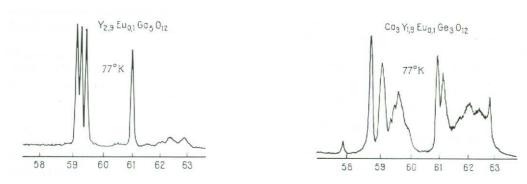# About of the limit of validity of the point groups' theory[1]

X. Oudet

Fondation Louis de Broglie, 23 rue Marsoulan, 75012 Paris, France
e-mail: xavier-oudet@wanadoo.fr

In crystallography, the atoms of a crystal are supposed to occupy a site having the properties of symmetry of a point group that is when applying these properties the site is reproduced a finite number of time.

Toward 1970, thank to a high pressure and high temperature 2000 bars-1200°C installation, the synthesis of $Ca_3Ln_2Ge_3O_{12}$ garnets has been successful [1], (Ln stand for the elements going from La to Yb to which one has to had Sc, Y and Lu). These garnets were questioning: which site the rare earths Ln occupy? Many researchers supposed that their place were the dodecahedral site at least in part, as in $Ln_3Fe_5O_{12}$. Indeed the rare earth elements are voluminous and it was a defendable argument. The calcium being equally voluminous there was reason to establish, using a different property that the volume alone, the place of these atoms. The rare earth elements are known to exhibit characteristic optical properties. The europium fluorescence gives results easy to use, in substituting a small amount of this element to yttrium. *Nevertheless, there is a trap to avoid, the selection rules based on the theory of the point groups, which are not always respected.* To avoid this theoretical approach I had chosen to compare the spectrum of $Ca_3Y_2Ge_3O_{12}$ to that of $Y_3Ga_5O_{12}$.

Figue 1. The fluorescence of europium, unit 100Å, in the garnets $Y_3Ga_5O_{12}$ and $Ca_3Y_2Ge_3O_{12}$

The results are given in the *figure 1*. The splitting of the levels is more important for the garnet of germanium with the largest lattice parameter (a = 12,810Å against 12,276Å for that of gallium). If the europium site was the same in the both garnets, the smallest splitting would be that of germanium [1]-[2].

These results do not condemn the validity of the point groups, which were and stay a precious help to determine the crystal structures. Nevertheless, before to utilise the point groups symmetry properties, it is important to remember that the crystallographic laws, as the law of the constancy of the angle between the faces of a crystal or Haüy's law also called law

---

of the simple rational troncatures, which leads to the indices of Miller, are limits laws [3]. These laws suppose perfect faces in others words a perfect crystal but there is no perfect crystals. As a result, the diagrams of X-ray are the result of a great number of diffractions of photons; they just give a mean effect upon the whole crystal. Experimentally the disorder appears through the mosaic structure of the crystals; Guinier thus concluded a discussion on the crystalline perfection: "In the great majority of the cases, the crystal ideally imperfect is a much better approximation that the perfect crystal" [4].

We find here the limit character of the point groups' theory, which is the result from the fact that the point does not have physical reality.

The optical transitions, compared to the diffraction, are reflects of what happens inside the atoms, there is no mean effect. Furthermore, the crystalline disorder can give the appearance of a higher symmetry as we already indicated with the structures cfc and La_2O_3 [5]. These remarks allow understand, that the selection rules are not always respected and confirm the occupation of the octahedral site of the rare earth in the garnets of germanium. In fact, the atom is an object for which, if to consider it as a point has allowed deducing the crystalline structures, this approximation is generally much roughly: the atom most often does not have the properties of symmetry of its site.

References

[1]   Oudet X., Synthèse en phase solide sous hautes pressions de quelques composés de type grenat et étude spectroscopique des sites de la terre rare; Ann. Chim., 8, 271-7, 1973.

[2]   Oudet X., Synthèse en phase solide sous hautes pressions de quelques composés de type grenat et étude des sites de la terre rare et de la nature des liaisons suivant le site; Thèse Orsay 1971.

[3]   G. Friedel, Leçons de Cristallographie, Librairie scientifique Albert Blanchard, 9 rue de Médicis, Paris, seconde édition, (1964)

[4]   Guinier A., « Théorie et technique de la radiocristallographie, page 141, Dunod (1956).

[5]   Oudet X., Ann. de Chimie, France, 33, 435-468, (2008).

Manuscript received the 22 november 2012