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## NEUTRON DIFFRACTION STUDY OF THE STRUCTURE OF LIQUID CERIUM AND PRASEODYMIUM

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**Résumé.** — Le facteur de structure du Cérium et du Praséodyme a été déterminé par diffraction de neutrons à la température de 1 100 C. Au préalable nous avons supposé que la diffusion paramagnétique du liquide est identique à celle du solide, pour des raisons théoriques et expérimentales. On a obtenu ensuite par transformation de Fourier la fonction de corrélation de paire et le nombre de coordination. Le facteur de structure  $S(k)$  se comporte de façon anormale, pour un ion métallique simple.

**Abstract.** — The structure factors of liquid Cerium and Praseodymium have been determined at 1 100 C by neutron diffraction. For theoretical and experimental reasons paramagnetic scattering has been assumed to be identical in both liquid and solid states. The pair correlation functions, neighbour distances and coordination number were then obtained by Fourier transform. The structure factor  $S(k)$  exhibits an anomalous behaviour compared with simple metallic ions.

**Introduction.** — During the last ten years liquid Rare Earths were the subject of important work, mainly with regard to their thermodynamic properties. However nothing was known about structural features.

A previous study of Lanthanum [1] showed evidence for an anomalous structure factor. Thus we found it interesting to investigate local order in Cerium and Praseodymium to try to observe whether or not this kind of structure was typical of the Lanthanides.

After a survey of the Rare Earths electronic properties we present the method used to estimate the paramagnetic scattering in the liquid state. Then we give the results of our measurements in the liquid phase at a temperature of 1 100 C.

We compare these data with the previous data for Lanthanum. Finally we propose various possible models to explain the observed structure factor.

**1. Rare Earths Properties.** — 1.1 ELECTRONIC PROPERTIES. — The Rare Earths are characterised by a  $4f^n$  Shell where  $n$  increases from 0 for Lanthanum to 14 for Lutetium [2]. The outer shells are 6s (2 electrons) and 5d (generally 1 electron). They both contribute to the conduction band.

The  $4f^n$  shell which produces paramagnetism is a very localized one. Its radius may be obtained as a

function of the electronic density  $\rho(r)$  :

$$\langle r^2 \rangle = \frac{\int_0^\infty \rho(r) r^4 dr}{\int_0^\infty \rho(r) r^2 dr}$$

Experiment gives [3, 4, 5] :

$$\sqrt{\langle r^2 \rangle} \simeq 0,3 \text{ \AA}.$$

Using the hydrogenoid approximation we get :

$$\Psi_{4fm} = \alpha \left( \frac{Z^*}{a_0} \right)^{3/2} r^3 r^{-r/a} Y_{3m}(\theta, \Phi)$$

where

$$a = \frac{4 a_0}{Z^*} \quad \text{and} \quad \sqrt{\langle r^2 \rangle} = \frac{2 \sqrt{56}}{Z^*} a_0$$

i.e. for an effective charge  $Z^*$  equal to 20 [3, 4, 5]

$$a_0 \simeq 0.05 \text{ \AA}.$$

Furthermore the width of 4f band is very narrow (about 0.02 eV) [3].

Thus following de Gennes [6] we assume that the 4f electrons are bonded and in this model a Rare Earth metal appears essentially as a collection of trivalent ions. The sf exchange interaction is neglected and the ff interaction lifts the degeneracy of the  $4f^n$  levels. Levels may then be classified using the values

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of orbital  $L$  and spin  $S$  quantum numbers given by Hund's rules.

The strong spin orbit coupling resulting from the high effective charges lifts the  $LS$  degeneracy. The total angular momentum  $J$  may then be used to classify levels and for light Rare Earth atoms :  $J = L - S$ . In this thesis [14] Saint-James pointed out that influence of the crystal field on the cross section for paramagnetic scattering appears to be very weak (at high temperature).

**1.2 PARAMAGNETISM.** — If melting does not affect the 4f shell we may keep the de Gennes model in the liquid state. It seems that because of their short radius the 4f orbitals are not modified at high temperature. This point seems to be entirely confirmed by experiments on transport properties. There is no change in the resistivity and Hall coefficient at the melting point [7]. Furthermore, high temperature measurements of magnetic susceptibility [8, 9, 10] have shown that the only change at the melting point is fully explained by a volume change [11]. Moreover these measurements are in full agreement with the Curie-Weiss law :

$$\chi = \frac{C}{T - \theta_c}.$$

This allows us to obtain an experimental value of the magnetic moment  $\mu$  from the well known expression :

$$C = \frac{N\mu^2}{3K_B} \quad (1)$$

and from  $\mu$  we can derive the intensity of the paramagnetic scattering at  $k = 0$ .

Thus, for experimental and theoretical reasons it seems very well justified to assume the same paramagnetic form factor for both solid and liquid states.

**2. Structure factor and correlation function.** — For a complete description of a fluid structure we need the pair correlation function,  $g(r)$  which is the Fourier transform of the structure factor  $S(k)$ . These functions were previously described [12, 13] and we shall use the same formalism.

However for a paramagnetic ion, together with the nuclear scattering these also appears a magnetic term due to the neutron electron spin interaction. So therefore a knowledge of the paramagnetic form factor  $F(k)$  is necessary to obtain the atomic structure factor  $S(k)$ .

As pointed out by D. Saint-James [14] in the static approximation we may write the cross section for paramagnetic scattering as follows :

$$\frac{d\sigma}{d\Omega} = \left( \frac{\gamma e^2}{2mC^2} \right)^2 \frac{2}{3} N g^2 J(J+1) |F(k)|^2 \quad (2)$$

$m$  = electron rest mass,

$e$  = electron charge,

$N$  = number of atoms,

$C$  = the light velocity,

$J$  = total angular momentum,

$k$  = modulus of scattering vector,

$g$  is the lande factor given by the following well-known expression :

$$g \cdot \mathbf{J} = \mathbf{L} + 2 \mathbf{S}$$

and  $\gamma$  the magnetic moment of the neutron

$$\gamma = \frac{1,91 \cdot e}{M_n C} \quad (3)$$

$M_n$  = neutron mass,

$L$  = orbital momentum,

$S$  = spin momentum.

We have already seen (1.2) that for the Rare Earths there is no change in the magnetic properties on melting. The magnetic contribution measured in the solid state can then be subtracted from the total diffusion to obtain the nuclear term.

We are now in the classical situation where we can write the differential scattering cross section per unit solid angle  $d\Omega$  and momentum transfer  $d\omega$  as follows [15] :

$$\left( \frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{\text{coh}} = N \langle b \rangle^2 \cdot \frac{K}{K_0} \cdot S \text{ coh}(k, \omega) \quad (4)$$

$N$  is the number of atoms and  $\langle b \rangle$  the coherent nuclear scattering length averaged over the spin and isotropic distributions. Then, after a double Fourier transformation of  $S(k, \omega)$  we get the correlation function  $G(r, t)$  and, within the limits of the static approximation we may write :

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{coh}} = N \langle b \rangle^2 S(k). \quad (5)$$

In order to justify the static approximation we computed the first order correction using a Placzek type method for a detector efficiency  $E \sim 1 - e^{-\gamma(k_0/k)}$  following Yarnel *et al.* [16]. The difference between the theoretical and measured intensity is proportional to  $\sin^2 \theta$  and its order of magnitude is about 0.5 % for  $2\theta = 120^\circ$ , which is smaller than the statistical counting error. Thus the static approximation appears fully justified.

**3. Experimental.** — We used the H 10 spectrometer of the Saclay EL 3 reactor which provided us with a monochromatic neutron beam of wavelength

$$\lambda = 1.132 \text{ \AA}.$$

High temperatures are obtained by high frequency induction heating (0.7 MHz). The apparatus was described in a previous paper [12]. We used cylindrical samples of Cerium and Praseodymium (9.5 mm diameter and 50 mm height) in tantalum containers.

The sample and inductors were inside a large experimental chamber (600 mm diameter, 500 mm

height) with a continuously pumped vacuum of  $10^{-6}$  torr. This chamber, already used for a study on liquid selenium [13] is large enough to give a very weak background.

Measurements were performed with angular steps of 0.25 degree. In order to obtain good statistical accuracy the counting time was about 10 min for each point.

**4. Measurements.** — **4.1 PARAMAGNETIC SCATTERING.** — As previously stated (1.2) the paramagnetic contribution to the scattering is deduced from solid state measurements. If we look at the geometry defined by our sample we can consider three regions (Fig. 1).

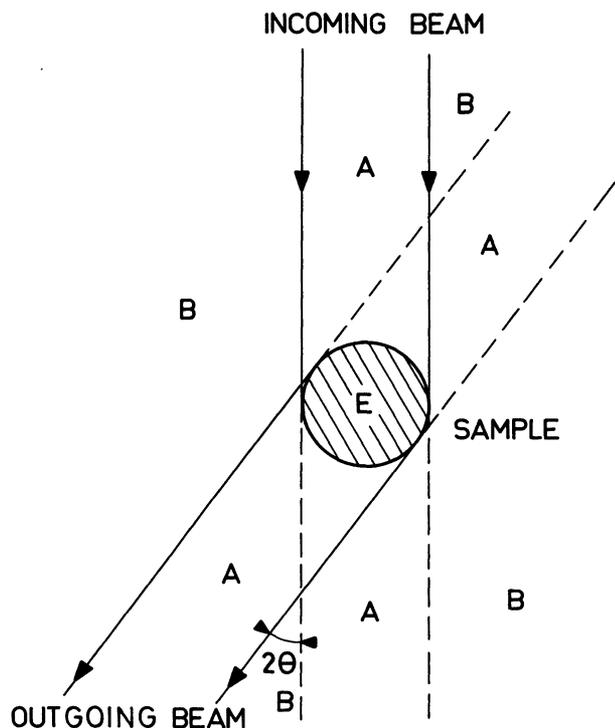


FIG. 1. — Measurement of the sample scattering at room temperature.

E : is the space occupied by the sample itself.

A : is defined by the incoming and outgoing beam as in our figure.

B : is the remaining region.

We first measure the background without any sample :

$$N_1 = i_A + i_B + i_E. \quad (6)$$

Then using a perfectly absorbing sample of the same geometry, we measure :

$$N_2 = i_B. \quad (7)$$

Then with the Rare Earths sample

$$N_3 = i_B + [A(\mu R)] i_A + i_S. \quad (8)$$

Where  $i_S$  is the sample scattering at room temperature from which we subtract the nuclear contribution and the incoherent part. In this expression  $A(\mu R)$  is

the absorption factor for a sample of radius  $R$  and linear absorption coefficient  $\mu$  [17]. Furthermore we should note, if  $2\theta > 6^\circ$ , that :

$$N_1 \simeq N_2 \quad \text{i.e.} \quad i_A + i_E \simeq 0.$$

Both of these terms are essentially due to air scattering outside the sample chamber and geometrical considerations show that in any case  $i_E$  is an order of magnitude lower than  $i_A$ . So we can take  $i_E \simeq 0$  and get a system of three equations which can be solved to obtain  $i_S$  as follows :

$$i_S = (N_3 - AN_1) - (1 - A)N_2. \quad (9)$$

A Debye-Waller correction has to be applied to  $i_S$ . This correction is of the form :  $1 - e^{-2\omega}$  with  $\omega = \alpha T$  (see Appendix).

To compute this factor, our measurements were carried out first at room temperature  $T_1$ , and later just below the melting point at temperature  $T_2$ . From the difference between these curves we deduce the coefficient  $\alpha$ , compute the Debye-Waller factor and obtain a corrected value for the paramagnetic scattering. Then, it is easy to subtract the nuclear scattering from the total scattering.

**4.2 NUCLEAR SCATTERING.** — We have measured the total intensity scattered by our liquid samples in the following conventional way :

1.  $I_1$  is the intensity scattered by the sample in its container ;
2.  $I_2$  is the intensity scattered by the empty container ;
3.  $I_3$  is a background measurement for the experimental chamber without sample or container.

Temperature tests have shown that the experimental chamber was always at room temperature so we get a system of three equations from which we can obtain the sample diffusion  $I(2\theta)$  after correction for absorption. Therefore subtraction of the paramagnetic part gives the intensity of the purely nuclear scattering.

**4.3 RESULTS.** — The experimental paramagnetic form factors for Cerium and Praseodymium are presented in figure 2 and figure 3.

We have plotted on these figures the same curves computed by D. Saint-James [14]. They are in agreement within the accuracy of our measurements (a few percent).

In figures 4 and 5 we give the structure factors  $S(k)$ . For liquid Cerium the first maximum at  $2.11 \text{ \AA}^{-1}$ , has an intensity of 1.95. For Praseodymium the intensity is 1.99 for an identical value of  $k$ . The pair correlation functions which are plotted in figure 6 and figure 7 exhibit a nearest neighbour distance of about  $3.55 \text{ \AA}$  for both Cerium and Praseodymium. Table I gives some important numerical values of  $g(r)$  for these two Rare Earths.

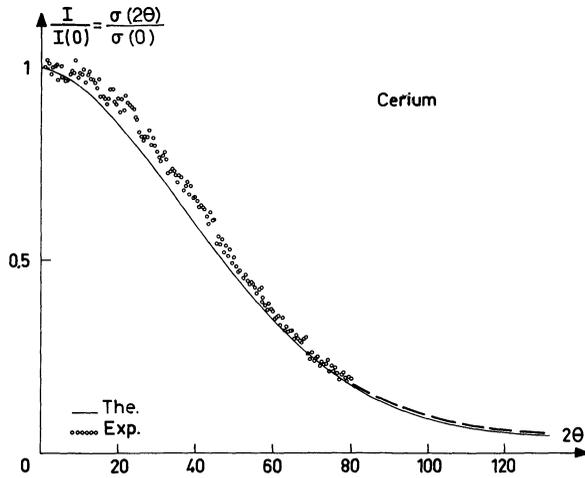


FIG. 2. — Measured and theoretical paramagnetic form factors of Cerium.

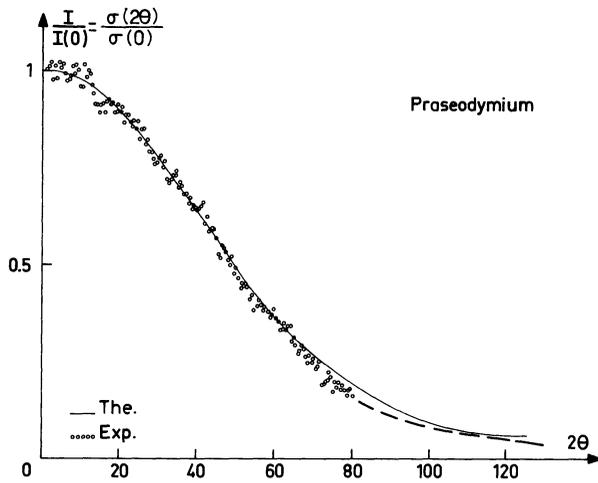


FIG. 3. — Measured and theoretical paramagnetic form factor of Praseodymium.

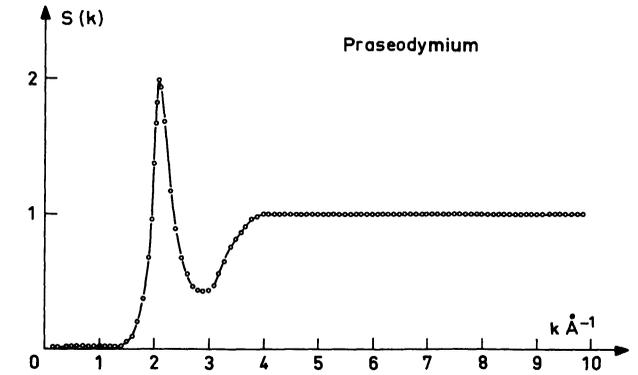


FIG. 5. — Structure factor  $S(k)$  for liquid Praseodymium at 1100 C.

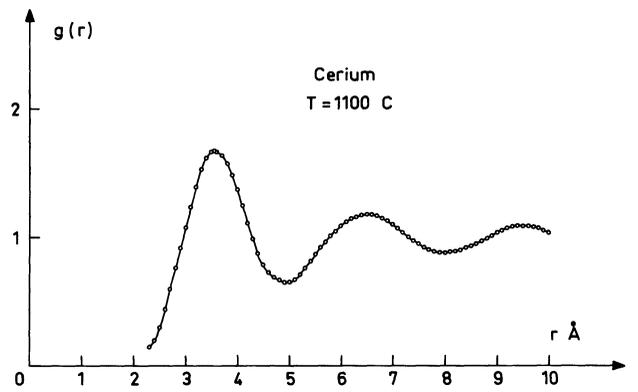


FIG. 6. — Pair correlation function  $g(r)$  of Cerium.

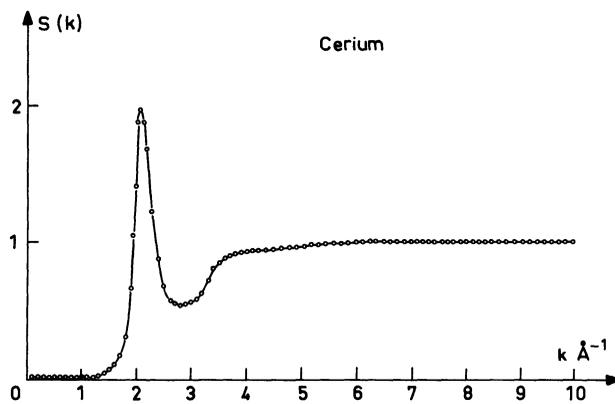


FIG. 4. — Structure factor  $S(k)$  for liquid Cerium at 1100 C.

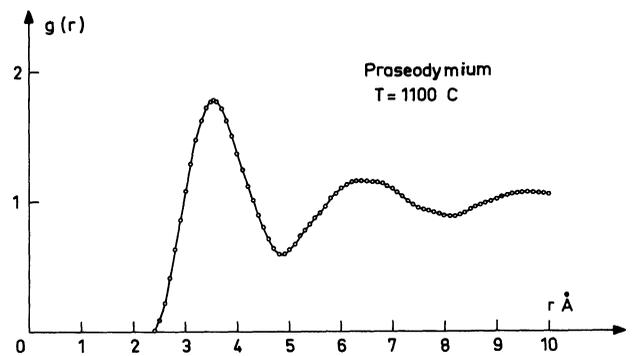


FIG. 7. — Pair correlation function  $g(r)$  of Praseodymium.

TABLE I

Peak positions of the atomic radial distribution function  $g(r)$  and coordination number  $n_1$  (temperature 1100 C).  
 Experimental errors in  $S(k)$  and  $g(r)$  are about 3% for the intensity and 1% for  $k$ .

	1st peak			2nd peak		3rd peak	
	$n_1$	Amplitude	$r$ (Å)	Amplitude	$r$ (Å)	Amplitude	$r$ (Å)
Cerium	12.3	1.68	3.57	1.18	6.50	1.09	9.45
Praseodymium	11.9	1.77	3.55	1.16	6.40	1.07	9.65

5. **Discussion.** — A look at the pair correlation function shows that the first and second neighbour distances are exactly those observed in the crystalline solid. This point can be explained by a very slight volume expansion with temperature in the solid phase and a negative volume change at the melting point [11].

The coordination numbers : 12.3 for Cerium and 11.9 for Praseodymium, are in good agreement with the compact structure of the solid.

However the structure factors  $S(k)$  have a strongly anomalous behaviour since they have only one maximum (for a  $k$  value of  $2.11 \text{ \AA}^{-1}$ ).

In this respect it appears that Cerium and Praseodymium behave like Lanthanum. This is an a posteriori argument confirming the hypothesis of a bonded 4f shell.

Local order seems therefore to be the same for all Rare Earths. However if there is an identical structure, this structure seems very difficult to explain since  $S(k)$  has only one maximum and it is very small one.

The hypothesis of a *soft potential* cannot explain our  $S(k)$  since D. Schiff has shown [18] that even for a Coulomb interaction the intensity of the first maximum is at least 2.4 and that the second one cannot be neglected. It would be possible to obtain such  $S(k)$  with extremely elongated particles (\*) but such a model seems unrealistic for the Rare Earths since we have proved that the 4f shell, which may cause anisotropy has no detectable effect on structure.

It seems that the hard sphere model of melting itself would be unrealistic for the Rare Earths. So we have to look for a mechanism able to explain a very fast disappearance of order above the melting point.

**Conclusion.** — In this work we have shown that because of the electronic properties of the 4f shell as well as the experimental high temperature data on transport properties, paramagnetic scattering for Ce and Pr has the same behaviour in both solid and liquid states. We have then measured the paramagnetic form factor  $F(k)$  at room temperature. These measurements are in full agreement within experimental errors with the theoretical values computed by D' Saint-James. Then we have performed scattering measurements in the liquid state. By subtracting the paramagnetic form factor  $F(k)$  from  $I(k)$  we deduce the structure factor  $S(k)$  of the liquid. At last by a Fourier transform, we get the pair correlation functions.

The structure factors as well as the pair correlation functions behave like those previously measured for Lanthanum.

However this kind of structure factor is very difficult to explain as it presents only one small peak.

We have shown that a soft potential model cannot explain these features. Furthermore a calculation based on ellipsoids appears to be very unrealistic for the Rare Earths.

Thus it seems that there is still no model capable of explaining short range order in the liquid Rare Earths.

## APPENDIX

Thermal motion weakens the Bragg peaks of a crystalline system by a factor  $D$  and produces a thermal diffuse scattering whose scattering cross section is proportional to :

$$(1 - D) \sigma_{\text{coh}} \quad [19].$$

In our study of paramagnetic scattering we disregard the coherent scattering term by cutting the Bragg peak. Then we have to compute the thermal diffuse scattering i.e.  $D$  factor.

According to Guinier [20] we express  $D$  in terms of the mean square displacement of the atoms  $\Delta X^2$  :

$$D = \exp \left( - \frac{16 \pi^2 \sin^2 \theta}{\lambda^2} \cdot \frac{\Delta X^2}{3} \right)$$

$D$  being the so-called Debye Waller factor. We can now compute  $\Delta X^2$  using an Einstein model :

$$\Delta X^2 = \frac{9 h^2}{4 \pi^2 m K \theta_D} \cdot \frac{T}{\theta_D} \left[ \frac{1}{4} \cdot \frac{\theta_D}{T} + \varphi \left( \frac{\theta_D}{T} \right) \right]$$

with

$$\varphi \left( \frac{\theta_D}{T} \right) = \frac{T}{\theta_D} \int_0^{\theta_D/T} \frac{x dx}{\exp x - 1}.$$

However if the experimental temperature  $T$  is above the Debye temperature  $\theta_D$  the expression :

$$M(T) = \frac{1}{4} \frac{\theta_D}{T} + \varphi \left( \frac{\theta_D}{T} \right)$$

is nearly equal to 1 as shown in the following table II.

$\frac{1}{4} \left( \frac{\theta}{T} \right) + \varphi \left( \frac{\theta}{T} \right)$  versus  $\frac{\theta}{T}$  after Guinier [20], p. 514.

We are in very close agreement with the above approximation because the Debye temperature is about 140 K for Cerium and Praseodymium. Thus we can write :

$$D = \exp - \alpha k^2 T.$$

Then the thermal diffuse scattering is

$$I_T = A \sigma_{\text{coh}} [1 - \exp(-\alpha k^2 T)].$$

We have performed two measurements at different temperatures in the paramagnetic phase. First at

(\*) Schiff, D., Private communication.

TABLE II

$\frac{\theta}{T}$	0	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	1.8	2.0	2.5
$\frac{1}{4} \left( \frac{\theta}{T} \right) + \varphi \left( \frac{\theta}{T} \right)$	1.000	1.001	1.004	1.010	1.018	1.028	1.040	1.054	1.069	1.087	1.104	1.164

room temperature :  $T_R$  and then just below the melting point :  $T_A$ . The difference pattern gives :

$$I_A(k) - I_R(k) = I_{T_A}(k) - I_{T_R}(k) = \\ = A\sigma_{\text{coh}}[\exp(-\alpha k^2 T_R)] - \exp(-\alpha k^2 T_A).$$

The knowledge of this difference for all  $k$  values allows us to compute  $\alpha$ .

We can deduce the thermal diffuse scattering value at the experimental temperature and thus obtain the paramagnetic scattering term.

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### References

- [1] BREUIL, M., TOURAND, G., *Phys. Lett.* **29A** (1969) 506.
- [2] COUBLIN, B., cours 2A, 3<sup>e</sup> cycle Orsay (1970).
- [3] KOEHLER, W. C., Thesis University of Tennessee (1953).
- [4] KOEHLER, W. C., WOLLAN, E. O., WILKINSON, M. K., *Phys. Rev.* **92** (1953) 1380.
- [5] KOEHLER, W. C., WOLLAN, E. O., *Phys. Rev.* **110** (1958) 37.  
MOON, R. M., KOEHLER, W. C., CABLE, J. W. and CHILD, H. R., *Phys. Rev. B* **5** (1972) n° 3.
- [6] DE GENNES, P. G., *C. R. Hebd. Séan. Acad. Sci.* **247** (1958) 1836.
- [7] BUCH, G., GUNTHERODT, H. J., KUNZI, H. U., MEIER, H. A., SCHLAPBACH, L., *Mat. Res. Bull.* **5** (1970) 76.
- [8] SAVITSKY, E. M. *et al.*, *Rare Earth Research*, p. 301, J. F. Nachman ed. (Gordon and Breach NY) 1962.
- [9] GUNTHERODT, H. J., SCHLAPBACH, L., *Physica* **44** (1971) 575.
- [10] ARAJSS, COLVIN, R. V., *Rare Earth Research* p. 178, J. F. Fachman ed. (Gordon and Breach NY) 1962.
- [11] PERKINS, R. H., GEOFFRION, L. A. and BIERY, J. C., *Trans. Metallurgical Society of Aime* **233** (1965) 1703.
- [12] TOURAND, G., BREUIL, M., *J. Physique* **32** (1971) 813.
- [13] TOURAND, G., *J. Physique* **34** (1973) 937.
- [14] SAINT-JAMES, D., Thèse Université de Paris (1912).
- [15] VAN HOVE, L., *Phys. Rev.* **95** (1954) 249.
- [16] YARNELL, J. L., KATZ, M. J., WENZEL, R. G. and KOEINIG, S. H. Los Alamos Rep. LA-UR-73-43 (1973).
- [17] MERIEL, P., BOUTRON, F., *Bull. Soc. Fse. Minér. Crist.* **83** (1960) 125.
- [18] HANSEN, J. P., SCHIFF, D., *Molecular Physics* **25** (1973) n° 6, 1281, 1290.
- [19] BACON, G. E., *Neutron Diffraction* (Oxford Clarendon Press) 1962.
- [20] GUINIER, A., *Théorie et Technique de la Radiocristallographie* p. 513 (Dunod, Paris) 1956.