EPR of Fe^{3+} in Low Quartz Isomorphs $A(III)B(V)O_4$

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(Z. Naturforsch. **30 a,** 28–34 [1975] ; received November 28, 1974)

Electron spin resonance spectra of Fe^{3+} in hydrothermally grown single crystals of $AlPO_4$, $GaPO_4$, $AlAsO_4$ and $GaAsO_4$ were measured at X-band and analyzed using a Spin-Hamiltonian for rhombic symmetry. The zero field splitting was found to be between about one and two times the microwave frequency, increasing regularly from $AlPO_4$ to $GaAsO_4$. This increase is largely due to an increase in the axial parameter D whereas the second order rhombic parameter E is practically constant. The fourth order parameter a increases exponentially with the lattice parameter ratio c_0/a_0. The variation of D indicates a site distortion for $GaPO_4$ about twice as large as in $AlPO_4$. For the arsenates, influences of increased covalency are apparent in addition to site distortions of comparable size. Halfwidths in the range of 18 Gauss for the phosphates and 38 Gauss for the arsenates indicate hyperfine interactions with ^{31}P and ^{75}As, and estimates of 0.5 and 1% spin density resp. at these nuclei are obtained, again showing increased covalency for the arsenate compounds.

Introduction

The ternary compounds $A(III)B(V)O_4$ with A = Al, Ga, Fe, Mn and B = P, As have a structure derived from α-quartz by alternating substitution of Si by A and B. The bonds in these compounds cannot be described as purely ionic or purely covalent and these substances seem ideally suited for systematic studies of trivalent transition metal ions in tetrahedral surrounding of oxygen. Optical spectra of Fe^{3+} in $AlPO_4$, $GaPO_4$ and $AlAsO_4$ have been reported some years ago [1]. They showed substitutional incorporation of this ion in A sites whereas Cr^{3+} in $AlPO_4$ almost exclusively occupies interstitial sites of distorted octahedral symmetry [2]. No systematic investigation of EPR spectra in such a system has been reported so far, but data for Mn^{2+} in binary chalkogenides of Zn and Cd [3] and for Mn^{2+} [4] and Fe^{3+} [5] in ternary chalkogenides of composition $A(II)B(III)_2X_2$ are available. They show increasing covalent bonding to contribute significantly to the spin Hamiltonian parameters D and a as also indicated by theoretical calculations [6]. For a quantitative experimental assessment of this covalency effect, however, rather precise knowledge of the crystal structures in terms of site distortions in the neighborhood of the transition metal ion is required. In the absence of such detailed structural information a semiquantitative separation of the influences of covalency and site distortions still seems possible in the present case, since the crystal structure of one compound ($AlPO_4$) [7] is known precisely and a second compound with equal covalent character ($GaPO_4$) is available. For the other two compounds the change in covalency can be estimated within rather narrow limits from optical absorption data. It is also hoped that the results of this work in terms of predicted distortions will prompt structure refinements for the other compounds.

A number of different centers of Fe^{3+} was found in α-quartz crystals, both natural and synthetic [8–12]. But in this system the spin Hamiltonian parameters for substitutional Fe^{3+} are largely determined by the type and location of the charge compensating positive ion. Interstitial incorporation of Fe^{3+} could be deduced for one of these centers from the optical spectra [13]. Therefore no close similarity of the crystal field parameters with those in the ABO_4 compounds can be expected for any one of these centers.

Crystallography and Growth of the ABO_4 Crystals

The room temperature modifications of $AlPO_4$, $GaPO_4$, $AlAsO_4$ and $GaAsO_4$ crystallize in the space group $P3_{2,1}21$. Only for $AlPO_4$ a detailed structure determination was performed [7], the NMR spectrum of ^{27}Al in this compound has also been measured [14]. The AlO_4 tetrahedra were shown to be more distorted than the PO_4 tetrahedra, the site symmetry of Al is C_2. Table 1 summarizes the lattice parameters of these compounds in comparison to those of α-quartz.

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Table 1. Lattice parameters of ABO_4 compounds.

Compound	$c_0/Å$	$a_0/Å$	c_0/a_0	Literature
$AlPO_4$	10.94761	4.94291	2.215	7
$GaPO_4$	11.05	4.902	2.255	15
$AlAsO_4$	11.224	5.030	2.230	16
$GaAsO_4$	11.38	5.01	2.271	15
"$SiSiO_4$"	10.8104	4.9138	2.200	17

Stanley was the first to grow large crystals of $AlPO_4$ [18] and $AlAsO_4$ [19] hydrothermally from homogeneous acidic solutions by slowly increasing the temperature. Our method differs from his in two respects: We did not normally use seed crystals and maintained a temperature gradient between nutrient material and growth region. In this way larger amounts of material could be deposited without need for opening the glass tubes to add fresh solution. The danger of cloudy inclusions in the crystals was effectively avoided in this way and crystals with dimensions up to 25 mm were obtained. Acid concentrations and temperature ranges for the growth of $AlPO_4$ and $AlAsO_4$ were the same as used by Stanley. For the gallium compounds optimum temperatures in the same region as for $AlAsO_4$ were determined, their solubility also decreases with temperature. It was not possible to grow crystals of $FePO_4$, $FeAsO_4$ or $MnPO_4$ in this way, possibly due to too small temperature dependence of their solubility. The material was either not transported at all or, at lower temperatures, dihydrates of the iron compounds were formed. The crystals were grown in thickwalled sealed glass tubes placed in a tubular furnace with two temperature zones. Size and quality of the crystals considerably improved when the glass tubes (with outer dimensions up to 48 mm) contained a narrow middle portion of only a few mm inner diameter and the two halves of the tubes were placed in separate aluminium blocks that were inserted into the tubular furnace. In the beginning of each run the side containing the raw material was placed in the hotter part of the furnace to allow all material to deposit on this side. After about 24 hours the temperature gradient was reversed, but kept below about 20 °C to allow seed formation to take place. After a few days the temperature gradient was raised to the final value near 30 °C. The crystals preferentially grew at the liquid/gas interphase. Doping level of Fe^{3+} was below 1 mole % in every case. The following table lists growth temperatures, average duration of each run and maximum size of the crystals achieved under these growth conditions. The low quartz crystal structure of these crystals was verified by X-ray powder diagrams.

Table 2. Hydrothermal growth of ABO_4 crystals.

Compound	Temperatures	Duration	Maximum length
$AlPO_4$	160/190 °C	20 days	25 mm
$GaPO_4$	210/240 °C	27 days	20 mm
$AlAsO_4$	230/255 °C	25 days	11 mm
$GaAsO_4$	210/240 °C	25 days	16 mm

Details of EPR Measurements

EPR spectra were taken at about 9.6 GHz with a Bruker spectrometer B-ER 414s employing a dual rectangular cavity vibrating in the TE 104 mode. The maximum magnetic field attainable with the BE-22-C3 magnet was in the range of 10.5 kG. Magnetic fields were measured using an AEG proton resonance unit, the microwave frequency was determined with a standard pitch sample in the second vacity having a g-value of 2,0024. Crystals with well-developed rhombohedral faces were oriented optically under a polarizing microscope. Due to the higher solubility at lower temperatures these faces often were etched preventing exact optical alignment via an optical two-circle goniometer. In these cases final alignment was accomplished by the Laue back-reflection technique using a Polaroid Laue camera. These crystals were glued onto a quartz rod fastened to a goniometer head. In this way the crystals could be rotated about a prealigned axis perpendicular to the magnetic field. In some experiments a Bruker 400 X G-2 goniometer was used allowing sample rotation in the microwave cavity about two mutually perpendicular axes. Due to excessive damping of the microwaves by this unit, however, these measurements were difficult. Normally the crystals were rotated about the threefold c_0-axis and one of the twofold a_0-axes. In some cases a rotation about an axis perpendicular to these (a b_0- or Y-axis) was also performed.

Results

For rotation about the threefold axis three identical spectra displaced by 60° each were observed as expected for Fe^{3+} substituting A (III) on the three twofold axes. In contrast to the substitutional centers of Fe^{3+} in α-quartz these spectra were of equal intensity within the limits of error. For all compounds the largest fine structure splitting was observed for $H_0 \parallel a_0$, the other two symmetry axes of the centers lie along the c_0 and b_0 axes resp. Figures 1 and 2 show the spectra in $AlPO_4$ for rotations about the c_0- and a_0-axes resp. The spectra in the other compounds are quite similar, but not all transitions occur within the range of our magnet. A spin Hamiltonian of the form

$$h\nu = g\beta H + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \frac{a}{6}[S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{3}S(S+1)(3S^2+3S-1)] \qquad \mathbf{(1)}$$

was used for their analysis. In accordance with all previous experience g was assumed to be isotropic and set equal to 2.0024. Rough estimates of D and E were obtained from the observed fine structure splittings using the diagrams of Dowsing and Gibson[20]. Final values for the parameters D, E and a were obtained using a slightly modified least squares fitting computer program QCPE 69 developed by Gladney *. Agreement between observed and calculated microwave frequencies was in the range of a few percent. Table 3 lists the fine structure parameters obtained. Absolute signs were not determined. Addition of an axial fourth order term

$$b[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2] \qquad (1\,\mathrm{a})$$

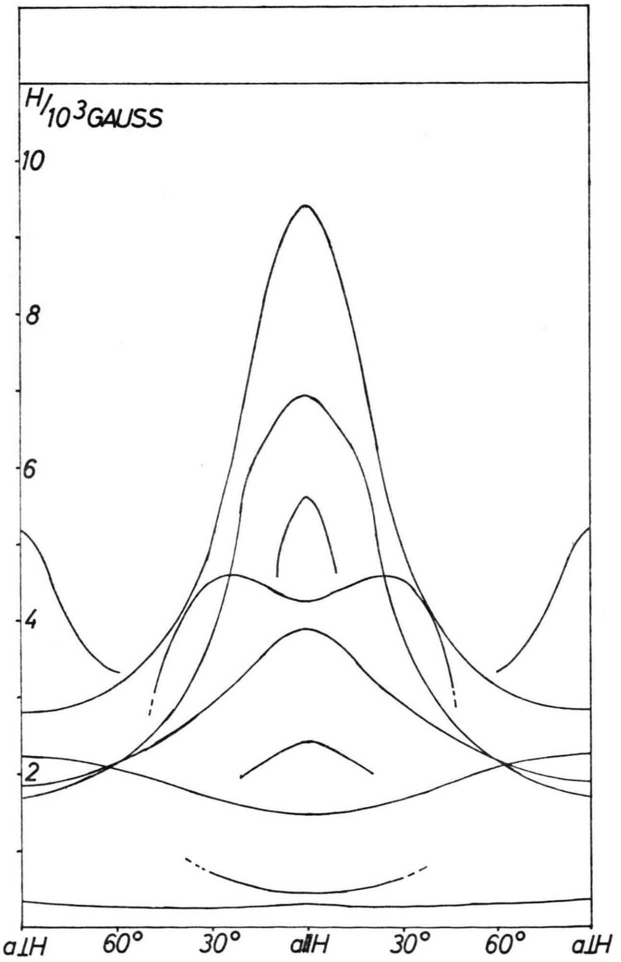

Fig. 1. Fe^{3+} in $AlPO_4$. Angular variation of line positions at 9.6 GHz for rotation about the threefold axis. For clarity only one of the three equivalent centers is shown.

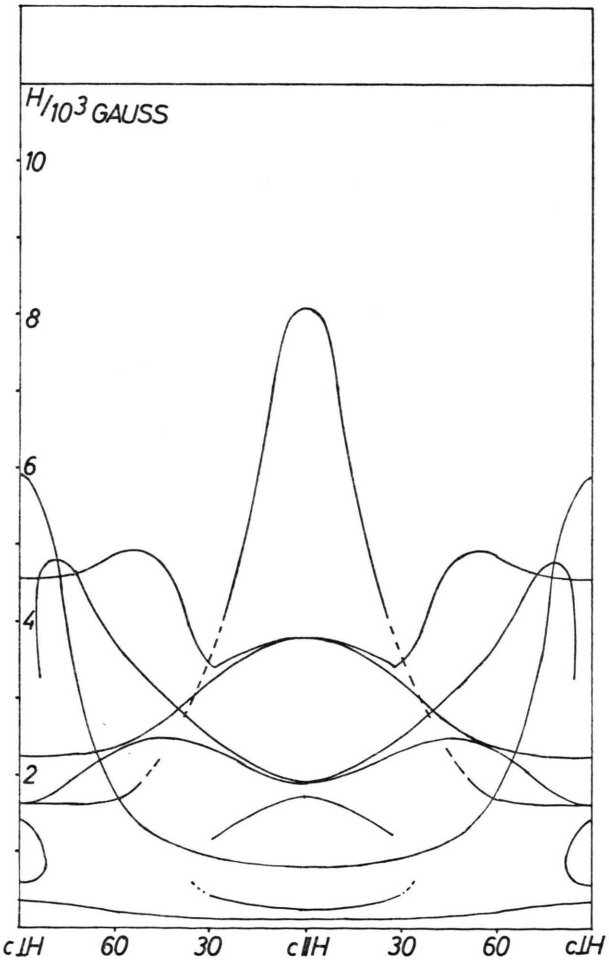

Fig. 2. Fe^{3+} in $AlPO_4$. Angular variation of line positions for rotation about the twofold axis.

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* Available from Quantum Chemistry Program Exchange Bloomington, Ind., USA.

did not improve the agreement significantly. From these fine structure parameter values the zero field splittings were calculated. As shown in Table 3, they are in the range between about one and two times the microwave frequency employed. Figure 3 shows the energy level diagram for $GaAsO_4$.

Table 3. EPR parameter values of Fe^{3+} in ABO_4 crystals.

Crystal	D/GHz	E/GHz	a/GHz	δ/Gauss *	E_1/GHz **	E_2/GHz ***
$AlPO_4$	3.33	1.14	0.67	18	7.90	11.11
$GaPO_4$	5.89	1.17	1.04	19	9.38	17.28
$AlAsO_4$	6.57	1.11	0.82	38	10.23	19.07
$GaAsO_4$	6.77	1.17	1.53	39	9.72	20.57
α-quartz (I-center) [11]	2.06	0.92		3−7	7.08	9.09

* Halfwidth (distance between extrema of derivative curve).
** Zero field splitting (±1/2, ±3/2).
*** Zero field splitting (±3/2, ±5/2).

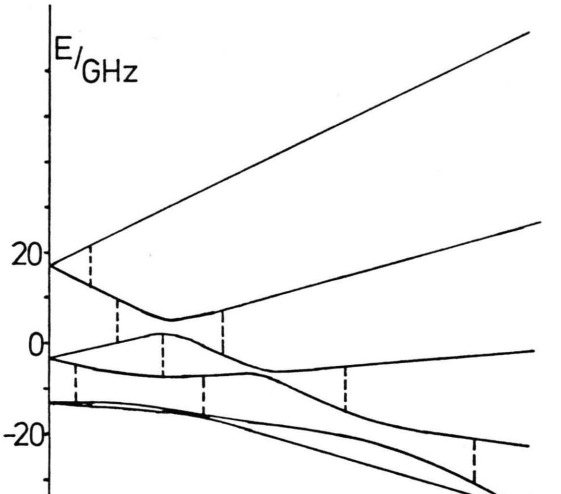

Fig. 3. Fe^{3+} in $GaAsO_4$. Energy level diagram calculated from the parameters given in Table 3.

The linewidths were considerably broader than for Fe^{3+} in quartz. For the phosphates they were in the range of 18 Gauss and near 38 Gauss for the arsenates. They are also listed in Table 3.

Discussion

Fine Structure Parameters

The similarity among the EPR spectra of the four compounds is immediately apparent from the identical positions of the symmetry axes x, y and z and the systematic variation of the fine structure parameters from $AlPO_4$ to $GaAsO_4$. It can be regarded as proof for substitutional incorporation of Fe^{3+} in $GaAsO_4$ also for which hitherto no optical spectra were measured. The lack of any crystal field stabilization energy immediately explains the difference to Cr^{3+} which in the $AlPO_4$ lattice almost exclusively occupies interstitial sites of distorted octahedral symmetry [2]. Size and variation of the crystal field parameters then remain to be explained. Starting with the second order parameters D and E we note a regular increase in D whereas E is essentially constant in this series. Two origins for the variation of these parameters are discussed in the literature: the amount of lattice site distortion and the degree of covalency. Low [21] gives a distortion in the range of 10^{-10} cm for D of the order of 0.1 cm^{-1} (or about 3 GHz) as observed for $AlPO_4$. From the Al-O distances of $d_1 = 1.7327$ and $d_2 = 1.7452$ Å resp. and the angles O-Al-O of $\alpha_1 = 112.30°$ and $\alpha_2 = 112.03°$ given by Schwarzenbach [7] we calculate a distortion along the z-axis of

$$\Delta x = d_1 \cdot \cos \alpha_1/2 - d_2 \cdot \cos \alpha_2/2 = 0.96 \cdot 10^{-10} \text{ cm}.$$

The agreement is surprisingly good, but due to the larger radius of the Fe^{3+} compared to Al^{3+} the site distortion in pure $AlPO_4$ cannot be set equal to the local site distortion of a substitutional Fe^{3+}. Furthermore, an influence of asymmetries beyond the first coordination sphere can also not be excluded since in the electrostatic point-multipole approximation we have

$$D \, \alpha \sum_j q_j/R_j^3 \qquad (2)$$

with q_j the charge of the jth atom and R_j its distance from the paramagnetic ion. Taking the Fe-O distance in $AlPO_4$ to be the arithmetic mean between the Al-O and the normal Fe-O distance for tetrahedral coordination one would expect D to be about 10% lower in $GaPO_4$ for comparable distortion. The experimental value of 5.89 GHz for $GaPO_4$ corresponds to a site distortion about twice as large as that in $AlPO_4$. Influences of covalency are completely neglected here, but covalency of the Fe-O bond does not change from $AlPO_4$ to $GaPO_4$. This is immediately apparent from the identical position of the first charge transfer band at 46,000 cm^{-1} in both systems[1]. The site distortions in $AlAsO_4$ and $GaAsO_4$ are more difficult to predict due to increased covalency. From the position of the first charge transfer band of Fe^{3+} in $AlAsO_4$ at 42,300 cm^{-1} (see [1]) an increase in optical electronegativity compared to the phosphates of 0.12 units can be deduced. Taking the covalency as c/n where $n=4$ is the coordination number and c is a function of the electronegativity difference given by Hannay and Smith[22] as:

$$c = 1 - 0.16\,(X_A - X_B) - 0.035\,(X_A - X_B)^2 \qquad \textbf{(3)}$$

we get covalencies of

$c/n = 0.201$ for Fe^{3+} in the phosphates and
$c/n = 0.209$ for Fe^{3+} in the arsenates.

Both absolute value and difference are comparable to the systems Mn(II) – S and Mn(II) – Se[4]. Whereas there may be some doubt about the absolute scale of covalency chosen, the difference definitely indicates an increase in covalency.

Differences in site distortion among these isomorphs can be assumed to have two causes:

a) The size of the cations A and B in relation to the size of the oxygen anions. This influence can be respresented by the sum of the radii $r_A + r_B$ as done in Figure 4.

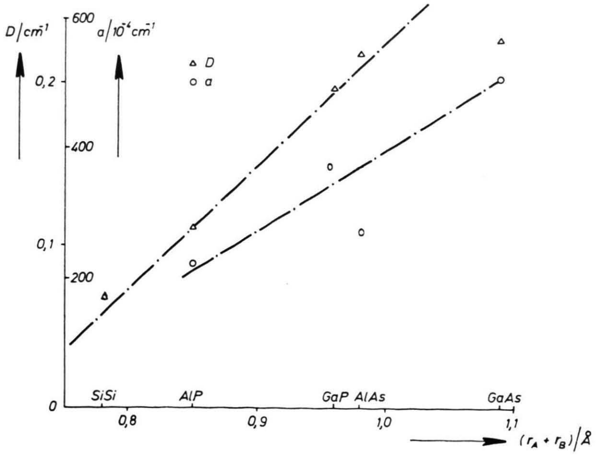

Fig. 4. Variation of D and a with the sum of the cation radii.

b) The relative size of the ions A and B. A correlation with the ratio r_A/r_B suggests A site distortions for the arsenates smaller than for $AlPO_4$ and consequently a more than twofold increase of the axial parameter D due to increased covalency in the arsenates. However, it is possible that the optimum ratio r_A/r_B varies with the sum of these radii. Knowing that for quartz and $AlPO_4$ the A site distortion increases with the ratio of the lattice constants c_0/a_0, we take this ratio as a measure of the relative distortions (see Figure 5).

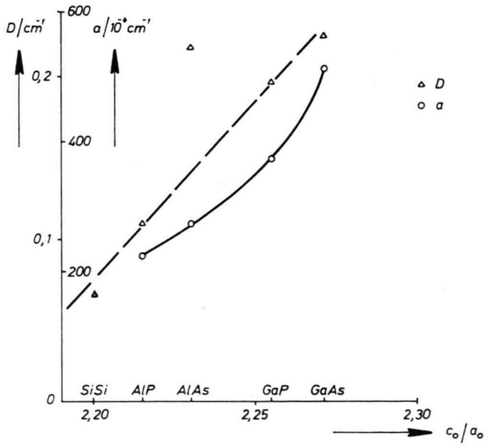

Fig. 5. Variation of D and a with the ratio of the lattice parameters c_0/a_0.

The correlation with the sum of the radii tends to indicate distortions for both $AlAsO_4$ and $GaAsO_4$ comparable to $GaPO_4$ and only small influences of increased covalency. The correlation with the ratio of the lattice constants suggests a considerable influence of increased covalency for $AlAsO_4$ alone. Due to the larger radius of As(V) compared to P(V) the distortions in the arsenates are presumably more evenly distributed among the A and B sites. The distortions of the A sites in the arsenates are therefor likely to be below the amount inferred from the phosphates, of comparable size for both $AlAsO_4$ and $GaAsO_4$ and not larger than in $GaPO_4$. For Mn^{2+} in $CdGa_2Se_4$ a value of D four times as large as in $CdGa_2S_4$ was observed[4]. While the site distortions in these compounds are also not known exactly, some of this larger increase certainly must arise from increased site distortion.

Also included in Figs. 4 and 5 is D for an Fe^{3+} center in quartz first identified in brown synthetic samples[11]. This value is nicely compatible with substitutional Fe^{3+} not having charge compensators in close neighborhood as suggested by Matarrese et alias[11]. The evidence from other, widely differing sources, however, conclusively proves interstitial incorporation of this ion[13]. The conclusion is inevitable then that considerable relaxation must take place in the neighborhood of this interstitial Fe^{3+}. This conclusion is supported by the pronounced influence of small concentrations of interstitial ion on the overtone vibrations of quartz[23].

Turning now to the first order parameter a, we immediately note its large size compared to many other systems. For site symmetries as low as C_2 the axes of the different crystal field parameters may not be collinear. This fact may also in part be responsible for the relatively large deviations between observed and computed microwave frequencies (in addition to the comparable sizes of the Zeeman and crystal field splittings). The more sophisticated ways of analysis developed by White et al.[24] and Michoulier and Gaite[25] would be appropriate, but they require measurements at higher microwave frequencies in these cases. Thus we can say that our a term certainly must contain fourth order contributions of lower than cubic symmetry. In principle it should reflect the crystal field in the first coordination sphere of Fe^{3+}, but we cannot draw any definite conclusions from the exponential increase of a with the c_0/a_0 ratio indicated in Figure 5. Certainly the almost twofold increase in going from Al to Ga is at variance with a purely ionic model.

It would be very interesting to compare the predicted distortions with values directly determined by X-ray structure refinements.

Linewidths

As shown in Table 3 the linewidths in the ABO_4 compounds are considerably broader than for Fe^{3+} in quartz. They are largely determined by the type of B atom, and the most likely source of broadening is hyperfine interaction with the nuclear spins of ^{31}P and ^{75}As resp. The lineshape is intermediate between Gaussian and Lorentzian indicating contributions of both isotropic and anisotropic interactions. Assuming hyperfine interactions with two nonequivalent pairs of nuclei we can try to simulate the observed resonance lines. Rough estimates of about 0.5% spin density at the ^{31}P nucleus and about 1% spin density at the ^{75}As are obtained from the observed hyperfine splittings of 3555 Gauss for PO_4^{2-}[26, 27] and 4320 Gauss for AsO_4^{2-}[27, 28]. Again the increased covalency in the arsenates is apparent from these estimates. It is not possible, however, to completely duplicate the observed structureless absorption lines using components of only 3 Gauss halfwidth. Compared to quartz some additional mechanism of broadening must therefor be operative with linewidths in the range of 10 Gauss for the phosphates. Dipolar broadening can hardly be the dominant source since the Fe^{3+} ions are at least 4.4 Å apart and no significant sharpening was observed with reduced concentration of Fe^{3+}. A disorder of A and B atoms is very unlikely in view of the different size and charge of these ions. Also, the effect of such a disorder can be estimated to be larger than the Al, Si disorder in feldspars where linewidths of the order of 150 Gauss are observed. Structural defects may be the cause of this extra broadening. Even in quartz halfwidths of 3 Gauss are exceptional, and a value of 6 Gauss may be more representative giving a closer agreement with our data in the ABO_4 compounds. The smallest halfwidth ever observed for Fe^{3+} in $AlPO_4$ was a value of 13 Gauss.

ENDOR measurements would be very helpful for a quantitative determination of the hyperfine interactions.

We acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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