

Neutron diffraction studies of $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ at 296–4°K

Masao Atoji

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Neutron diffraction studies of $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ at 296–4 °K^{a)}

Masao Atoji

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439
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Neutron diffraction measurements have shown that in the ternary CaC_2 -type compounds, $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$, the cubic NaCl -type structure, which is usually stable above about 1000 °C, can be arrested down to 4 °K due to a large strain energy of the disordered lattice. Also retained down to 4 °K are a random distribution of Ce and U atoms, as well as the orientational disordering of C_2 molecules. The lattice parameters at 296–4 °K indicate no valency change, such as $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$. $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ showed no magnetic ordering at 296–4 °K in 0–21 kOe. $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ becomes a weak ferromagnet below 17 °K in 21 kOe, with the moment direction parallel to the [111] direction.

I. INTRODUCTION

In the phase immediately below the melting point, the CaC_2 -type MC_2 (M =alkaline earth, rare earth, or U) exhibits a cubic NaCl -type structure in which the C_2 molecule undergoes an orientational disorder having a cubic site symmetry.¹ At lower temperatures the structure becomes tetragonal, due to the alignment of the C_2 molecules parallel to the c axis. The transition temperature is the lowest in M =alkaline earths (e.g., CaC_2 , 450 °C),² the intermediate in M =rare earths (RE) (e.g., CeC_2 , 1109 °C),^{3–7} and the highest in M =U, 1765 °C.⁸

In some ternary carbides $\text{M}_x\text{M}'_{1-x}\text{C}_2$ with the CaC_2 -type structure, the cubic structure can be arrested down to room temperature. This occurs when the strain energy caused by the disordering of M and M' is large enough to suppress the cubic–tetragonal transformation. Such case has been observed in $\text{La}(\text{RE})\text{C}_2$ ($\text{RE}=\text{Dy–Tm}$), $\text{Ce}(\text{RE})\text{C}_2$ ($\text{RE}=\text{Er, Lu}$), $\text{Pr}_x\text{Lu}_{1-x}\text{C}_2$,^{5–7} $\text{La}_x\text{U}_{1-x}\text{C}_2$, and $\text{Ce}_x\text{U}_{1-x}\text{C}_2$.⁹ $\text{Ce}_x\text{U}_{1-x}\text{C}_2$ was selected for our neutron diffraction study in conjunction with the carbide nuclear-fuel program.

McColm *et al.*,⁹ found that $\text{Ce}_x\text{U}_{1-x}\text{C}_2$ at room temperature exhibits a single-phase, cubic structure in the range $0.16 < x < 0.45$ and $0.65 < x < 0.84$, and a two-phase, cubic structure in $0.45 < x < 0.65$. McColm *et al.*,⁹ also found that the lattice-parameter dependency on x is very small in $0.16 < x \leq 0.6$, implying the smallest possible atomic radius for Ce and, hence that all Ce atoms are in the Ce^{4+} state. The lattice parameter variation becomes much larger in the range $0.6 < x \leq 0.84$, meaning that a considerable portion of Ce atoms is in the Ce^{3+} state. These interpretations were supported by their magnetic susceptibility measurements at $x=0.32$ and 0.66 at room temperature.⁹ We selected these two compositions so as to explore the low-temperature properties of a disordered structure that is usually stable only at very high temperatures. We have previously carried out neutron diffraction studies of most of the tetragonal CaC_2 -type carbides, including CeC_2 and UC_2 at 296–4 °K.^{10–12} These results were characterized by a strong anisotropic, competing interaction between crystal field

and exchange energy. The present study of $\text{Ce}_x\text{U}_{1-x}\text{C}_2$ is of interest in view of the change in the crystal field from tetragonal to cubic.

II. EXPERIMENTAL AND STRUCTURAL

Samples of $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ were prepared by arc-melting compressed pellets composed of cerium metal chips, uranium metal turnings, and spectroscopic graphite powder. Each alloyed boule was inverted and remelted. The further melting did not improve the quality of the product, and tended to shatter the boule unless it was heated very slowly. The arc melting was also performed using large pieces of UC_2 and CeC_2 as the starting material, since their powders do not cohere well in the pellet formation. Further in this process, the shattering of pellets and boules occurs more readily, and the quality of the product was, in general, inferior to those prepared from the elements. For the quality evaluation of the samples, both neutron and x-ray diffraction methods were employed. The major impurities were UC (up to about 10 wt. %) and the tetragonal CaC_2 -type $\text{Ce}_x\text{U}_{1-x}\text{C}_2$ (up to about 5 wt. %). We chose the samples with the least impurity content, and utilized a comprehensive lattice-parameter table⁹ for the composition determination. The uncertainty in our composition value is about 10%.

TABLE I. The observed and calculated integrated intensities of $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ at 4 °K, where $I_{\text{calc}} = jLF^2 \exp[-0.4(\sin\theta/\lambda)^2]$ in 10^{-26} m^2 , j is multiplicity, L is Lorentz factor and F is structure factor per unit cell for the statistical orientation of the C_2 molecular axis along four body diagonals.

Indices	$\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$		$\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$	
	I_{obs}	I_{calc}	I_{obs}	I_{calc}
111	2	1.5	4	3.8
200	30	31.3	30	30.4
220	20	20.4	18	18.4
311	4	3.9	1	1.1
222	6	6.5	5	5.0
400	1	0.7	2	1.7

^{a)}Work performed under the auspices of the Division of Basic Energy Sciences of the U. S. Department of Energy.

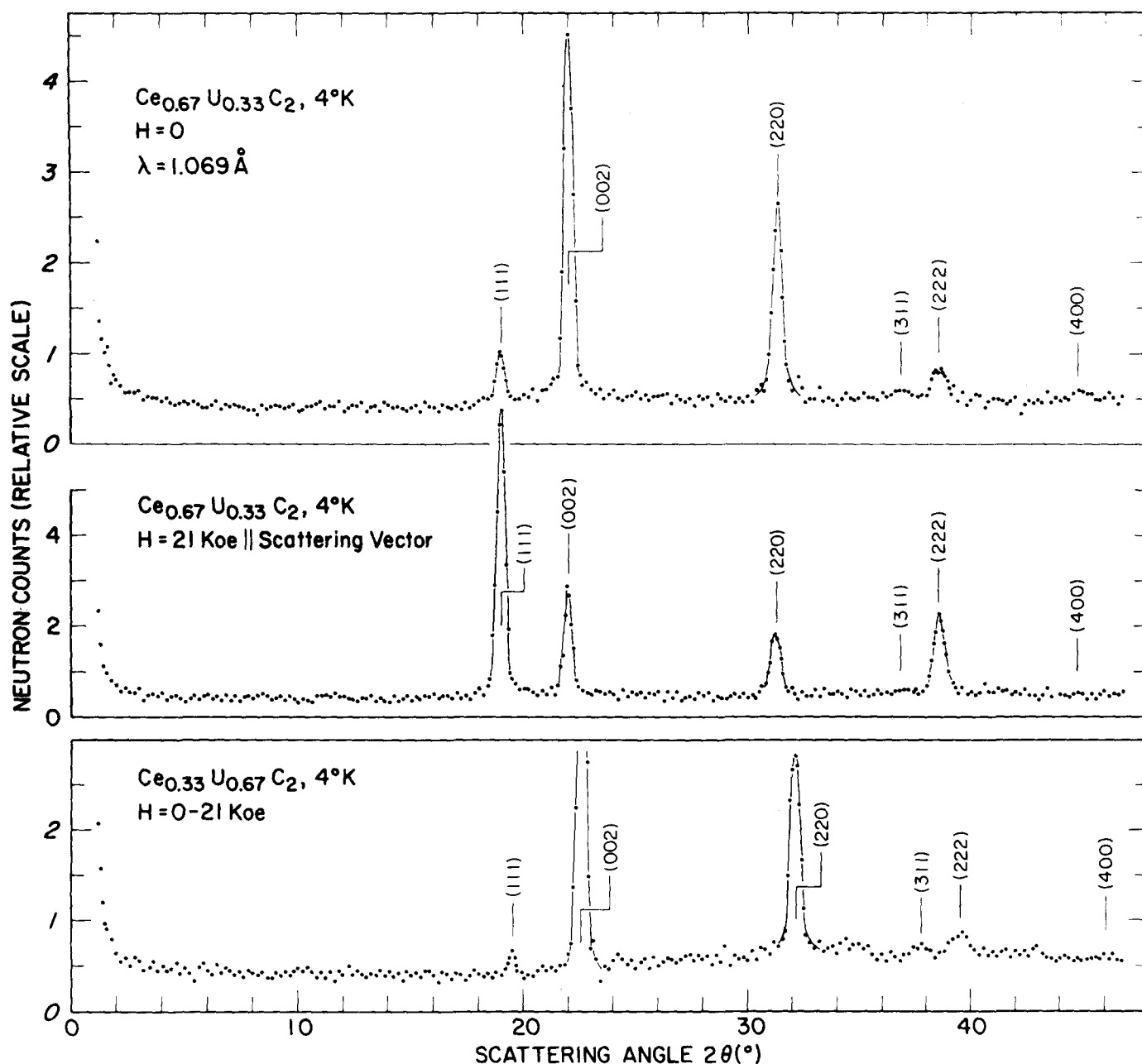


FIG. 1. The upper and middle diagrams represent the powder neutron diffraction patterns of $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ at 4 °K, respectively, before and after the external magnetic field H is applied parallel to the scattering vector in the $\theta - 2\theta$ scan. The randomly oriented crystallites in $H=0$ tend to align their ferromagnetic moments in the direction of the applied field. The resultant intensity modulation indicates that the moment is parallel to the $[111]$ axis. Note that the neutron count ordinate of the middle diagram is scaled down 50%. The lowest diagram represents the diffraction pattern of $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ at 4 °K, which is uninfluenced by $H=0-21$ KOe. The reflections of major impurities have been subtracted out in these diffraction patterns.

$\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ is grayish metallic, similar to UC_2 ,¹⁰ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ is golden metallic, like CeC_2 .¹² The diffraction data of the pulverized samples were taken with 1.069 Å neutrons at various temperatures between 296 and 4 °K. The higher-order wavelength contamination is less than 0.04%. Cubic lattice parameters at 296 and 4 °K are $a=5.474$ and 5.462 Å for $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$, and $a=5.624$ and 5.614 Å for $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$, respectively, all with ± 0.002 Å (standard deviation). The linear thermal expansion coefficient in the 4–296 °K range is $(6 \pm 2) \times 10^{-6} \text{ deg}^{-1}$ for both compounds. This value is

typical in most metallic compounds, and indicates no change in the valency state, such as the electronic transition from Ce^{3+} to Ce^{4+} found in Ce metal¹³ and Ce_2C_3 .¹⁴

The diffraction patterns in the range 296–4 °K showed no detectable change except for a variation in the Debye–Waller temperature factor. Nuclear superlattice reflections were not detectable, meaning that U and Ce atoms are distributed at random among the cation sites. The intensities were calculated for free rotation of the C_2 molecule, and for random orientation of the C–C axis

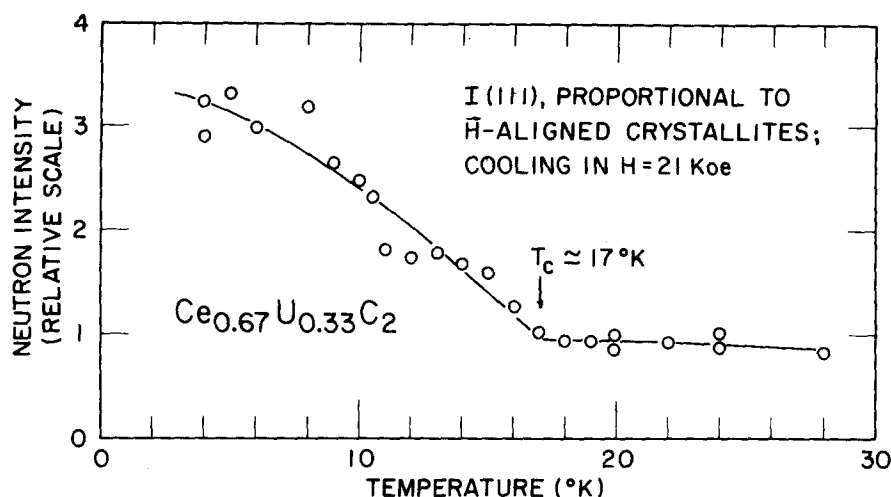


FIG. 2. Temperature dependence of the (111) intensity of $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ in cooling. The 21 KOe field is being applied parallel to the scattering vector. The intensity enhancement involves the nuclear contribution only and is proportional to the field-induced preferred orientation of the crystallites, hence approximately to the square of the ferromagnetic moment.

parallel to $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 100 \rangle$, all in the cubic space group $O_h^5\text{-}Fm\bar{3}m$. The intensity differences in these four models are hardly significant, in view of large uncertainties (about 10%) in the observed intensities which are compared with the most reasonable model, the $\langle 111 \rangle$ orientation, in Table I. The scattering lengths employed were 0.48, 0.85, and 0.665 in 10^{-14} m for Ce, U, and C, respectively.¹⁵ Similar results were obtained in the neutron diffraction studies of the high-temperature cubic phases of CaC_2 ,¹⁶ LaC_2 ,¹⁷ and UC_2 .¹⁸

III. MAGNETIC STRUCTURE

McColm *et al.*,⁹ obtained the effective Bohr magneton numbers (μ_{eff}) of $\text{Ce}_{0.34}\text{U}_{0.66}\text{C}_2$ and $\text{Ce}_{0.66}\text{U}_{0.32}\text{C}_2$ at room temperature as 2.1 and 2.2 Bohr magnetons (μ_B), respectively. The μ_{eff} values of U^{3+} , U^{4+} , Ce^{3+} , and Ce^{4+} are 3.68, 3.62, and 2.54 and 0 μ_B , respectively. McColm *et al.*,⁹ hence assigned U^{3+} or U^{4+} for U in both compounds; Ce^{4+} for Ce in $\text{Ce}_{0.34}\text{U}_{0.66}\text{C}_2$; 50% Ce^{3+} and 50% Ce^{4+} for Ce in $\text{Ce}_{0.66}\text{U}_{0.32}\text{C}_2$. These interpretations are in accordance with an unusual lattice-parameter dependency on x , as described before.

The paramagnetic scattering of the tetragonal CeC_2 gave $\mu_{\text{eff}} = 2.54 \mu_B$, meaning that Ce in the paramagnetic CeC_2 is equivalent to the free Ce^{3+} ion.¹⁰ The CeC_2 becomes a first-kind antiferromagnet below 33°K with the moments aligned parallel to the c axis. The saturation ordered moment per CeC_2 is $1.74 \mu_B$,¹⁰ showing a 19% suppression by the crystal field from the maximum possible ordered moment of $2.15 \mu_B$. The tetragonal UC_2 possesses a very weak, temperature-dependent, paramagnetic moment of about 8×10^{-4} emu/mole, which gives rise to no detectable paramagnetic scattering down to 5°K.¹²

If $\mu_{\text{eff}} = 2 \mu_B$ is also assigned to our $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ and $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ samples, the resulting paramagnetic scattering near $2\theta \approx 0$ corresponds to about 0.04 on the relative neutron count scale of Fig. 1. Such weak scattering is difficult to evaluate, because of a large uncertainty in the impurity scattering. On the other hand, the detectability on the coherent magnetic reflection is much higher. Careful search for magnetic reflections was, however, fruitless. Also, no ferromagnetic intensity

was detected at the nuclear reflections. The low limit of detectability is about 0.5 μ_B /chemical formula for CeC_2 -type antiferromagnetic ordering, and the same for the ferromagnetic alignment.

The diffraction patterns were then taken in an applied magnetic field. $\text{Ce}_{0.33}\text{U}_{0.67}\text{C}_2$ showed no change in the range 296–4°K in $H = 0$ –21 KOe. On the other hand, $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ at low temperatures, the applied field induces a strong preferred orientation of the crystallites, revealing the development of a ferromagnetic moment. In our loosely packed powder sample, the torque induced by the applied field is strong enough to orient even a very weakly magnetized crystallite. The preferred orientation axis can then be determined in the $\theta - 2\theta$ scan with the field direction parallel to the scattering vector.¹⁹ Such a scan is shown in Fig. 1. It is immediately obvious that the easy direction of magnetization in $\text{Ce}_{0.67}\text{U}_{0.33}\text{C}_2$ is the $[111]$ axis, because of an enormous enhancement in the (hhh) intensities and the largest diminution in (hko) intensities. These intensity variations involve the nuclear contribution only. In fact, the diffraction pattern showing the preferred orientation at 4°K (the middle diagram of Fig. 1) was virtually unchanged by warming up to 296°K. Diffraction intensities for preferred orientation in cubic powders have been formulated by Järvinen *et al.*, (1970).²⁰

The field-induced torque is proportional to (the applied field) \times (the square of the net moment) in the uniaxial ferromagnet. Accordingly, the intensity enhancement of the (111) reflection gives a crude measure of the magnetization. The temperature dependency curve of the (111) intensity, with $H = 21$ KOe being applied parallel to the (111) scattering vector, shows that a change of the slope occurs near 17°K, which can be designated as the Curie temperature (T_c) in 21 KOe (Fig. 2). In the weaker field, T_c became less distinctive, and the accurate extrapolation of T_c to $H = 0$ could not be made. This ferromagnetism is likely attributable to an RKKY-type interaction, enhanced by the randomly distributed Ce^{3+} ions in the cation sites. Among probable ordered magnetic structures are ferrimagnetic, metamagnetic and parasitical ferromagnetic. Unique magnetic structure determination requires neutron and magnetic measurements using a single crystal.

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