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Nuclear and Magnetic Structure of $U_3Ga_2Ge_3$: A Neutron Powder Diffraction Study

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The crystal structure of $U_3Ga_2Ge_3$ has been investigated by means of neutron powder diffractometry in the range from 1.5 to 100 K. Full matrix full profile refinements of the nuclear structure at 100 K revealed a new structure type with almost fully ordered distribution of Ga and Ge atoms in the 8*c* sites of space group *I*4. The new $U_3Ga_2Ge_3$ type is a low symmetry derivative of the ordered antitype-Cr_5B_3 (*I*4/*mcm*), $R_I = 0.032$, $R_F = 0.030$. From model refinements, eventual interstitial nonmetal occupation in the metal octahedra $U_1Ge_1Ge_2Ga_2$ or $U_2Ge_2Ga_2$ or in metal tetrahedra Ge_2Ga_2 is ruled out. At temperatures lower than $T_c = 90$ K uranium atoms order ferromagnetically as monitored by the intensity of the magnetic reflection $^MI_{(011)}$. Due to the observation of the ^{M}(011) reflection, the magnetic spin structure is consistent with the symmetry of the noncentrosymmetric space group *I*422. The lower symmetry invokes a splitting of the 4*a* sites of the parent Cr_5B_3 type (*I*4/*mcm*) into two twofold uranium sites 2*a* and 2*b* of *I*422. Besides the uranium atoms in 8*j* ($\mu_U = 2.57\ \mu_B$), only the uranium atoms in 2*a* were found to carry a magnetic moment $\mu_U = 2.45\ \mu_B$. All moments are parallel to the crystallographic *a* axis. To comply with the symmetry of the Ge/Ga atoms, magnetic and nuclear structure have to be described in space group *I*4. The reliability values for the 1.5 K diffractogram were: $R_I = 0.024$, $R_F = 0.019$, and $R_{mag} = 0.033$.

1. INTRODUCTION

U_3Si_2 dispersion in an aluminium matrix has proven to be a useful high-density uranium and proliferation-resistant fuel for research and test reactors (1). Preliminary investigations of analogous gallium-containing fuels revealed rather high changes in volume after heat treatment for 100 h at 400°C and these fuels were therefore rated with poor irradiation performance (2). With respect to the lack of information on the true nature of the ternary systems U–Ga–Si(Ge), we have started a systematic study of the phase equilibria and the crystal chemistry in the ternary combinations U–(Al, Ga)–Si(Ge) with particular emphasis on the magnetic properties of novel ternary compounds. In a recent paper we dealt with the crystal structure of novel ferromagnetic compounds with the formula $U_3M_2M'_3$, where M and M' are metals from the third and fourth main group, respectively (3). The present paper is designed to provide details regarding the Ga/Ge atomic site distribution and details on the low-temperature ferromagnetic structure of $U_3Ga_2Ge_3$.

2. EXPERIMENTAL DETAILS

A sample with a total amount of ca. 7 g was prepared by argon arc-melting ingots of the elements. Starting from a nominal composition, 37.5 at.% U, 22.0 at.% Ga, and 40.5 at.% Ge, a single phase and well-crystallized product was obtained. Further details of sample preparation and heat treatment, as well as handling of the specimens in glove boxes, can be found in our previous paper (3). Precise lattice parameters and standard deviations were obtained from a least squares refinement of room temperature (RT) Guinier–Huber X-ray powder data, using monochromatic Cu$K\alpha_1$ radiation with an internal standard of 6N-pure Ge ($a_{Ge} = 0.5657906$ nm at RT).

Neutron powder diffraction in the temperature range from 1.5 to 100 K was performed at the ORPHEE 14MW-reactor (CEN-Saclay) using the G4-1 double-axis multidetector neutron powder diffractometer with a helium cryostat (wavelength $\lambda_n = 0.2426$ nm; resolution $\Delta d/d \geq 4 \times 10^{-3}$; see Ref. (4)). Preferred orientation effects were minimized by powdering the sample in a steel mortar to a grain size smaller than 30 μm. Further details concerning the experiment are summarized in Table 1.

Precise atom parameters, occupation numbers, individual isotropic thermal factors, and profile parameters were derived from a least-squares full-matrix Rietveld refinement

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TABLE 1
Experimental Data for $U_3Ga_2Ge_3$

Sample container	Aluminium cylinder $R_i = 4$ mm
Temperature [K]	1.5 to 100 K, helium cryostat
Radiation wavelength [nm]	$\lambda_n = 0.2426$
Absorption correction	$\mu R = 0.0$
Reactor	ORPHEE, CEN-Saclay
Monochromator	Pyrolytic graphite
Detector	800 cells linear multidetector, BF_3
2Θ range [°]	20.03 to 99.93
Step-scan increment [2Θ]	0.10
Coherent scattering lengths [fm]	U 8.417
	Ga 7.288
	Ge 8.193
	O 5.803
Number of contributing reflections	30
Background	Interpolation for 25 values (100 K)
	Interpolation for 14 values (1.5 K)
Preferred orientation	Zero
Number of variables	15 (data at 100 K); 9 (data at 1.5 K)
Largest element of correl. matrix	0.7 (100 K); 0.9 (1.5 K)
Maximal Δ/σ	< 0.01 (120 K); < 0.01 (1.5 K)
Residual values	$R_I = \sum \lvert I_i(\text{obs}) - (1/c) I_i(\text{calc})\rvert / \sum \lvert I_i(\text{obs})\rvert$
	$R_F = \sum \lvert [I_i(\text{obs})]^{1/2} - [I_i(\text{calc})]^{1/2}\rvert / \sum [I_i(\text{obs})]^{1/2}$
	$R_P = \sum \lvert Y_i(\text{obs}) - (1/c) Y_i(\text{calc})\rvert / \sum Y_i(\text{obs})$
	$R_{\omega P} = [\sum \omega_i \lvert Y_i(\text{obs})(1/c) Y_i(\text{calc})\rvert^2 / \sum \omega_i \lvert Y_i(\text{obs})\rvert^2]^{1/2}$
	$R_{\text{mag}} = \sum \lvert {}^M I_i(\text{obs}) - (1/c)^M I_i(\text{calc})\rvert / \sum {}^M \lvert I_i(\text{obs})\rvert$
	$R_e = \{(N - P + C)/\sum \omega_i Y_i^2(\text{obs})\}^{1/2}$
	$\chi^2 = \{R_{\omega P}/R_e\}^2$

Note. Symbols used: I_i, integrated intensit of reflection i; ω_i, weighting function; Y_i, number of counts (background corrected) at 2Θ; c, scale factor.

routine (5, 6). Neutron scattering lengths were taken from a recent compilation by Sears (7). The various reliability factors calculated are defined in Table 1.

3. RESULTS AND DISCUSSION

3.1. Refinement of the Crystal Structure of $U_3Ga_2Ge_3$ at 100 K

3.1.1. The crystal structure of $U_3Ga_2Ge_3$. Refinement of the neutron powder spectrum collected at 100 K (above the magnetic ordering temperature of $T_c = 90$ K, see below) was based on the atom parameter set obtained from a preliminary single crystal X-ray study of $U_3Al_2Si_3$ and particularly of the homologous $U_3Al_2Ge_3$ (see Ref. (3)). The refinement in $I4/mcm$ converged to a rather low residual value (U1 in 4*a*, U2 in 8*h* [0.1635(9), $y = x + \frac{1}{2}$, $z = 0$], Ge in 4*c* and a random distribution of (0.5Ge + 0.5Ga) in 16*l* [0.1416(5), $y = x + \frac{1}{2}$, 0.1859(6); for standardization of the atom parameters see Ref. (8)]; $R_I = 0.032$, $R_F = 0.026$). However, a slight further decrease was achieved introducing Ga/Ge atom order reducing the crystal symmetry to space group $I4$ (Ga in $8c_1$, Ge in $8c_2$). This space group not only complies with the request for Ga/Ge atom ordering but also with the conditions for the magnetically ordered state (loss of the *c*-glide plane and center of symmetry; see below). The final structural and profile parameters, as well as the residual values obtained from the full-matrix Rietveld refinement, are presented in Table 2. The occupancies of all metal sites have been refined; however, no significant deviation from a full occupation was revealed. Due to the small difference in the X-ray scattering power of the neighboring elements Ga and Ge, their true site occupation could not be resolved from X-ray methods. With neutron scattering lengths differing by about 15% (see Table 1), identification of Ge in the (4*c*) sites was unambiguous and no Ga was found in the (4*c*) sites. This result inferred a reinvestigation of the crystal structure of $U_3Al_2Ge_3$ on new and better quality single-crystals of homologous $U_3Al_2Ge_3$ by X-ray single-crystal diffractometry to make use of the larger difference in the X-ray scattering power of Al and Ge. Although deviations of the atom parameters from the high symmetry arrangement ($I4/mcm$) are small, indeed significant improvement of the R values was observed when a practically full

TABLE 2
Crystallographic (Neutron) Data for $U_3Ga_2Ge_3$

(A) Refinement at 100 K[a]

Atom	Site	x	y	z	B [nm$^2 \times 10^2$]
U1	2*a*	0	0	0.2404(8)	0.05
U2	2*a*	0	0	$\frac{3}{4}$	0.05
U3	8*c*	0.1617(9)	0.3383(9)	0	0.09
Ge1	2*a*	0	0	0	0.16
Ge2	2*a*	0	0	$\frac{1}{2}$	0.16
0.97Ge3 + 0.03Ga1	8*c*	0.1424(5)	0.3576(5)	0.3143(5)	0.21
0.18Ge4 + 0.82Ga2	8*c*	0.3576(5)	0.1424(5)	0.1857(5)	0.21

Asymmetry parameter ($< 20^\circ$), $a \cong 0$; preferred orientation, $p \cong 0$.
Residual values: $R_I = 0.032$, $R_F = 0.030$, $R_P = 0.112$, $R_{\omega P} = 0.122$, $R_e = 0.035$, $\chi^2 = 12.1$

(B) Refinement at 1.5 K[b]

Atom	Site	x	y	z	μ_U [μ_B]***a***	B [nm$^2 \times 10^2$]
U1	2*a*	0	0	$\frac{1}{4}$	2.45 (15)	0.07
U2	2*a*	0	0	$\frac{3}{4}$	0.0	0.07
U3	8*c*	0.1628(10)	0.3372(10)		0 2.57(7)	0.13
Ge1	2*a*	0	0	0	—	0.15
Ge2	2*a*	0	0	$\frac{1}{2}$	—	0.15
0.89Ge3 + 0.11Ga1	8*c*	0.1414(5)	0.3586(5)	0.3138(5)	—	0.19
0.05Ge4 + 0.95Ga2	8*c*	0.3586(5)	0.1414(5)	0.1862(5)	—	0.19

Asymmetry parameter ($< 20^\circ$), $a \cong 0$; preferred orientation, $p \cong 0$.
Residual values: $R_I = 0.024$, $R_F = 0.019$, $R_{mag} = 0.033$, $R_P = 0.094$, $R_{\omega P} = 0.101$, $R_e = 0.029$, $\chi^2 = 12.1$.

Note. The expression for the individual isotropic temperature factor is: $T = \exp[-B(\sin\Theta/\lambda)^2]$. Standard deviations are in parentheses.

[a]Space group $I4$–C_4^5, No. 79, $Z = 2$, origin at 4. Lattice parameters [nm]: $a = 0.77528(13)$, $c = 1.10290(20)$. Atom parameters: Due to the small deviations from $I4/mcm$ the constraint $y = x + \frac{1}{2}$ for the sites 8*c* was kept througout the refinement in $I4$.

[b]Space group $I4$–C_4^5, No. 79, $Z = 2$, origin at 4. Lattice parameters [nm]: $a = 0.7749(1)$, $c = 1.1021(2)$.

atom order was assumed for the Al/Ge atoms in space group $I4$. The X-ray data are summarized in Table 3 and this type of atom order may infer a general feature for all isotypic and homologous compounds $U_3M_2M'_3$ reported in (3).

3.1.2. Nonmetal occupation in $U_3Ga_2Ge_3$. The generally weak X-ray scattering factors of small nonmetal atoms such as carbon, nitrogen, or oxygen in interstitial lattice sites may hide their detection by X-ray diffraction techniques and actually no residual electron density was seen in a corresponding difference Fourier synthesis for the crystal structure of $U_3Al_2Ge_3$. With respect to the much higher sensitivity of neutrons for light atoms, the unit cell of $U_3Ga_2Ge_3$ was analyzed with respect to suitable voids for nonmetal occupation. For simplicity the analysis was performed in the parent symmetry $I4/mcm$ and revealed three possible sites: (a) $U_1Ge_1(Ge,Ga)_4$ octahedra in 8*f* (0, 0, *z*), (b) $U_2(Ge,Ga)_4$ octahedra in 8*g* ($0, \frac{1}{2}, z$) and (c) $(Ge,Ga)_4$ tetrahedra in 4*b* ($0, \frac{1}{2}, \frac{1}{4}$). For the latter case, occupation by nitrogen and/or oxygen atoms indeed was found for La_5Pb_3 with the Cr_5B_3 type (La_4 tetrahedra, Ref. (9)). Model refinements of the 100 K neutron data assuming nonmetal occupation of the afore-mentioned coordination figures, however, rule out any significant amount of interstitial atoms in these sites. Individual calculations in all cases showed strong correlation between nonmetal atom occupancies and their isotropic temperature factors, either resulting in giant temperature factors at constant (full) site occupation or reducing the occupancies to virtually zero at a given value of $B = 0.5 \times 10^2$ nm^2. These results clearly confirm the truly ternary, i.e., uncontaminated, nature of $U_3Ga_2Ge_3$.

3.2. Magnetic Structure of $U_3Ga_2Ge_3$ at 1.5 K

The powder spectrum observed at 1.5 K, as shown in Fig. 1, reveals the appearance of a significant reflection of magnetic origin at $2\Theta \cong 22^\circ$, which perfectly indexes as the $^M(011)$ reflection on the basis of the tetragonal cell derived at 100 K or RT. Violating the law of extinctions for the parent symmetry in space group $I4/mcm$, $(0kl)$ is extinct for $l, k = 2n + 1$; the existence of the $^M(011)$ reflection requires

TABLE 3
Crystallographic Data for $U_3Al_2Ge_3$ (X-Ray Single Crystal Refinement at RT)

Atom	Site	x	y	z	B [nm$^2 \times 10^2$]
U1	2*a*	0	0	$\frac{1}{4}$	0.45(1)
U2	2*a*	0	0	0.7495(2)	0.5
U3	8*c*	0.15978(9)	0.34026(9)	0.0167(1)	0.50(1)
Ge1	2*a*	0	0	0.0005(5)	0.81(3)
Ge2	2*a*	0	0	0.5009(5)	0.80
0.15Ge3 + 0.85Al1	8*c*	0.1336(8)	0.3650(5)	0.3329(5)	1.3(1)
0.92Ge4 + 0.08Al2	8*c*	0.3499(3)	0.1501(3)	0.2085(2)	0.49(3)

Interatomic distances within the first gap (standard deviations $\leq$ 0.0009 nm)

U1	1 Ge1	0.2759	Ge1	1 U1	0.2759
	1 Ge2	0.2759		1 U2	0.2764
	4 Al1	0.2989		4 U3	0.2922
	4 Ge3	0.3151			
	4 U3	0.3890	Ge2	1 U2	0.2753
	4 U3	0.4143		1 U1	0.2789
				4 U3	0.2922
U2	1 Ge2	0.2753			
	1 Ge1	0.2764	Al1	1 Ge4	0.2597
	4 Ge4	0.2988		1 Ge4	0.2606
	4 Al1	0.3166		1 Ge4	0.2735
	4 U3	0.3886		1 Al1	0.2947
	4 U3	0.4147		1 U3	0.3036
				1 U3	0.3055
U3	1 Ge2	0.2922		1 U1	0.3151
	1 Ge1	0.2922		1 U2	0.3166
	1 Ge4	0.2972		1 U3	0.3501
	1 Al1	0.3036			
	1 Al1	0.3054	Ge4	1 Al1	0.2597
	1 Al1	0.3064		1 Al1	0.2606
	2 Ge4	0.3204		1 Al1	0.2735
	(1 Ge4	0.3403)		1 U3	0.2972
	(1 Al1	0.3501)		1 U2	0.2988
	1 U3	0.3506		1 U1	0.2989
	1 U2	0.3886		2 U3	0.3204
	1 U1	0.3890		(1 Ge4	0.3294)
	4 U3	0.4124		1 U3	0.3403

Note. Space group, $I4$–C_4^5, No. 79, $Z = 2$, origin at 4. Lattice parameters [nm]: $a = 0.7758(1)$, $c = 1.1036(3)$. Residual values: $R_F = 0.031$, $R_{\omega F} = 0.032$, GOF = 1.006.

a reduction of symmetry for the arrangement of the ferromagnetic uranium spin structure consistent with the tetragonal subgroup $I422$ of highest symmetry, splitting the U1 4*a* site of space group $I4/mcm$ into two subsets (2*a*) and (2*b*) in $I422$ after a shift of the origin by $\boldsymbol{v} = (0, 0, \frac{1}{4})$. For this reduction a simple crystallographic group–subgroup relationship exists: $I4/mcm \Rightarrow (t2;\ \boldsymbol{a}, \boldsymbol{c}) \Rightarrow I422$. Furthermore, a regrouping of the twofold sites is possible in the space group $P4/m$ (sites 2*g*, 2*h*) in addition to providing a splitting of the eightfold uranium position 8*h* of $I4/mcm$ into two individual sites 4*j* and 4*k*. The Rietveld refinement of the difference spectrum ($I_{\text{obs. } 1.5\,\text{K}} - I_{\text{nuclear, } 100\,\text{K}}$), allowing a variation of the U-magnetic moments in various (parallel) spin directions, finally converged to the spin arrangement in $I422$ with all the uranium moments parallel to the $\boldsymbol{a}$ axis (see Table 2). Besides the uranium atoms in 8*j* ($\mu_U = 2.57\ \mu_B$) only the uranium atoms in 2*a* were found to carry a magnetic moment $\mu_U = 2.45\ \mu_B$. A model refinement allowing individual moments for the eight U atoms in triclinic symmetry revealed virtually zero deviation from the common moment of $\mu_U = 2.6\ \mu_B$. Similarly, a regrouping of the uranium atoms in the twofold sites 2*g* and 2*h* of $P4/m$ immediately led to unacceptably high residual values and to divergence of the refinement. A final analysis of various

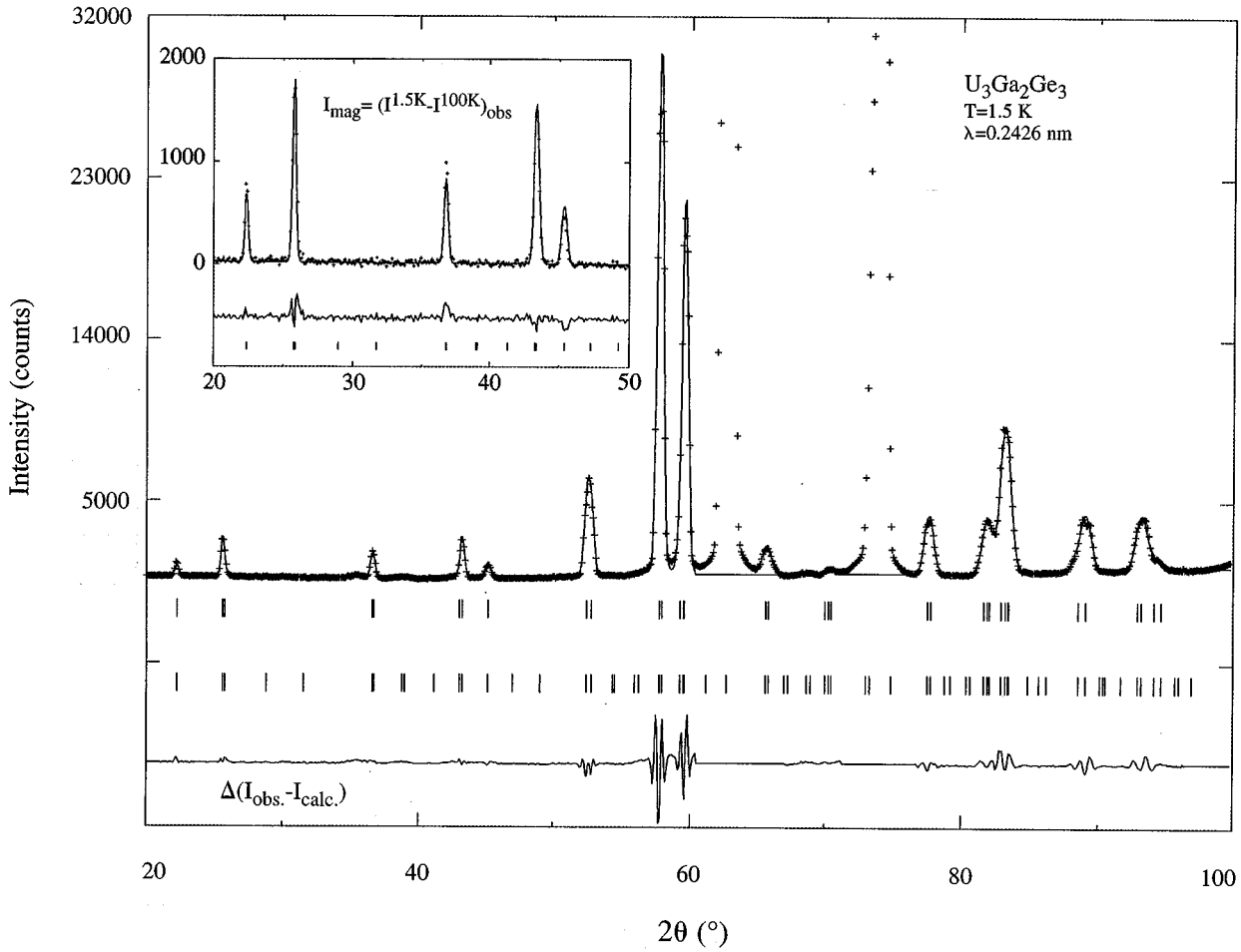

FIG. 1. Observed and calculated neutron powder diffraction patterns of $U_3Ga_2Ge_3$ at 1.5 K. Excluded regions correspond to two neutron peaks from the Al-sample environment. The difference spectrum $I_{obs.} - I_{calc.}$ and indexation of reflections are shown at the bottom of the graph. *Inset*: difference pattern $I_{mag.} = I_{obs.(1.5K)} - I_{obs.(100K)}$ of the low angle region revealing ferromagnetic uranium contributions.

possible moment directions revealed within $\pm 4^\circ$ no significant deviation from the ***a*** axis. The *I*422 symmetry of the spin structure, however, does not comply with the observed Ge/Ga atom sublattice (*I*4). Consistency between magnetic and nuclear structure is obtained, transferring the atom and spin arrangement to the low symmetry subgroup *I*4 (*I*422 $\Rightarrow$ (*t*2; ***a***, ***c***) $\Rightarrow$ *I*4). The final structural and profile parameters, as well as the residual values obtained from the full matrix Rietveld refinement, are presented in Table 2, including interatomic distances up to 0.45 nm. The residual values in Table 2 finally obtained (with temperature factors fixed from an earlier refinement of the nuclear part of the pattern) were below 7% for both the nuclear and the magnetic part. The magnetic moments derived are consistent with those evaluated from magnetic susceptibility and magnetization measurements on nonoriented, polycystalline samples (Fig. 2). This is particularly true for the magnetic ordering temperature $T_c = 90$ K, as measured from susceptibility data (see inset of Fig. 2) and monitored on the intensity of the $^M(011)$ reflection (see Fig. 2; $[^MI(011)]^{1/2} \approx M/M_0$; $T_c = 92$ K). The rather large inter-uranium distances revealed ($d_{U-U} > 0.35$ nm, average $d_{U-U} \sim 0.40$ nm, Table 2) favor magnetic moment localization on the uranium and on the (ferro)magnetic interactions observed. The variation of M/M_0 versus the reduced temperature T/T_c, however, shows little resemblance to the $J = 9/2$ ground state of trivalent uranium and rather reflects a pronounced mode of *f–sp* hybridization also conceived from the short U–Ge and U–(Ga, Ge) distances that are well below the sum of the corresponding atom radii. A three-dimensional presentation of the crystal structure and of the alignment of the uranium spins is shown in Fig. 3. It should be mentioned at this point that the neutron data for all the intermediate temperatures measured (30, 60, 80, and 84 K) confirm both the nuclear and the magnetic structure as derived from the refinements at 1.5 and 100 K.

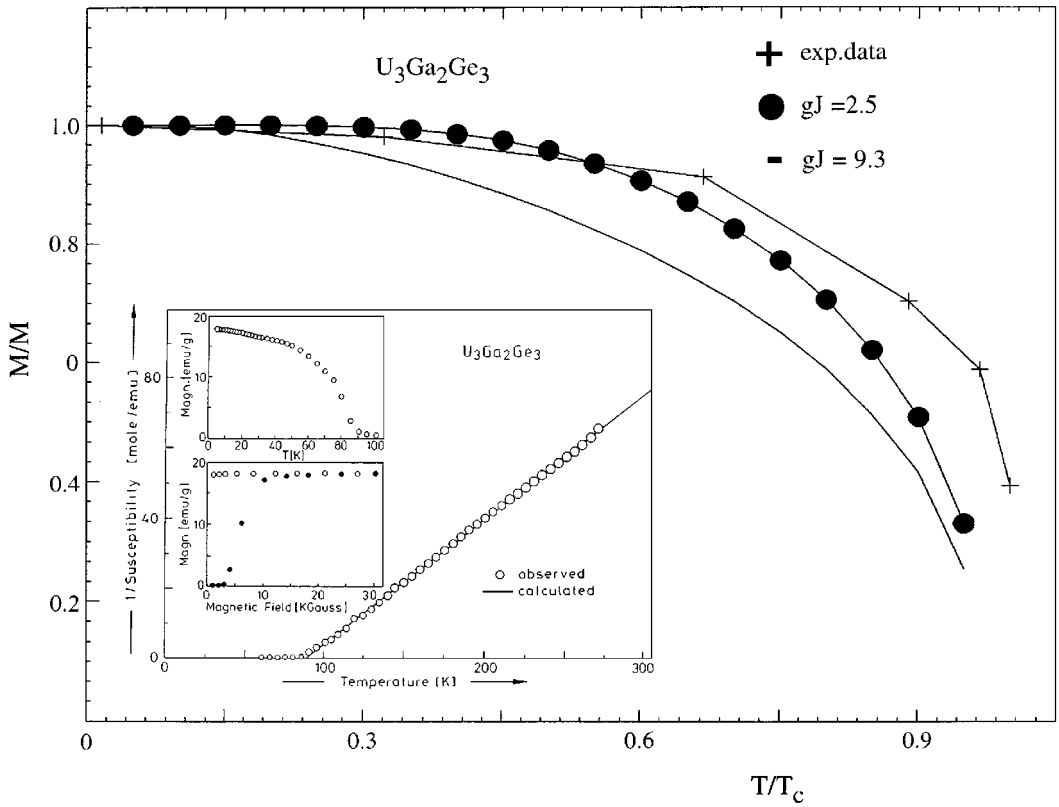

FIG. 2. Reduced integrated magnetic intensity ${}^{M}I_{(011)}$ ($\approx M/M_o$) versus reduced temperature T/T_c for ferromagnetic $U_3Ga_2Ge_3$ and comparision with various spin moments. *Inset*: magnetization versus temperature and magnetization versus field.

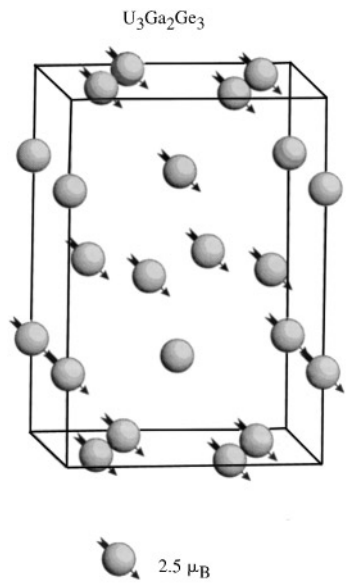

FIG. 3. Crystal structure and magnetic spin structure in three-dimensional view (vertical axis ***c***, horizontal axis ***b***, and axis toward viewer ***a***).

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