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PARAMAGNETIC O_2^- DEFECTS IN APATITES

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Résumé. — La R. P. E. permet la mise en évidence et la caractérisation de l'ion superoxyde O_2^- dans les tunnels de différentes apatites oxygénées. On compare leur situation à celle que ces ions occupent dans les halogénures alcalins.

Abstract. — The superoxide O_2^- ion is studied by E. S. R. in various oxygenated apatites. It allows to state its position and its orientation in the channel of the apatites. One compares these results with those obtained in alkali-halides.

Before presenting some results about O_2^- defects in apatite structures it is important to define what is an apatite.

The simplest and chemically stablest apatite is the fluoro-phosphate calcium apatite, the formula of which is

Its crystal structure is hexagonal. Projecting it on the (00.1) plane one obtains the figure 1 [1]. A first

FIG. 1. — Projection of the apatite structure on the (00.1) plane.

peculiarity is the existence of two kinds of sites for the calcium ions. The 0.0 and 0.5 ones are in a trigonal neighbourhood while the others have no symmetry element.

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One can substitute some of them by transition or rare earth ions which award interesting fluorescence properties to the apatites which are commonly used as inner coating in the strip lighting. It provides at the same time laser crystals.

Except in its crystal parameters, this structure is not appreciably modified if all the fluorines are substituted by chlorine, bromine, hydroxyl, carbonate ions. In the same way, all the calciums may give up their place to strontium or barium ions, while arsenate or vanadate ions may play the same part than the phosphates do.

For us, it is important to notice that the anions such as halogens, hydroxyls,... always stay along linear channels which run parallel to the c -axis of the hexagonal structure. According to their size the sites they occupy in the channel are different. Fluorines may stay at $c/4$ and $3c/4$, in the middle of alkaline earth triangles; bigger chlorines have not enough room and must remain near $c/2$.

When alkaline earth nitrates are dropped in solutions of diammonium hydrogen phosphate (or arsenate) containing hydrogen peroxide, one obtains at 80 °C apatite precipitates the channel of which contains OH^- , O_2^{2-} , O_2^- ions [2].

The last ones are paramagnetic and E. S. R. experiments provide informations about their behaviour in the lattice.

The results we present here, have been obtained on phosphate and arsenate apatites with calcium, strontium and barium cations. Hitherto we have not been able to work out sufficiently large single crystals, however, as we go to see now, E. S. R. results permit

TABLE I

Oxygenated apatite compounds	Calcium	Phosphate Strontium	Barium	Calcium	Arsenate Strontium	Barium
$\overline{g_z}$	2.058	2.081	2.147	2.06	2.090	2.158
$\overline{g_x = g_y}$	2.003	2.000	1.998	2.001	2.001	1.999

to put forward a proposal for the situation and the orientation of the O_2^- ion in the channel.

All the measurements were achieved with an X-band homodyne spectrometer at liquid nitrogen temperature where the spectra were spectacularly enhanced.

With such powdered samples, all these averaged spectra are characteristic of an anisotropic g -factor with two well resolved components. In the calcium arsenate apatite alone it were more difficult to determine a correct g_z value. In the table I are gathered the different g components for all the studied apatites.

These results have to be compared with those which have already been obtained by Kanzig *et al.* [3] with the same superoxide ions in alkali halides. Typically for KCl, g -components are :

$$g_x = 1.951, \quad g_y = 1.955, \quad g_z = 2.436$$

and thus the g -shifts appear being greater than in our case. Zeller and Kanzig [4] have related these g -shifts to the crystal field effect. Indeed in superoxide O_2^- ions, the unpaired electron is in an orbitally degenerated $^2\pi_g$ level. In a crystal, if the neighbourhood has not the same axial symmetry, this degeneracy is split. Taking in account, at the same time, the spin-orbit coupling interaction $\lambda L.S$ and this crystal field splitting Δ one obtains at first order :

$$g_x = g_y = g_e \cos x$$

$$g_z = g_e + 2 \sin x$$

where such is x that $\tan x = \lambda/\Delta$.

Then, it is found that the greater is the crystal field effect the weaker are the g -shifts.

At the light of these calculations what may be the interpretation of our results ?

First, the molecular axis of the O_2^- ion cannot lie along the channel axis, otherwise the molecular symmetry would not be perturbed, the orbital degeneracy would not be split and the g -shifts would be much more important.

Then, what is the position of O_2^- in the channel ? If its center stays, as the fluorines do, at $c/4$ and $3c/4$ in middle of calcium (or Sr, Ba) triangle, the surroundings would tend to make the molecular axis parallel to the channel one. It may be not the case.

Another, more interesting possibility consists to put its center at $c/2$. Then it stays in an octaedron of alkaline-earth ions as it does in alkali-halides where the octaedron is formed with alkaline ions. Proceeding on this comparison, from crystal parameters we are able to compute the dimensions of these octaedrons in the apatites. One observes first that they are slightly stretched along the c axis except for the calcium arsenate apatite in which it is slightly flattened. This distortion may be measured by the ratio p of the distances between two alkaline earth ions lying in the same (a, b) plane and two staying at two different levels along c . The table II gives these ratios. One observes that they regularly decrease from calcium to barium apatites. Furthermore the diagonal lengths l which are also given in table II, are approximatively the same than those of the alkaline octaedrons in the alkali halides (6.29 Å in KCl), but the 2^+ charges of the alkaline earth ions increase, as observed, the crystal field effect.

Now we may suppose that the orientation in the octaedron is the same as in alkali halides, that is to say, that the O_2^- ions are along medians of alkaline earth squares with their π lobes towards each of these ions. This situation is represented in figures 2a

FIG. 2a. — Projection of the channel neighbour ions on the (a, c) plane in the case of the calcium phosphate apatite.

TABLE II

Oxygenated apatite compounds	Calcium	Phosphate Strontium	Barium	Calcium	Arsenate Strontium	Barium
$\overline{\rho}$	0.982	0.967	0.955	1.004	0.975	0.966
$\overline{l (\text{\AA})}$	5.85	6.11	6.41	6.04	6.26	6.55

and 2b which are the projections of the channel neighbourhood either on the (a, c) plane or on the plane containing the c -axis and perpendicular to the a -direction. Only the ions near these planes have been drawn.

FIG. 2b. — Projection of the channel neighbour ions on the plane containing c and perpendicular to the a axis.

Another possibility would be to put, in the same square, the molecular axis perpendicular to the channel axis. However in this situation, the π lobes would be forwards the negative charges of oxygens belonging to phosphate or arsenate ions. Thus such orientation seems unlikely except, perhaps, in the case of the calcium arsenate apatite where the slight flattening of the octaedron might promote it and that would not be at variance with the experimental result.

In our hypothesis for the general case, the superoxide ion axis is slanted by an angle θ on the c -axis. We represented in figure 3 the relative variation of Δ (derived from the g_z shifts) versus the tangent of θ .

FIG. 3. — Variation of the crystal field splitting versus the tangent of the angle θ between the O_2^- molecular and the channel axes.

Except for the calcium arsenate apatite for which we saw O_2^- presents a particular behaviour, a linear variation is observed with the same slope for phosphate and arsenate apatites. We see here that the more stretched is the host octaedron the weaker is the crystal field effect, but weaker is the angle θ . So it appears that the farther neighbourhood with its axial symmetry plays an important part in the rhombic crystal field undergone by the superoxide ion.

To conclude, after these observations and their interpretations, we want point out that it is possible to obtain essentially calcium phosphate apatites with very large concentrations of such magnetic dipoles. They may stay then in neighbour sites along the channel and form linear chains. Magnetic measurements at very low temperature are at the present time in progress.

References

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DISCUSSION

J. ARENDS. — To produce your O_2^- ions you must have heated your specimen for a long time at high temperature this might change the stoichiometry considerably. In fact you are most likely not dealing with a regular apatite structure.

J. DUGAS and C. REY. — O_2^- ions are introduced in the structure during the precipitation of apatites from solutions at about 80 °C.

The samples were never heated before experiments.