U4+ form factor in UGa2

Rafik Ballou, A. Deriagin, F. Givord, R. Lemaire, R. Levitin, F. Tasset

► To cite this version:

Rafik Ballou, A. Deriagin, F. Givord, R. Lemaire, R. Levitin, et al.. U4+ form factor in UGa2. Journal de Physique Colloques, 1982, 43 (C7), pp.C7-279-C7-285. 10.1051/jphyscol:1982740 . jpa-00222347

HAL Id: jpa-00222347

<https://hal.science/jpa-00222347>

Submitted on 1 Jan 1982

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

U^{4+} FORM FACTOR IN UGa_2

R. Ballou*, A.V. Deriagin⁺, F. Givord*, R. Lemaire*, R.Z. Levitin** and F. Tasset⁺⁺

*Laboratoire Louis Néel, C.N.R.S., 166X, 38042 Grenoble Cedex, France

⁺Ural State University, Sverdlovsk, U.S.S.R.

**Moscow State University, Moscow, U.S.S.R.

⁺⁺Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France

Résumé. - UGa_2 cristallise dans la structure hexagonale de type AlB_2 et une forte distorsion orthorhombique est observée dans l'état ferromagnétique ($T_C = 125$ K) due à une magnétostriction gigantesque. Nous avons effectué une étude par neutrons polarisés à 4,2 K dans un champ magnétique de 46,2 kOe, appliqué parallèlement à l'axe de facile aimantation $\vec{a}$. Nous avons mesuré les intensités intégrées afin d'affiner les facteurs de structure nucléaires dans la structure distordue. La projection de la densité magnétique sur un plan (100) met en évidence une forte densité sur les sites d'uranium presque sphérique, l'absence de densité sur les sites de gallium et une faible polarisation positive entre les atomes. Le facteur de forme de l'uranium déduit a été analysé afin de déterminer l'état fondamental. Nous pensons que les atomes d'uranium sont dans l'état de valence U^{4+} . Le facteur de forme observé correspond à une délocalisation des électrons 5f plus grande que celle calculée dans l'approximation du couplage de Russell-Saunders. Un premier calcul, utilisant l'approximation dipolaire dans le cadre du couplage intermédiaire, associée à la contribution d'une polarisation positive, a pu rendre compte de la variation observée du facteur de forme de l'uranium.

Abstract. - UGa_2 crystallizes in the hexagonal AlB_2 type structure and a large orthorhombic distortion is observed in the ferromagnetic state ($T_C = 125$ K) due to a giant magnetostriction. A polarized neutron study has been performed at 4.2 K in a magnetic field of 46.2 kOe, applied parallel to the easy magnetization axis $\vec{a}$. Integrated intensities have been measured for the refinement of the nuclear structure factors in the distorted structure. The projection of the magnetic density on the (100) plane evidences a large and almost spherical density on U sites, no density on the Ga sites, and a slight positive polarization between the atoms. The deduced U form factor has been analyzed in order to determine the magnetic ground state. We think that the uranium atoms are in the $4+$ state. The observed form factor corresponds to a larger delocalization of the 5f electrons than that calculated in the Russell-Saunders coupling approximation. A first calculation using the dipole approximation in the intermediate coupling framework, associated with the contribution of a positive polarization can account for the observed variation of the U form factor.

1. Introduction

UGa_2 crystallizes in the hexagonal AlB_2 -type phase structure (space group $P6/mmm$) with the lattice parameters $a = 4.213$ Å and $c = 4.017$ Å at room temperature. The compounds RGa_2 , R being a Rare Earth, crystallize in the same structure(1), in particular the lattice parameters of $NdGa_2$ at 300 K are $a = 4.27$ Å and $c = 4.27$ Å(2), values slightly larger than those of UGa_2 .

UGa_2 is ferromagnetic below $T_C = 125$ K. Its magnetostatic behaviour has been studied previously on a single crystal(3). A large orthorhombic distortion of the hexagonal lattice is observed in the ferromagnetic state due to a giant magnetostriction ($\lambda_{Y,2} = -4 \times 10^{-3}$ at 4.2 K). The easy magnetization axis is the $\vec{a}$ -axis. A huge magnetocrystalline anisotropy is observed : at 4.2 K, the anisotropy field is

of the order of 10^6 Oe. It should be noticed that this anisotropy field is comparable with the magnitude of the molecular field ($H_M \sim 2 \times 10^6$ Oe). Magnetization curves at 4.2 K in magnetic fields applied along the three principal symmetry

Figure 1 : Magnetization curves at 4.2 K in magnetic fields applied along the three principal directions of symmetry in the single crystal of UGa_2 .

directions in the crystal are shown in figure 1. At this temperature, the spontaneous magnetization is $2.71 \mu_B$ per uranium atom. In the paramagnetic state, the susceptibility is highly anisotropic. To the contribution of 5f electrons which follows a Curie-Weiss law is superposed a temperature independent component χ_0 . Depending whether the susceptibility is measured in a direction parallel to the $\vec{a}$ -axis or $\vec{c}$ -axis, the paramagnetic Curie temperature reaches $\theta_p // \vec{a} = 134$ K and $\theta_p // \vec{c} = -64$ K. The effective magnetic moment has a value $2.8 \mu_B$ which is quite lower than those of U^{3+} ($3.62 \mu_B$) and U^{4+} ($3.58 \mu_B$) ions, calculated in the Russell-Saunders coupling framework: $\mu_{eff} = g_J(J(J+1))^{1/2}$.

The deficient value of the saturation magnetic moment in UGa_2 can either be due to crystal field effects also responsible for the magneto-crystalline anisotropy and the magnetostriction or to a possible delocalisation of the 5f electrons corresponding to a large hybridization with the conduction band. However a recent X-ray photo-emission study⁽⁴⁾ of UGa_2 pointed out the presence in the spectra of satellites due to two-hole final states which is an indication for a weak fd hybridization, that is an increase of the 5f localization as compared to that in other uranium compounds.

The determination of the magnetic density in UGa_2 by diffraction of polarized neutrons on a single crystal has been undertaken to specify the degree of localization of the 5f electrons. The analysis of the form factor allowed us to characterize the nature of the ground state and to show the crystal field effects.

2. Experimental

Measurements were performed at 4.2 K on the D3 (I.L.L.) polarized neutron diffractometer ($\lambda = 0.9$ Å). The single crystal is nearly parallelepipedic ($1.5 \times 1.2 \times 0.9$ mm³) with the largest dimension along the $\vec{a}$ -axis; it was placed in a superconducting split-coil magnet with the easy magnetization axis $\vec{a}$ vertical and parallel to the applied magnetic field of 46 kOe. It was cooled in the applied field in order to avoid domain formation.

To refine the nuclear structure factors in the orthorhombic symmetry associated with the magnetocrystalline distortion, measurements of integrated intensities of all Bragg reflections of the type (0kl) and (lkl) (orthorhombic indices), out to $\sin\theta/\lambda = 0.53$ Å⁻¹, have been undertaken first, for one fixed polarization state of incident neutrons.

We have then carried out measurements of the so-called polarization ratio R, for all Bragg reflections out to $\sin\theta/\lambda = 1$ Å⁻¹ in the zero layer ($h = 0$) and first upper layer ($h = 1$). The value of R for a given reflection may be written as :

$$R = \frac{1 + 2q^2\gamma + q^2\gamma^2}{1 - 2q^2\gamma + q^2\gamma^2}, \quad \text{where } q^2 = \sin^2\alpha,$$

with α being the angle between the scattering vector k and the field H and $\gamma = F_M/F_N$, where F_M and F_N are the magnetic and nuclear structure factors, respectively. This relation between γ and R has to be modified to take account of imperfections of the instrument and of perturbing characteristics of the sample. In particular,

correction for incomplete incident polarization and depolarization by the sample was made by studying the thermal variation of the polarization ratio of the (001) reflection which goes through a minimum at 50 K. A comparison of the polarization ratio for several reflections measured at different wavelengths has shown that in the limit of experimental precisions the correction of extinction was negligible. From the observed values of R_p , precise values of γ were deduced except for reflections with large R ($\gamma \sim 1$).

3. Results

The only reflections observed were those satisfying the equality $h+k = 2n$ which is a characteristic existence rule of space group $Cmmm$. The lattice parameters at 4.2 K are $a = 4.190 \text{ \AA}$, $b = 7.287 \text{ \AA}$ and $c = 4.011 \text{ \AA}$. The crystallographic structure at 4.2 K was refined from the integrated intensities corrected by the Lorentz factor and absorption. The magnetic contributions to these intensities were taken into account with the aid of γ values deduced from the measurements of the polarization ratios. The position of the atoms in the lattice cell, their nuclear scattering lengths and their temperature factors are collected in the Table 1.

The corresponding reliability factor defined as

$$\sqrt{\sum_{hkl} \frac{1}{\sigma} |F_{Ncalc} - F_{Nobs}|^2 / \sum_{hkl} \frac{1}{\sigma} |F_{Nobs}|^2} \text{ is equal to } 2 \text{ \%}.$$

In conclusion, the magnetocrystalline distortion affects essentially the lattice parameters and not the positions of the atoms in the lattice cell, since, in an orthorhombic description, the value of the parameter y corresponding to an undistorted structure is $1/3$.

Table 1 : Results of the crystallographic refinement in the orthorhombic structure.

atom	nuclear scattering length	site	positions	Debye-Waller factors
U	0.842 (5)	2a	(000)	$B_{11}^U = 0.48 (8)$ $B_{22}^U = 0.48 (8)$ $B_{33}^U = 0.42 (6)$
Ga	0.720 (4)	4j	$(0, y, \frac{1}{2})$ $y = 0.333 (1)$	$B_{11}^{Ga} = 0.46 (8)$ $B_{22}^{Ga} = 0.46 (8)$ $B_{33}^{Ga} = 0.45 (7)$

The magnetic structure factors have been obtained from the values of γ and the nuclear structure factors deduced from the nuclear structure refinement. Their values are sorted in table 2 according to their $\sin\theta/\lambda$ value and their type of geometric nuclear structure factor. The determination of the magnetic structure factor is less precise for some reflections of type 4 because of their large polarization ratio value.

The deduced magnetic structure factors $F_M(0kl)$ for a section in reciprocal space lead by Fourier inversion to the projection of the magnetic density on the (100) plane. The value of the bulk magnetization is introduced as a constant $F_M(000)$ term in the series. The projection is shown in fig. 2. The magnetization is essentially localized on the uranium site and shows little anisotropy. A weak positive diffuse density can be noticed. The variation of the magnetic structure factor with $\sin\theta/\lambda$ shown in figure 3 is then characteristic of the uranium form factor in UGa_2 . The anisotropy of this form factor is weak. The solid line in figure 3 represents a guide for the eye through the observations, it is divided by the uranium bulk magnetic moment ($2.72 \mu_B$)

Table 2 : Magnetic structure factors for UGa_2 at 4.2 K. F_{M1} , F_{M2} , F_{M3} , F_{M4} correspond respectively to the geometric nuclear structure factor $b_U + 2b_{Ga}$, $b_U + b_{Ga}$, $b_U - 2b_{Ga}$ and $b_U - b_{Ga}$.

h k l	sin θ/λ	$F_{M1} (u_B)$	$F_{M2} (u_B)$	$F_{M3} (u_B)$	$F_{M4} (u_B)$
0 0 1	0.1247			5.24 (20)	
0 2 0	0.1372				4.96 (6)
1 1 0	0.1377				4.88 (13)
0 2 1	0.1854		4.45 (3)		
1 1 1	0.1857		4.33 (4)		
1 3 0	0.2379	3.65 (3)			
0 0 2	0.2493	3.67 (2)			
1 3 1	0.2686			3.36 (11)	
0 4 0	0.2745				3.68 (9)
0 2 2	0.2846				3.57 (9)
1 1 2	0.2848				3.49 (6)
0 4 1	0.3014		3.10 (3)		
1 3 2	0.3446	2.60 (2)			
1 5 0	0.3632				2.82 (14)
0 4 2	0.3708				2.76 (12)
0 0 3	0.3760				
1 5 1	0.3840		2.28 (2)		
0 2 3	0.3984		2.14 (2)		
1 1 3	0.3985		2.16 (2)		
0 6 0	0.4117				
0 6 1	0.4302	1.99 (3)			
1 5 2	0.4406			1.91 (8)	
1 3 3	0.4432				1.89 (11)
0 4 3	0.4639		1.57 (2)		
0 6 2	0.4813	1.43 (2)			
1 7 0	0.4849				1.46 (16)
0 0 4	0.4986	1.35 (2)			
1 7 1	0.5104		1.26 (2)		
0 2 4	0.5172				1.69 (23)
1 1 4	0.5173				1.56 (21)
1 5 3	0.5213		1.18 (2)		
0 8 0	0.5489				1.52 (36)
1 3 4	0.5525	1.00 (2)			
0 6 3	0.5562			1.00 (5)	
0 8 1	0.5629		0.96 (3)		
0 4 4	0.5692				1.19 (26)
0 8 2	0.6029				0.34 (25)
1 7 3	0.6203		0.65 (2)		
0 0 5	0.6233			0.76 (6)	
1 9 0	0.6290	0.61 (2)			
0 2 5	0.6382		0.61 (2)		
1 1 5	0.6383		0.66 (3)		
1 9 1	0.6412			0.58 (6)	
0 6 4	0.6466	0.55 (2)			

h k l	sin θ/λ	$F_{M1} (u_B)$	$F_{M2} (u_B)$	$F_{M3} (u_B)$	$F_{M4} (u_B)$
0 8 3	0.6642		0.49 (2)		
1 3 5	0.6672			0.51 (5)	
1 9 2	0.6766	0.49 (2)			
0 4 5	0.6810		0.43 (2)		
0 10 0	0.6862				0.17 (17)
0 10 1	0.6974		0.39 (2)		
1 5 5	0.7214		0.32 (3)		
0 10 2	0.7300				0.19 (11)
1 9 3	0.7317			0.39 (5)	
8 4	0.7416				0.14 (12)
0 6 5	0.7470			0.29 (4)	
0 0 6	0.7479	0.30 (2)			
0 2 6	0.7604				0.21 (8)
1 11 1	0.7742		0.25 (3)		
0 10 3	0.7814		0.24 (2)		
1 3 6	0.7849	0.21 (2)			
1 7 5	0.7959		0.16 (3)		
0 4 6	0.7967				0.07 (5)
1 9 4	0.8026	0.15 (2)			
0 12 0	0.8234	0.14 (2)			
0 8 5	0.8305		0.14 (2)		
0 12 1	0.8328			0.18 (4)	
0 10 4	0.8482				0.07 (11)
1 11 3	0.8507		0.11 (4)		
0 6 6	0.8538	0.13 (2)			
0 12 2	0.8603	0.09 (4)			
0 0 7	0.8726			0.30 (10)	
0 2 7	0.8833		0.14 (3)		
1 1 7	0.8834		0.09 (2)		
1 9 5	0.8855			0.03 (11)	
0 12 3	0.9043			0.06 (5)	
1 3 7	0.9045			0.11 (17)	
1 13 1	0.9085		0.13 (3)		
0 4 7	0.9147		0.05 (2)		
0 10 5	0.9270		0.08 (2)		
0 8 6	0.9278				0.13 (12)
1 5 7	0.9452		0.10 (3)		
0 14 0	0.9606				-0.20 (41)
0 12 4	0.9626	0.03 (3)		0.07 (16)	
0 6 7	0.9648				
0 14 1	0.9687		0.04 (3)		
1 13 3	0.9746		0.06 (3)		
1 9 6	0.9772			0.07 (3)	
1 11 5	0.9861		0.04 (2)		

4. Discussion

Strictly speaking, in uranium, the spin-orbit interaction cannot be considered

Figure 2 : Projection of the magnetic density on the (100) plane.

as a small perturbation to the Coulomb interactions that is the mixing of spectral terms due to spin-orbit interaction is no longer negligible⁽⁶⁾. However, as a first attempt to interpret the observed form factor, we consider that the ground state results from the application of the Russell-Saunders coupling and, thus is a linear combination of states $|JM\rangle$: $|\Psi\rangle = \sum_M \lambda_M |JM\rangle$.

Within the tensor-operator method^(7,8), the magnetic scattering length is defined as a vector $\vec{E}$ with spherical components E_q given by

$$E_q(h) = - \sum_{K''Q''} \sqrt{4\pi} Y_{Q''}^{K''}(h) \sum_{K'Q'} \left[\sum_{MM'} \lambda_M \lambda_{M'} (A(K'',K') + B(K'',K')) \right] \langle K'Q'JM' | JM \rangle \langle K''Q''K'Q' | 1q \rangle$$

Figure 3 : Variation of observed magnetic structure factors with $\sin\theta/\lambda$.

$Y_{00}^{K''}(h)$ are spherical harmonics depending on the orientation of the vector $\vec{h}$ in the reciprocal space. $A(K'',K')$ represents the orbital contribution to the form factor, $B(K'',K')$ represents the spin contribution. They can be expressed in terms of quantities A' and C' and of radial integrals $\langle j_k(h) \rangle$ which depend on the radial part of the one electron wave function (10,11). The quantities A' and C' being independent on the principal quantum number n , we have used for U^{3+} ($4f^3$) and for U^{4+} ($3f^4$) values tabulated⁽⁹⁾ for Nd^{3+} and Pr^{3+} respectively. The form factor analysis has been carried out with equatorial plane reflections (0kl) since only the component E_0 is required.

In the dipole approximation the form factors corresponding to the ground multiplet $3H_4$ and $4I_{9/2}$ of the free ions U^{4+} and U^{3+} respectively are close together (figure 4) and none of them correspond to our observed mean form factor which decreases more rapidly.

The effects of crystal field due to an uniaxial environment allow to determine the valence state of uranium. The magnetic moment of uranium is largely reduced it is at most equal to $2.72 \mu_B$. Only a combination $0.84|44\rangle - 0.54|42\rangle$ in the ground multiplet $3H_4$ of the U^{4+} ion leads to a form factor practically isotropic and in reasonable agreement with the observed form factor. As a matter

Figure 4 : U^{3+} and U^{4+} form factors in the dipole approximation. The solid line represents a guide for the eye through the observation.

of fact, all the magnetic amplitudes expressions calculated with wavefunctions corresponding to the U^{3+} ion exhibit large anisotropic contributions. This is illustrated in figure 5 as explained in its caption. This result is coherent

Figure 5 : Magnetic form factors mf calculated in two orthogonal directions ($0k0$, $00l$) for the U^{3+} ground state $0.79|9/2 - 9/2\rangle - 0.61|9/2 - 5/2\rangle$ ($m = 2.72 \mu_B$)

Figure 6 : Magnetic form factors calculated as in figure 5, but for two different ground states of the U^{4+} ion : $0.84|44\rangle - 0.54|42\rangle$ ($m = 2.72 \mu_B$) (—) $0.75|44\rangle - 0.66|42\rangle$ ($m = 2.5 \mu_B$) (-----)

with the values of the lattice parameters in UGa_2 which are very close to those of the isomorphic compound $NdGa_2$. Indeed, uranium having an atomic number larger than the neodymium, one must be in a valence state greater than +3 to have practically the same dimension as the ion Nd^{3+} in $NdGa_2$. However, the decrease of the apparent observed form factor is more rapid than the one calculated (figure 6). This effect may be due to the superposition of a positive polarization of the conduction band in agreement with the map of magnetization density. The best fit can be obtained with a diffuse polarization of $0.22 \mu_B$ per uranium atom. Nevertheless, this polarization is far from being uniform for it affects the observed form factor until $\sin\theta/\lambda = 0.3 \text{ \AA}$. Such a positive polarization often found in cerium compounds⁽¹²⁾ ($CeAl_2$) is characteristic of fd hybridization.

The above calculations carried out with the Russell-Saunders coupling approximation is not very rigorous since when working in the intermediate coupling framework we obtain a ground state $|\psi\rangle$ of the U^{4+} ion which is a combination of states with only 89 % of components of the multiplet 3H_4 ⁽¹³⁾. This state is written in the $|LSJM\rangle$ basis as :

$$|\psi\rangle = 0.945|^3H_4M\rangle - 0.314|^1G_4M\rangle + 0.093|^3F_4M\rangle.$$

The values of L_z and S_z corresponding to this state with $M = J$ are respectively 4.714 and -0.714 while those corresponding to the principal component (3H_4) are 4.8 and -0.8. The form factor of this state has been calculated in the dipole approximation :

$$(L_z + 2S_z)f = 2\langle j_o \rangle S_z + (\langle j_o \rangle + \langle j_2 \rangle)L_z$$

Figure 7 : U^{4+} form factor in the dipole approximation respectively within the Russell-Saunders and intermediate coupling.

In figure 7, it is compared with the one calculated for 3H_4 multiplet. Its more rapid decrease is due to the component 1G_4 of spin zero and leads to a best agreement with the form factor observed in UGa_2 .

Finally, the polarized neutron study of UGa_2 allowed us :

- i) to determine the valence state U^{4+} of the uranium ion
- ii) to show that the uranium form factor when calculated in the intermediate coupling framework gives a better agreement with experimental results
- iii) to evidence a positive diffuse polarization of the electrons in the conduction band.

Presently we are calculating the crystal field effects within the intermediate coupling in order to define more precisely this positive polarization and the ground state wave function.

Acknowledgements

We would like to thank J.X. Boucherle, D. Gignoux and D. Givord for helpful and profitable discussions.

References

- (1) RAMAN A., Z. Metallk. 58 (1967) 179.
- (2) IANDELLI A., PALENZONA A., in Handbook on the physics and chemistry of rare earth, Ed. by K.A. Gschneidner, Jr. and L. Eyring (North Holland Publishing Company, Amsterdam) 2 (1979) 32.
- (3) ANDREEV A.V., BELOV K.P., DERYAGIN A.V., KAZEI Z.A., LEVITIN R.Z., MENOVSKY A., POPOV Yu.F., SILANT'EV V.I., Sov. Phys. JETP 48 (1978) 1187.
- (4) SCHNEIDER W.D., LAUBSCHAT C., Phys. Rev. Letters 46 (1981) 1023.
- (5) KOESTER L., RAUCH H., Table of neutron scattering length (Favoprint, Austria, 1981).
- (6) CHAN S.K., LAM D.J., in The actinides : electronic structure and related properties, Ed. by A.J. Freeman and J.B. Barby, Jr. (Academic Press, New York) 1974, p. 14.
- (7) JOHNSTON D.F., Proc. Phys. Soc. 88 (1966) 37.
- (8) LOVESEY S.W., RIMMER D.E., Rep. Prog. Phys. 32 (1969) 333.
- (9) LANDER G.H., BRUN T.O., J. Chem. Phys. 53 (1970) 1387.
- (10) FREEMAN A.J., DESCLAUX J.P., LANDER G.H., FABER J. Jr., Phys. Rev. B 13 (1976) 1168.
- (11) DESCLAUX J.P., FREEMAN A.J., J.M.M.M. 8 (1978) 119.
- (12) BOUCHERLE J.X., International Conference on Valence Instabilities, Zurich (1982).
- (13) RAHMAN H.U., RUNCIMAN W.A., J. Phys. Chem. Solids 27 (1966) 1833.