has C_s symmetry. The direction of the z axis of largest hyperfine splitting should be at least approximately along the V–O bond direction. Because the crystallographic **c** axis coincides with the y axis of VO²⁺, one of the V–O bonds in the mirror plane must be involved. With an angle of -61.5° between the V–O(I) direction and the **a** axis, the near coincidence of A_{zz} with this bond direction shows that the V–O bond is formed from this combination. Within the

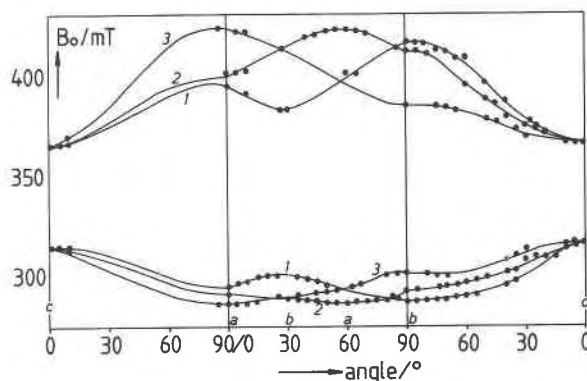


Fig. 2. Angular variation of the outermost components of the octets due to V⁴⁺ at 9.3 GHz and 300 K for rotations around **b** ($= \mathbf{a} \times \mathbf{c}$), **a**, and **c** axes (from left to right). Experimental values are indicated by dots; the lines are calculated.

rather large limits of error of the crystal-structure determination, the bond lengths of the V–O(I) and the V–O(II) bonds are equal, but longer than those of the two V–O(III) bonds. In other cases, e.g., in wavelite (Vassilikou-Dova et al., 1988), the shortest bond is highly favored energetically for formation of the V–O bond. In addition to these static properties, however, differences in the dynamic ones may also be of considerable influence, because a drastic shortening of the V–O distance of more than 10 pm is expected with formation of the double bond. An approximately inverse relationship between the size of A_{zz} and the V–O bond distance can be expected, but no quantitative relation can yet be established, because practically all EPR data are obtained for small concentrations of VO²⁺ in host sites of diamagnetic ions for which the true bond distances are still unknown.

In some cases, including cristobalite (Grunin, 1971), zoisite (Hutton, 1971), garnets (Havlicek et al., 1974), and zircon (Ball and Wanklyn, 1976; di Gregorio et al., 1982), EPR spectra of V⁴⁺ in distorted tetrahedral sites can only be observed at or below 77 K because the spin-lattice relaxation times are too short. In other cases like SbVO₄ (Zapart et al., 1988) and the cristobalite and berlinite modifications of AlPO₄ (de Biasi, 1980, 1982), V⁴⁺ was easily detectable at room temperature. Thus it appears that the actual spin-lattice relaxation times of this ion depend critically on the energy of the first excited state, which increases with site distortion because of increasing splitting of the $e (d_{x^2-y^2}, d_{z^2})$ level, which is degenerate in ideal tetrahedral symmetry. It must also be

TABLE 1. Spin-Hamiltonian parameters for V⁴⁺ in vanadinite

Component	g	$A \times 10^4$ (cm ⁻¹)	Orientation
zz	1.9025(6)	175.9(3)	56.5° from a
xx	1.9870(5)	106.8(3)	33.5° from a
yy	1.9681(6)	66.8(3)	parallel to c

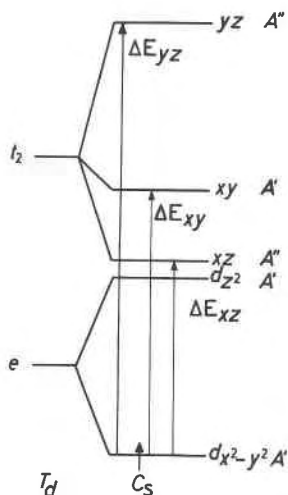


Fig. 3. Energy-level diagram for V⁴⁺ in ideal (T_d) and distorted (C_s) tetrahedral symmetries. The ordering and energy separations of levels connected by vertical arrows follow from the principal values of the g matrix.

noted that in several of the above cases the actual V⁴⁺ site was not determined with certainty.

Our crystals are too small for conventional measurement of optical absorption spectra. Their gray color suggests a very indistinct spectrum covering the visible range more or less uniformly. This color cannot be explained by the presence of V⁴⁺ in fourfold coordination alone, because this environment should result in either green or blue colors, as observed in zircon-type crystals (di Gregorio et al., 1982) and garnets (Weber and Riseberg, 1971). Although no colors were reported for V⁴⁺ in AlPO₄ (de Biasi, 1980, 1982), similar colors can be inferred from the reported photoacoustic absorption spectra. Simultaneous presence of a radiation defect in lower concentrations, as investigated in detail in red vanadinites and assigned to a Pb⁺ ion (Vassilikou-Dova and Lehmann, our unpublished results), certainly also contributes to the color. The red color of these vanadinites has been ascribed to a charge-transfer transition of the VO₃⁻ (Nagara et al., 1986). However, this interpretation must be questioned, because this color should dominate in every vanadinite if it were a property of the pure compound and not a result of a certain defect. In any case, intervalence transfer transitions between V⁴⁺ and V⁵⁺ should not significantly contribute to the optical absorption spectrum, because the VO₄ groups are isolated in the structure.

The positions of three of the four predicted ligand-field bands of VO²⁺ can be estimated from the first-order relations for the principal values of the g matrix (see Fig. 3):

$$g_{zz} = 2.0023 - (8\lambda/\Delta E_{xy}) \quad (1)$$

$$g_{yy} = 2.0023 - (2\lambda/\Delta E_{yz}) \quad (2)$$

$$g_{xx} = 2.0023 - (2\lambda/\Delta E_{xz}). \quad (3)$$

These relations yield values of about 12000, 19600, and 8800 cm⁻¹, respectively, with the usual value of 150 cm⁻¹ for the spin-orbit coupling constant. Of these values, only the second one falls in the visible range, although the high-energy tail of the first one may extend into the visible range. The fourth band corresponding to excitation of the electron into the d_{z^2} level is expected to lie close to that of the d_{xz} level, i.e., also in the infrared range.

The occurrence of a small portion of the V in the four-valent state could be due to either reducing conditions during crystal growth or to subsequent ionizing radiation. Because this ion is not observed in vanadinites from other localities that contain different radiation defects (Vassilikou-Dova and Lehmann, our unpublished results), a charge imbalance near these V⁴⁺ ions may lead to their preferential capturing of an electron as a result of ionizing radiation.

Incorporation of trivalent rare-earth-element ions on adjacent Pb sites is a likely cause of such a local charge imbalance. Of these, only Gd³⁺ would be detectable by EPR at normal temperatures, but was not observed. Two observations suggest that at least the major part of the V⁴⁺ is not due to ionizing radiation, but was formed during crystal growth as a result of low oxygen fugacity. (1) The concentration of V⁴⁺ in the unheated sample is more than an order of magnitude higher than the limiting upper concentration of radiation defects of about 100 ppm per lattice site. At higher concentrations, electron and hole centers spontaneously recombine via tunneling because the spatial separation between them is too small. (2) The incomplete bleaching at 770 K is also not compatible with a radiation defect, because this temperature exceeds the limit of their thermal stability.

Future experiments must show whether the concentration of V⁴⁺ in vanadinites is a suitable sensor of oxygen fugacity. The vanadinite from Keban was found in large limestone cavities, but we are unable to assess the oxygen fugacity during its formation because no occurrence of other minerals in this locality was reported by the supplier.

Note added in proof: The unpublished results alluded to in this paper will appear in the following:

Vassilikou-Dova, A.B., and Lehmann, G. (1989) A radiation defect in pyromorphite and vanadinite. *European Journal of Mineralogy*, in press.

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