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Citation: The Journal of Chemical Physics **89**, 3295 (1988); doi: 10.1063/1.454935
View online: http://dx.doi.org/10.1063/1.454935
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Magnetic structure and Pu ground state in β-Pu_2O_3

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(Received 22 April 1988; accepted 13 May 1988)

Neutron diffraction from a polycrystalline sample of $^{242}Pu_2O_3$ (La_2O_3 structure) has been used to solve the magnetic structure below $T_N = 19$ K. The magnetic unit cell requires a doubling in all three crystallographic directions of the chemical unit cell. Below 4 K the magnetic and chemical unit cells become identical. The moments point along the unique c axis at all temperatures below T_N. The magnetic moment is $0.60(2)\mu_B$ per Pu ion and the C_2 coefficient in the Pu^{3+} form factor is 4.5(3). The value of the moment, its direction within the unit cell, and the C_2 coefficients are all consistent with the $|\pm 3/2\rangle$ Kramers doublet being the ground state of the Pu^{3+} ion.

I. INTRODUCTION

In earlier studies performed at Argonne National Laboratory, reports were presented of the preparation,[1] heat capacity, magnetization,[2] and magnetic structure[2] of β-Pu_2O_3 in the temperature range ~3 to 350 K. These studies give a fairly complete picture of the properties of this compound, with one exception. The determination of the magnetic structure of Pu_2O_3 was not resolved, nor was the second transition at $T \sim 4$ K understood. Our motivation in the present work was to resolve those questions.

β-Pu_2O_3 has the hexagonal La_2O_3 unit cell with one molecular per unit cell. The Pu configuration is trivalent Pu^{3+}:$5f$.[5] At low temperature the ion should therefore be magnetic. As reported earlier[1,2] this is indeed the case; the material exhibits an antiferromagnetic transition at ~19 K. The crystal-field interaction will give rise to the $J = 5/2$ manifold being split into three Kramer's doublets. The total manifold splitting as deduced from thermodynamic data is between 100 and 300 cm^{-1}, with the first excited state at ~50 cm^{-1}. No information is available on the precise eigenfunction of the ground state.

One of the most intriguing aspects of Pu_2O_3 was the discovery by neutron diffraction of a second magnetic transition below T_N at ~4 K. No sign of this was reported in the magnetization experiments[2] reported in the same paper. (The heat capacity data[1] did not extend to low enough temperature to address this issue.) Although the magnetization is not sensitive to all changes of magnetic structure, the particular change proposed by McCart *et al.*[2] involved a reorientation of the spin direction, and such a transmission should drastically affect the magnetization. Furthermore, spin reorientations are extremely rare in actinide systems because such systems usually exhibit very large magnetic anisotropy. A spin reorientation must therefore either overcome a large anisotropy barrier or change it.

In this paper we report neutron experiments that resolve some of the above dilemmas. We are also able to assign the eigenfunctions of the ground state of the Pu^{3+} ion.

II. EXPERIMENTAL

We have used *exactly* the same sample as used in the earlier neutron experiments. It consisted of 9.44 g of $^{242}Pu_2O_3$ powder, encapsulated first in a vanadium tube, and then further doubly encapsulated in aluminum. The inner vanadium container was 12 mm in diameter and 25 mm long, the outer Al container had a diameter of 35 mm. This rather unusual configuration was simply to accomodate the original Argonne V container into a standard double Al container accepted by the Institut Laue Langevin as safe for neutron experiments on transuranium samples. The capsule was then placed in a modified ILL (orange) cryostat capable of temperatures between 1.5 and 300 K. As can be realized form the above description of the sample the loose powder, which itself has a poor thermal conductivity, was not in good contact with the cold plate of the flow cryostat. As a consequence it proved impossible to lower the temperature of the sample below the second transition ($T < 4$ K), despite reaching 1.5 K in the He bath. The implications of this will be discussed later.

The neutron experiments were conducted on the D2B powder diffractometer at the High-Flux reactor of the ILL, Grenoble, France. An incident beam of $\lambda = 2.396$ Å neutrons was diffracted from a curved pyrolitic graphite monochromater. The collimation before the sample was 0.5° giving a resolution $\Delta d/d = 4.3 \times 10^{-3} \cot\theta$, where θ is the Bragg angle, in the high-intensity lower resolution configuration. A full description of the instrument is given by Hewat.[3]

III. RESULTS AND ANALYSIS

A. Atomic structure

A complete study of atomic structure was reported in Ref. 2 both below (13 K) and above (40 K) the magnetic transition temperature. Our results here are completely consistent with the earlier results, and are given in Table I. Note that we have not attempted a complete refinement of the atomic structure in this experiment; for a start, because we chose a long wavelength to resolve the magnetic lines, our data on D2B extend only to $\sin\theta\lambda \sim 0.4$ Å^{-1}, whereas those previously taken in Ref. 2 extend to $\geqslant 1$ Å^{-1}, so that the larger error bars do not reflect the capability of D2B. However, the parameters are in good agreement, and that this is a good description of the structure can be seen by the good

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TABLE I. Atomic parameters either refined (with standard deviation referring to least significant digit) or assumed for Pu_2O_3. Atoms positions are $Pu(\frac{1}{3},\frac{2}{3},z)$; $O_1(0,0,0);O_2(\frac{1}{3},\frac{2}{3},z)$. The structure is centrosymmetric, space group 164.

		Ref. 2	This work
Lattice parameters	a	3.8380(5)	3.838(1) Å
	c	5.9175(5)	5.918(1) Å
Scattering lengths	b_0	0.5803	0.5803×10^{-12} cm
	b_{Pu}	0.798(7)	0.80
O/Pu ratio		1.481(5)	1.48
Atomic positions	$z(Pu)$	0.2422(4)	0.2408(8)
	$z(O_2)$	0.6489(4)	0.6451(8)

agreement between the observed and calculated nuclear intensities in Table II.

The principle purpose of this refinement is to establish a scale factor between the nuclear and magnetic intensities; this scale factor gives the magnetic moment/Pu atom.

B. Magnetic structure: $4<T<19$ K

As found previously we find $T_N\sim19$ K. The subtraction spectra $I(6\text{ K})$-$I(27\text{ K})$ are shown for $20°<2\theta<100°$ in Fig. 1. The positions of the nuclear peaks are marked above the figure; note that these do not always perfectly subtract as a small thermal contraction takes place. The magnetic peaks are on the average 20–40 times weaker than the nuclear peaks.

The magnetic peaks can all be indexed on a unit cell that is *doubled* in all directions as compared to the chemical unit cell. Thus $\mathbf{a}_M=2\mathbf{a}$; $\mathbf{b}_M=2\mathbf{b}$; and $\mathbf{c}_M=2\mathbf{c}$, where **a**, **b**, and **c** refer to the chemical unit cell. Under these conditions the $(hk.l)$ integers of the magnetic reflections may be indexed with those of the chemical cell by using half integers, e.g., $M(11.1)\equiv(\frac{1}{2}\frac{1}{2}\cdot\frac{1}{2})$ and $M(31.2)\equiv(\frac{3}{2}\frac{1}{2}\cdot1)$, etc. On the figure all M-indexed peaks are in this notation. As can be seen from Table III we have succeeded in measuring 15 nonzero magnetic reflections.

TABLE II. Nuclear intensities in Pu_2O_3 at $T=25$ K. $(hk.l)$ is indexed on the chemical unit cell (**a**, **b**, **c**). θ is the Bragg angle ($\lambda=2.396$ Å). I_{obs} and I_{calc} are observed and calculated nuclear intensities, respectively. The standard deviation refers to the least significant digit. The column I_{mag} corresponds to the magnetic intensity expected in the low-temperature ($T<4$ K) phase at each nuclear reflection. The intensity scale is arbitrary.

$hk.l$	2θ	I_{obs}	I_{calc}	I_{mag}
10.0	42.25	699(10)	628	14
00.2	47.76	426(10)	442	0
10.1	48.83	1707(15)	1714	40
10.2	65.65	3235(25)	3269	3
00.3	74.79	161(8)	234	0
11.0	77.26	4286(30)	3982	7
10.3	89.85	1685(20)	1859	1
20.0	92.25	251(10)	185	1
11.2	96.16	1120(15)	938	3
20.1	96.96	741(15)	627	3
00.4	108.14	111(10)	108	0
20.2	111.54	1705(20)	1833	0
11.3	121.14	892(15)	963	0
10.4	124.83	317(10)	386	0

Before continuing to explain the magnetic structure in detail it seems worth while to point out why and how the previous work failed to get the correct structure. The first point to note is that the $M(10.1)$ is very close in position to the (00.1). The Δd space difference is 0.12 Å in 5.80 Å, i.e., $\Delta d/d\sim2\%$. In fact in the early (reactor) work at Argonne the instrumental resolution was about 1.5%, so this was misidentified as a magnetic peak at the nuclear (00.1) position. Since the magnetic interaction vector

$$q^2=\sin^2\alpha\,, \tag{1}$$

where α is the angle between the spin direction $\boldsymbol{\mu}$ and the scattering vector **Q**, a nonzero magnetic contribution at (00.1) would signify a component of $\boldsymbol{\mu}$ in the basal plane of the hexagonal structure. For $\boldsymbol{\mu}\|\mathbf{c}$ $q^2(00.1)=0$. Only two further magnetic peaks were seen in the first ANL experiments, $M(11.1)$ and $M(21.1)$. Other peaks were either too close to nuclear peaks or too weak. Having assumed a contribution at (00.1) the authors were unable to satisfactorily index the other two peaks. An attempt was later (1982) made on the pulsed source at ANL to see these peaks[4] but this was not successful. A powder diffractometer at a spallation source is based on the fixed angle, variable λ method. Thus in $2d\sin\theta=\lambda$ if θ is fixed at say 45° obtaining the $M(11.1)$ reflection, which has $d=3.651$ Å, requires $\lambda=5.16$ Å. However, pulsed sources with thermal moderators,[5] have their spectral peak ~1 Å. A cold neutron source is therefore required—as is now available at both the Rutherford (UK) and Argonne sources. The pulsed source has sufficient resolution for the problem but without a cold moderator it does not have enough intensity. Thus both previous neutron experiments failed for different reasons, first not enough resolution, second not enough intensity!

Table I gives all the magnetic intensities that have been measured. No peaks in the pattern are unassigned. Three things are immediately obvious by inspection in the Table. (1) l is odd only, (2) h and k are never both even, and (3) for reflections with h, k small and l large, e.g., (10.3), (10.5), etc. the intensities are small. It is relatively simple to derive the magnetic structure with these three pieces of information.

(1) l is odd only. The magnetic unit cell consists of two unit cells in the **c** direction, with Pu atoms at $(\pm z_{Pu})$. For l odd the relevant generator is $(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2\cos\pi l)$ where $\boldsymbol{\mu}_1=-\boldsymbol{\mu}_2$ and the translation is one chemical unit cell. Thus Pu atoms one chemical unit cell apart have *opposite* magnetic moments. The stacking along the **c** axis is $+\,+\,-\,-$, etc.

(2) h, k are not both even. This is more difficult and needs reference to Fig. 2. The spin structure may propagate in any one of three hexagonally equivalent directions, $\mathbf{a}_M$, $\mathbf{b}_M$, or $-(\mathbf{a}_M+\mathbf{b}_M)$. This can give rise to either three domains or a 3**k** structure.[6]

(3) The observation that for large l the magnetic intensities are small suggests that the moments point along **c**. For a hexagonal system q^2, the magnetic interaction vector is[7]

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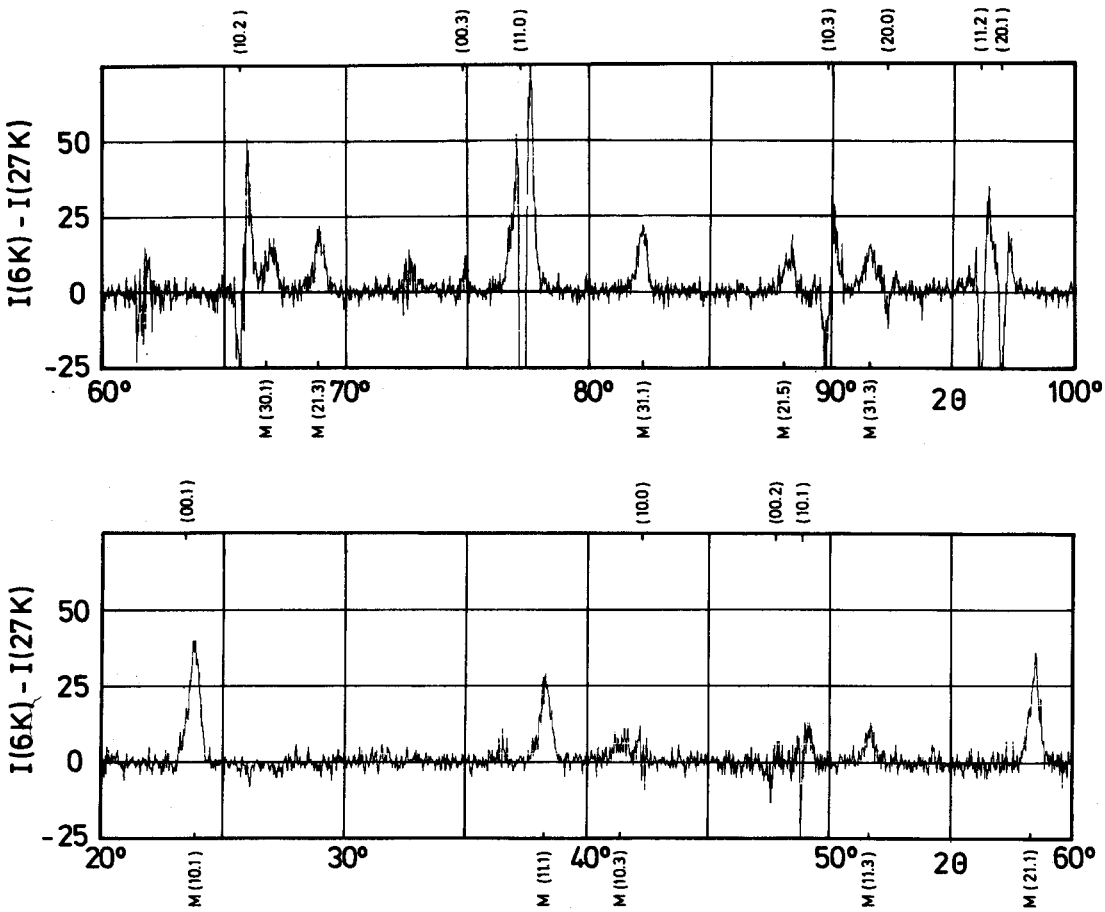

FIG. 1. Difference spectra $I(6\text{ K}) - I(27\text{ K})$ for β-Pu_2O_3 taken on D2B with $\lambda = 2.396$ Å. The $(hk.l)$ above the pattern give the positions of the nuclear reflections. The $M(hk.l)$ below give the magnetic Miller indices on a cell doubled in all three directions.

TABLE III. Magnetic reflections observed and calculated for Pu_2O_3 at 10 K. The $(hk.l)$ indices refer to the doubled unit cell (2**a**, 2**b**, 2**c**). θ is the Bragg angle ($\lambda = 2.396$ Å), I_{obs} is the observed intensity with the standard deviation referring to the least significant digit, I_{mag} is the calculated magnetic intensity. The intensity scale is arbitrary but the same as Table II.

$hk.l$	$2\theta°$	I_{obs}	I_{mag}
10.1	23.86	85(5)	92.8
11.1	38.31	59(5)	49.2
10.3	41.35	19(3)	14.2
11.3	51.63	20(3)	22.3
21.1	58.34	62(5)	59.0
10.5	64.99	<10	4.6
30.1	66.74	29(4)	27.0
21.3	68.84	38(4)	39.3
11.5	72.97	<15	4.6
30.3	76.64	~15	13.8
31.1	82.24	40(4)	40.4
21.5	88.10	22(3)	14.8
31.3	91.65	36(4)	26.6
10.7	93.95	<10	1.2
30.5	95.56	<15	11.4
11.7	101.47	<10	3.5
32.1	104.75	27(3)	29.2
31.5	110.90	22(3)	21.0
41.1	112.61	28(4)	30.4
32.3	114.74	19(3)	27.2
21.7	117.30	~10	10.4
41.3	123.26	29(4)	20.9
30.7	126.06	<10	3.1
50.1	130.12	~10	13.2
10.9	136.44	<10	0.4
32.5	138.28	~15	18.1

$$q^2 = 1 - \{\tfrac{1}{2}(h^2 + hk + k^2)a^{*2}\sin^2\Phi + l^2c^{*2}\cos\Phi\}d^2\,,$$

where **a*** and **c*** are reciprocal lattice vectors, and Φ is the angle the moment makes with the unique **c** axis. If $\boldsymbol{\mu}\|\mathbf{c}$ then $\Phi = 0$ so that

$$q^2 = 1 - l^2d^2/c^2\,.$$

Our refinements show that $\Phi \leqslant 10°$ and we assume that $\Phi = 0$.

We can now perform a least-squares analysis of the observed and calculated magnetic intensities. The calculated magnetic intensity is given by

$$I\,[M(hk.l)] = |F_{Pu}\,(hk.l)|^2 \tfrac{1}{3}Lq^2(0.2696)^2 \times [\mu f(\mathbf{Q})]^2 \times 10^{-24}\ \text{cm}^2\,, \qquad (2)$$

where $F_{Pu}\,(hk.l)$ is the trigonometric structure factor of Pu

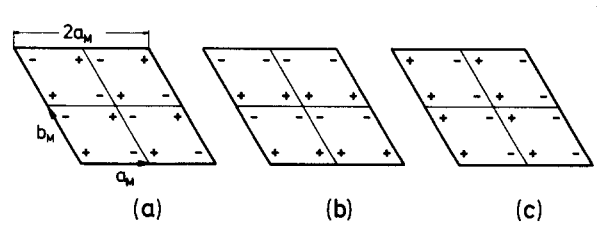

FIG. 2. Spin configurations in basal plane of Pu_2O_3. Each sign represents a Pu moment at a particular value of z_{Pu}. Similar spins can either be in the direction $(\mathbf{a}_m + \mathbf{b}_m)$ as in (a), or along $\mathbf{a}_m$ as in (b), or along $\mathbf{b}_m$ as in (c). The interference conditions give h odd, k odd for domains as in (a), h even, k odd as in (b), or h odd, k even as in (c).

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atoms only. We note that the magnetic structure does *not* contain an inversion center. The term $\frac{1}{3}$ is from the domains, or single component of 3k structure, L is the Lorentz factor, q^2 the magnetic interaction vector, μ the Pu moment, and $f(\mathbf{Q})$ its form factor. We neglect the Debye–Waller factor since our data is at relatively small $\sin\theta/\lambda$ and low temperature. Since the form factor of Pu^{3+} is of considerable interest,[8,9] we expand this as

$$f(\mathbf{Q}) \approx \langle j_0 \rangle + C_2 \langle j_2 \rangle ,$$

where $\langle j_0 \rangle$ and $\langle j_2 \rangle$ are tabulated functions relating to the spatial extent for the single electron wave function,[10] and C_2 is a constant.

The final refinement thus contains two parameters only, μ and C_2. The result is a good minimum with the observed and calculated intensities of Table III and

$$\mu = 0.60(2)\mu_B ,$$

$$C_2 = 4.5(3) .$$

We have also calculated the intensities of all other magnetic reflections for $2\theta < 140°$ and these are given in Table III. In every case these intensities are $\leqslant 15$, which is about the minimum we can detect; this gives additional weight to our model.

C. Magnetic structure $T<4$ K

As mentioned in Sec. II we were unable to reach this interesting region in our present experiment because of poor thermal contact. Instead we reproduce in Fig. 3 the original curve from Argonne (Fig. 4 of Ref. 2) but note that it represents the sum of $(00.1) + M(10.1)$. The three peaks $M(10.1)$, $M(11.1)$, and $M(21.1)$ *all* disappeared in the original ANL experiment. No new peaks were seen. An obvious explanation of this (and given in Ref. 2) is that the magnetic and chemical unit cells become identical at ~ 4 K. The spin structure is then a simple $+\ -$ configuration of the two Pu ions in one unit cell. The magnetic intensities then coincide with the nuclear intensities and, assuming $\boldsymbol{\mu}$ remains parallel to $\mathbf{c}$, we have calculated the "extra" intensity at each nuclear reflection $T < 4$ K and given it in the final column of Table II. Only in one case, the (10.1), does it exceed 2%, which was the standard deviation of the nuclear intensities in Ref. 2.

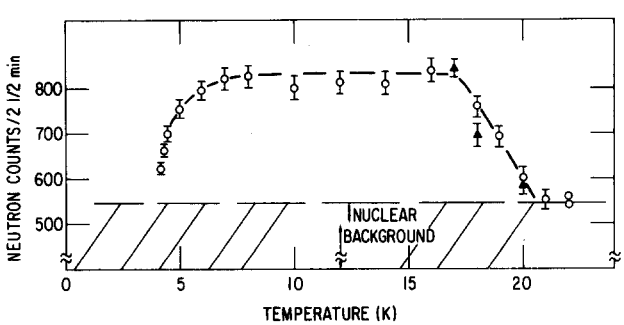

FIG. 3. This figure is taken from Ref. 2. It shows the combined intensity of the $M(10.1)$ and the "background" of the nuclear (00.1) reflection as a function of temperature. In Ref. 2 the T-dependent intensity was incorrectly assigned to a magnetic contribution at (00.1). The disappearance of the $M(10.0)$ below 5 K is connected with the change of the propagation vector, see the text.

The change of the propagation vector, with the direction of μ staying constant, also explains the absence of any effects in the magnetization. The latter is usually insensitive to such subtle changes.

IV. DISCUSSION

In the present study we have successfully resolved the magnetic structure of β-Pu_2O_3. We may also use the information about $\boldsymbol{\mu}$ and C_2 to deduce the ground state wave function. The Pu^{3+} ion in the structure has a site symmetry C_{3h}. The crystal field lifts the degeneracy of the $J = 5/2$ multiplet to give three Kramers doublets with M_J eigenfunctions $|\pm 1/2\rangle$, $|\pm 3/2\rangle$, and $|\pm 5/2\rangle$. Referring, for example, to the diagonalization performed by Segal and Wallace,[11] we see that the parallel (to the unique c axis) components of these three wave functions are 0.2, 0.6, and 1, respectively, whereas the perpendicular components are 0.6, 0, and 0. Since $\boldsymbol{\mu} \| \mathbf{c}$ in Pu_2O_3 this effectively eliminates the $|\pm 1/2\rangle$ component, which would prefer to order in the basal plane. These components are the moments divided by gJ. We use the intermediate coupling[12] g of 0.414 for Pu^{3+} so we obtain μ values of 0.62 μ_B and 1.04 μ_B for the $|3/2\rangle$ and $|5/2\rangle$ states, respectively. Our result of $0.60(2)\mu_B$ points strongly to the $|3/2\rangle$ ground state.

Further confirmation of the ground state can be deduced from the C_2 coefficient. Although the C_2 coefficient is in principle a function of the angle α, see Eq. (1), between the moment direction and scattering vector,[8,13] our data are not of sufficient accuracy to extract this dependence. The C_2 coefficients for the three components $|1/2\rangle$, $|3/2\rangle$, and $|5/2\rangle$ are approximately 4.3, 4.2, and 3.8. Our result of 4.5(3) is thus inconsistent with the $|5/2\rangle$ state, but in good agreement with the $|3/2\rangle$ state.

In conclusion we believe the ground state of the Pu^{3+} ion in β-Pu_2O_3 is the $|\pm 3/2\rangle$ Kramers doublet. This is similar to that deduced for Pu doped into ethylsulphate,[14] but different from the ground state in the trichloride.[15]

ACKNOWLEDGMENTS

We wish to thank M. Tetenbaum of ANL for producing this sample and A. Hewat of the Institut Laue Langevin, Grenoble for experimental assistance. The security aspects of this experiment were ably covered by the Radioprotection services of the ILL and J. Rebizant of EITU. The loan of the ^{242}Pu from the U. S. Department of Energy is gratefully acknowledged.

[1] H. E. Flotow and M. Tetenbaum, J. Chem. Phys. **74**, 5269 (1981).
[2] B. McCart, G. H. Lander, and A. T. Aldred, J. Chem. Phys. **74**, 5263 (1981).
[3] A. Hewat, Mat. Science Forum **9**, 69 (1986). Proceedings of the Meeting on High Resolution Powder Diffraction, Daresbury, UK, 1986, edited by C. R. A. Catlow.
[4] B. McCart and G. H. Lander (unpublished).
[5] C. G. Windsor, *Pulsed Neutron Scattering* (Taylor and Francis, London, 1981).
[6] See, for example, J. Rossat-Mignod, in *Methods of Experimental Physics*, edited by K. Skold and D. L. Price (Academic, New York, 1987), Vol. 23, p. 69.

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[7]G. Shirane, Acta Crystallogr. **12**, 282 (1959).
[8]G. H. Lander, A. Delapalme, P. J. Brown, J. C. Spirlet, J. Rebizant, and O. Vogt, Phys. Rev. Lett. **53**, 2262 (1984); J. Appl. Phys. **57**, 3748 (1985).
[9]M. Wulff, G. H. Lander, J. Rebizant, J. C. Spirlet, B. Lebech, C. Broholm, and P. J. Brown, Phys. Rev. B **37**, 5577 (1988).
[10]J. P. Desclaux and A. J. Freeman, J. Magn. Magn. Mater. **8**, 119 (1978).
[11]E. Segal and W. E. Wallace, J. Solid State Chem. **2**, 347 (1970).
[12]W. T. Carnall and B. G. Wybourne, J. Chem. Phys. **40**, 3428 (1964).
[13]E. Balcar, S. W. Lovesey, and F. A. Wedgwood, J. Phys. C **3**, 1292 (1970); G. H. Lander and T. O. Brun, J. Chem. Phys. **53**, 1387 (1970).
[14]H. Lämmermann and J. G. Conway, J. Chem. Phys. **38**, 259 (1963).
[15]E. R. Jones, M. Hendricks, J. A. Stone, and D. G. Karraker, J. Chem. Phys. **60**, 2088 (1974).

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