Neutron Diffraction Investigations of Metallic Cerium at Low Temperatures

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Neutron diffraction experiments have been performed on metallic cerium at a series of temperatures between room temperature and 4.2°K in an attempt to clarify the anomalous behavior which has been observed in previous specific-heat and magnetic-susceptibility measurements. Results on three specially prepared samples show that the interesting magnetic behavior can be correlated with the three crystallographic phases present in the samples. There is a change in the electronic configuration of the cerium atoms when the collapsed face-centered cubic phase is formed, and antiferromagnetic ordering occurs in the hexagonal close-packed phase at about 12.5°K.

INTRODUCTION

THE anomalous behavior that has been observed at low temperatures in specific heat[1,2] and magnetic susceptibility[3–5] measurements on metallic cerium has caused considerable interest in the magnetic properties of this metal. Both types of experiments have shown a large anomaly with considerable thermal hysteresis in the temperature range from 90°–190°K and a smaller anomaly at 12.5°K. Furthermore, the results are strongly dependent on the previous history of the sample. Lock[3] found that repeated thermal cycling of a specimen between room temperature and 20°K eliminated the thermal hysteresis in the susceptibility measurements near 100°K and approximately doubled the paramagnetic susceptibility below 50°K, while Parkinson and Roberts[2] observed an increase in the specific-heat peak at 12.5°K after similar cycling.

Recent x-ray investigations by McHargue and Yakel[6] have suggested that these anomalous results may be associated with the phase transformations that occur in metallic cerium at low temperatures. These experiments showed that three crystallographic forms exist below room temperature and that the relative concentrations are dependent both on the sample temperature and on the condition of the sample. At room temperature both a face-centered cubic structure (fcc) and a hexagonal close-packed structure (hcp), with an *ABAC* stacking sequence of close-packed planes, were observed. However, observations on samples cooled below about 100°K showed that these phases could transform to another face-centered-cubic structure (fcc′), in which the volume was decreased 16.5% below that of of the original fcc phase. For increasing sample temperatures, a large hysteresis existed in the phase transformations.

The collapsed fcc′ structure has been found previously[7,8] under different conditions of pressure and temperature, and the explanation suggested for the existence of a second fcc structure with a decreased volume has involved the promotion of a $4f$ electron to a $5d$ level.[9,10] This electron transfer has also been suggested as the mechanism responsible for the anomalous behavior of the magnetic susceptibility in the temperature region near 100°K. Consequently, it was of interest to investigate the magnetic properties of cerium under known crystallographic conditions. Neutron diffraction techniques are ideal for such an investigation, and these experiments would also give information on the cryomagnetic anomaly at 12.5°K. Lock suggested that this anomaly was due to an antiferromagnetic transition, and since x-ray patterns taken at room temperature showed that his samples were almost entirely the fcc phase, he inferred that the magnetic ordering occurred in this phase. An alternative explanation was offered by Parkinson and his co-workers, who suggested that the observed behavior might be due to excitation of electrons between energy levels produced by Stark splitting of the ground state.

EXPERIMENTAL PROCEDURE

The cerium used in this investigation was obtained from the Institute for Atomic Research, Iowa State College, and had the highest purity of any material available. It was melted in tantalum crucibles in a vacuum to outgas and to reduce volatile impurities. Spectroscopic and gas analyses indicated a purity of 99.9%.

Neutron diffraction measurements were obtained on three specimens which were prepared to give different concentrations of the crystallographic phases as a function of temperature. The following methods were used:

(a) Sample I was melted and cast in a cylindrical tantalum crucible which was approximately the size of the sample to be investigated. The crucible was then stripped away and the specimen was machined to the

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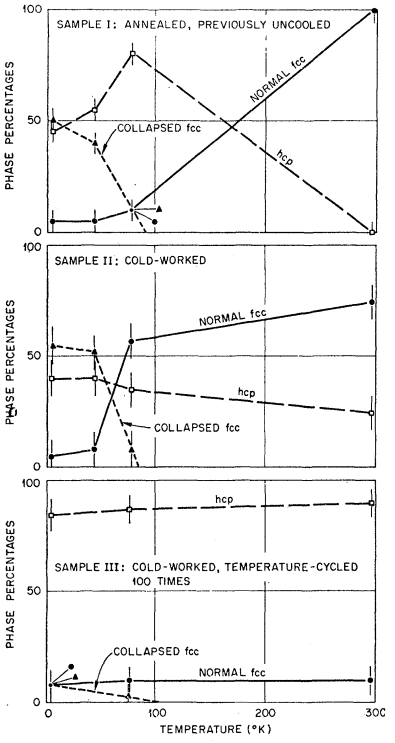

FIG. 1. Variation of crystallographic phases in three cerium samples with decreasing temperatures. Normal fcc ($a_0=5.15$ A); hcp ($a=3.68$ A, $c=11.91$ A); collapsed fcc ($a_0=4.85$ A).

proper dimensions, after which it was vacuum annealed at 350°C.

(b) Sample II was melted and cast in a tantalum crucible considerably larger than the desired sample size. After the crucible was stripped away, the specimen was given a reduction of about 50% in cross-sectional area to the proper dimensions by cold-rolling.

(c) Sample III was the same specimen as sample II, but at the conclusion of the investigations on that sample, it was thermally cycled 100 times between 4.2°K and room temperature. This procedure was followed in an attempt to duplicate the thermal cycling used by Lock and by Parkinson and Roberts.

The samples were polycrystalline cylindrical rods about 5-cm long and 1-cm diam. They were sealed in a helium atmosphere within thin-walled aluminum cells and mounted in a double-jacketed vacuum cryostat. Diffraction patterns were obtained at a series of temperatures from room temperature to 4.2°K.

EXPERIMENTAL RESULTS

Crystallographic Phase Determinations

The crystallographic phases at the various sample temperatures were determined from the nuclear reflections, and the phase percentages that were observed as the sample temperatures were decreased are shown in Fig. 1. Results for increasing sample temperatures were considerably different because of thermal hysteresis in the phase transformations. The points are plotted at the specific temperatures where data were obtained, and the straight lines merely connect the points without indicating the proper percentages at the intermediate temperatures. The feet on the points represent the estimated errors in the determinations, and these errors were due primarily to insufficient resolution in the diffraction patterns and preferred orientation in the samples.

The phases at room temperature and at 77°K for sample I agreed very well with those determined by x-ray analysis[6] on a sample prepared similarly. However, the phases in sample II did not agree with those observed by x-ray techniques for another sample which was cold-worked in a similar manner. Whereas the x-ray results indicated a sample which was essentially 100% fcc at room temperature, sample II contained about 25% of the hcp phase at that temperature. This difference may be associated with slightly different sample treatments, or it may indicate that the surface layer examined in the x-ray analysis was not representative of the bulk specimen.

Paramagnetic Scattering Analysis

The paramagnetic scattering from a magnetic material is proportional to $\mu_p^2 f^2$, where μ_p is the effective magnetic moment per atom in the paramagnetic state and f is the magnetic form factor. For rare-earth ions, in which the magnetic electrons obey Russell-Saunders coupling, $\mu_p=[g^2J(J+1)]^{\frac{1}{2}}$. Therefore, the paramagnetic scattering can be interpreted in terms of the spin and orbital angular momentum associated with the magnetic electrons within the atoms.

This type of analysis is particularly good for metallic cerium, since there is practically no diffuse scattering from the sample other than the paramagnetic scattering. There are two isotopes, Ce^{140} and Ce^{142}, which constitute 99.55% of the element, and since both have even-even nuclei, there is no nuclear-spin incoherent scattering. Furthermore, the two isotopes have closely the same values of nuclear coherent scattering amplitudes,[11] so that isotopic incoherence is essentially negligible. The only other sources of diffuse scattering, in addition to the magnetic scattering, are multiple scattering and disorder scattering due to lattice distortions. Both of these should be small for the samples that were investigated, and reasonable estimates could be made.

The diffuse scattering at small angles is shown in Fig. 2 for the three cerium samples at various temperatures. These curves, which have been corrected for background effects, show that a large decrease in scattering is associated with the presence of the fcc′ phase, an effect which would occur if the formation of this phase required a change in the electronic configuration of the atoms. Calculations have been made for the para-

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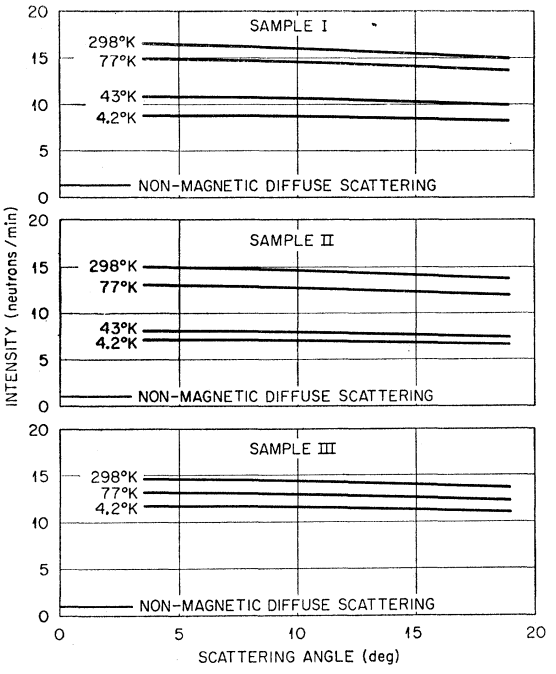

TEMP. (°K)	PHASE PERCENTAGES NORMAL fcc (%)	hcp (%)	COLLAPSED fcc (%)
298	100		
77	10	80	10
43	5	55	40
4.2	5	45	50

(°K)	(%)	(%)	(%)
298	75	25	
77	57	35	8
43	8	40	52
4.2	5	40	55

(°K)	(%)	(%)	(%)
298	10	90	
77	10	87	3
4.2	8	84	8

FIG. 2. Diffuse neutron scattering from three cerium samples at various temperatures.

magnetic diffuse scattering which would be expected with various possible electronic configurations, and these values have been compared with the experimental results. The intensities of all curves shown in Fig. 2 can be explained satisfactorily if the atoms in the fcc and hcp phases have one $4f$ electron in the $^2F_{\frac{5}{2}}$ state and the atoms in the fcc′ phase do not have a magnetic moment. Of the many configurations considered, this combination is the only one which gave satisfactory agreement with all of the data, and as shown in Table I, the agreement is well within experimental error.

Previous predictions that the formation of the fcc′ phase involves the promotion of a $4f$ electron to a $5d$ level are consistent with these results if the $5d$ electrons have compensating spins. The intensity of the diffuse scattering would not permit even a spin-only value for the magnetic moment of the atoms in this phase.

Investigations of Magnetic Ordering

The neutron diffraction patterns at 4.2°K for all three samples showed the presence of three additional very weak reflections, and Fig. 3 shows the development of these reflections in sample III. Although the intensities were very small, the reflection at a scattering angle near 13 deg was scanned with the sample at various temperatures above 4.2°K. Sample temperatures in this region were obtained with a small heater between the cerium and the container of liquid helium, and temperatures were measured with a calibrated copper-constantan thermocouple. The intensity of the reflection could be represented satisfactorily by a Brillouin-type curve which became zero at a temperature near 12.5°K. Therefore, the anomalies that were observed in the specific heat and magnetic susceptibility measurements at this temperature are undoubtedly associated with an antiferromagnetic transition.

The relative intensities of the antiferromagnetic reflections in the three samples at 4.2°K, when correlated with the three crystallographic phases existing at that temperature, indicated that these reflections must be associated with the hcp phase, and other analyses have substantiated this result. The reflections cannot be associated with the fcc′ phase, since their intensities disagree violently with the amount of this phase present at 4.2°K. Furthermore, the largest of the three reflections cannot be indexed by any sensible enlargement of the unit cell corresponding to the fcc structure. Of course,

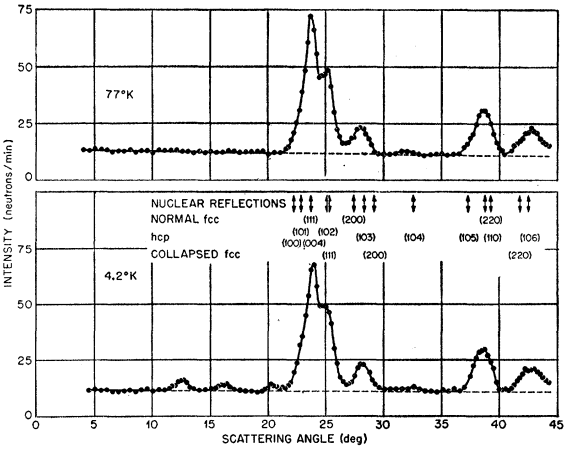

FIG. 3. Neutron diffraction patterns from cerium (sample III) at 77°K and 4.2°K.

TABLE I. Comparison of calculated diffuse scattering with experimental values (extrapolated to $2\theta=0°$).

Sample	Temperature (°K)	Phase concentrations (%) fcc	hcp	fcc′	Diffuse scattering (neutrons/min) Paramagnetic (calculated)[a]	Other (estimated)	Total	Observed
I	298	100			15.3	1.2	16.5	16.5
	77	10	80	10	13.8	1.2	15.0	15.0
	43	5	55	40	9.1	1.2	10.3	10.8
	4.2	5	45	50	7.3	1.2	8.5	9.0
II	298	75	25		14.0	1.0	15.0	15.0
	77	57	35	8	12.9	1.0	13.9	13.3
	43	8	40	52	6.7	1.0	7.7	8.0
	4.2	5	40	55	5.9	1.0	6.9	7.3
III	298	10	90		14.0	1.0	15.0	14.8
	77	10	87	3	13.5	1.0	14.5	13.5
	4.2	8	84	8	12.0	1.0	13.0	12.0

[a] Calculated values when the atoms in the fcc and hcp phases have one $4f$ electron in the $^2F_{5/2}$ state and there is no paramagnetic scattering from atoms in the fcc′ phase.

since the fcc phase is practically absent in all three samples at 4.2°K, it is not possible to show that this phase does not also experience antiferromagnetic ordering, but the largest reflection certainly appears to be the result of a transition that occurs in the hcp phase.

All three antiferromagnetic reflections can be indexed satisfactorily for a hexagonal cell with the same c axis as that of the chemical cell ($ABAC$ stacking sequence) and an a axis which is twice that of the chemical cell. Such a magnetic structure can be formed by stacking ferrimagnetic layers of moments of the type shown in Fig. 4(a), and calculations have been made for several models in which stacking sequences of $-+-+$ and $--++$ were considered. Since only three reflections were observed and these reflections were too weak to be measured accurately, it has been impossible to find a unique structure. However, there are models for both stacking sequences that predict the proper relative intensities within experimental error, provided the moments are oriented parallel to the c axis. The best agreement was obtained for a model with the $-+-+$ arrangement, and this model is shown in Fig. 4(b). Calculations of the value for the atomic magnetic moments varied between 0.50 μ_B and 0.75 μ_B for the various models, and for the model shown in Fig. 4(b), the value was 0.62 μ_B.

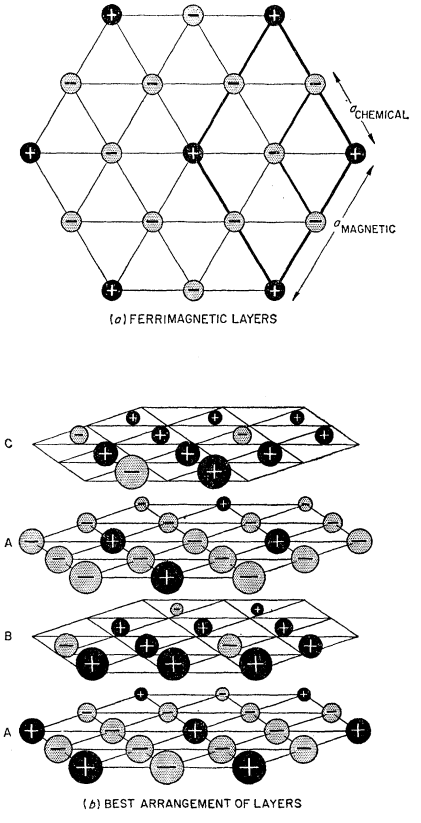

FIG. 4. Possible antiferromagnetic ordering in the hcp phase of cerium.

A determination of the magnetic moment was also obtained from the change in the diffuse scattering above and below the transition temperature, but this method was hindered by the change in diffuse scattering which accompanied the formation of the fcc′ phase. However, the maximum value of the ordered moment allowed by this calculation was 0.90 μ_B, and a more realistic value was 0.60±0.3 μ_B. Of course, the diffuse scattering analysis does not prove that any of the proposed magnetic structures are correct; it merely verifies that they predict a satisfactory value for the atomic moment in the ordered lattice.

DISCUSSION

In the rare-earth elements, the $4f$ sub-shell of electrons is progressively filled starting with cerium, and the magnetic properties of these elements arise from this incomplete shell. Since the $4f$ electrons are screened by eight electrons in the $5s$ and $5p$ sub-shells, the atoms within the metals should behave in a manner similar to the free atoms, except at low temperatures where crystal field effects can become important. The rare earths usually become trivalent ions in compounds, and they also have these trivalent characteristics in metals.

The results of the neutron diffraction investigation

on metallic cerium are consistent with these interpretations. At room temperature where the fcc and hcp phases were observed, the paramagnetic scattering from the cerium atoms corresponded to that from a trivalent ion with one $4f$ electron in the $^2F_{\frac{5}{2}}$ ground state. However, when the fcc′ phase was formed, the remaining $4f$ electron was presumably transferred to the conduction band, thereby giving the cerium atoms a tetravalent character and leaving them with no unpaired electrons. The low temperature data, however, indicate that the energy levels of the $^2F_{\frac{5}{2}}$ state are actually split by the crystal fields. The value of the atomic magnetic moment at 4.2°K for atoms in the ordered antiferromagnetic lattice is considerably smaller than the maximum value of $2.14\,\mu_B$ associated with this state. It should be mentioned that this effect was observed only in the coherent magnetic scattering at low temperatures. The absence of a change in the paramagnetic scattering indicates that the level splitting is small compared to the energy of the thermal neutrons incident on the samples.

The interpretation of the neutron diffraction results also appears to be completely consistent with the magnetic susceptibility measurements of Lock. From room temperature down to about 110°K, his results showed a Curie-Weiss behavior and gave an effective atomic moment in good agreement with that predicted for the free trivalent cerium ion in a $^2F_{\frac{5}{2}}$ ground state. Furthermore, if the anomalous behavior near 100°K was caused by a $4f \rightarrow 5d$ transition, Lock was able to predict that in cerium which is cooled for the first time, about half of the available $4f$ electrons are transferred. For the two samples (samples I and II) in this investigation which were previously uncooled, the phases that existed at room temperature and the phase transformations on cooling were different, but both samples showed about one-half of the sample transformed to the fcc′ phase at low temperatures. Of course, the reason that Lock's thermally-cycled sample showed no hysteresis in the magnetic susceptibility measurements is indicated by the phases that existed in sample III. This temperature cycling procedure apparently suppresses the transformation to the fcc′ phase and the corresponding electron transfer which is involved.

The antiferromagnetic structures that have been suggested to account for the magnetic ordering in the hcp phase cannot be considered definite because of the very weak reflections that were observed. However, the satisfactory agreement of the moment values obtained from the antiferromagnetic models with the value obtained from the diffuse scattering analysis indicates that these models are definite possibilities. It is also of interest that the experimentally determined moment values agree quite satisfactorily with those predicted from crystal field calculations. Murao and Matsubara[12] have calculated the level splitting of the $^2F_{\frac{5}{2}}$ state in the fcc phase, and their results predict a value of $0.71\,\mu_B$ for the atomic moment at low temperatures. Trammell[13] has extended these calculations to the hcp phase, and his results predict the same value for moments in the A layers but a slightly smaller value for the moments in the B and C layers where the crystal symmetry is different. Of course, if different moment values actually do exist for atoms in the two symmetries, then models of the $-+-+$ stacking sequence would give a magnetic structure that is slightly ferrimagnetic instead of antiferromagnetic.

Since the samples studied in this investigation contained only a small amount of the fcc phase at 4.2°K, it was not possible to make a definite determination concerning magnetic ordering in this phase. However, because of the similarity of this phase to the hcp phase and the presence of a $4f$ electron in the atoms, it seems logical to expect that antiferromagnetic ordering might also occur in the fcc phase. In fact, it is possible that the very small specific heat peak which has been observed[2] at about 7°K is the result of this antiferromagnetic transition.

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