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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF AMERICIUM LAVES PHASES*

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ABSTRACT

We have investigated a series of binary americium alloys with AB_2 stoichiometry (B = Al, Co, Fe, Rh and Ru) prepared from the ^{243}Am isotope. The C-15 ($MgCu_2$-type) structure appears in $AmAl_2$, $AmCo_2$, $AmFe_2$ and $AmRh_2$, whereas $AmRu_2$ is isostructural with $AmOs_2$ which has the C-14 ($MgZn_2$-type) structure.

The magnetic properties of the cubic americium Laves phases have been studied by means of magnetization and nuclear gamma-ray resonance (Mössbauer effect) measurements between 2.5 and 300 K. All the cubic Laves phases studied, except $AmFe_2$, exhibit almost temperature independent paramagnetism. The $AmFe_2$ sample is ferromagnetic with an estimated Curie temperature of ∿400 K. The hyperfine field at the Am site in all the compounds is small. The bulk magnetic moment of $AmFe_2$ ($\sim 3\mu_B$/F.U.) is thus associated only with the Fe atoms. The magnetic properties of the compounds are consistent with the assumption that the Am ion is in the +3 state($5f^6$).

I. INTRODUCTION

The importance of Laves phases to the alloy chemistry of intermetallic compounds arises from their widespread occurence (they form the largest known family of intermetallic compounds). Lam and Mitchell [1] showed that the Laves phases of the actinides Th, U, Np, and Pu obey the same general rules which govern the systematics of other Laves phases. In the present paper we report the existence of some new americium Laves phases and show that their alloy chemistry is consistent with the earlier results. In addition, we have studied the magnetic properties of some of these compounds by means of magnetization and NGR (nuclear gamma-ray resonance) experiments. Our interest in the magnetic properties arises from similar studies of the corresponding U, Np, and Pu Laves phases [2-5] that show a variety of magnetic behavior.

II. EXPERIMENTAL

The compounds were prepared by arc melting the requisite amounts of the constituent metals in an argon-helium atmosphere; the resultant buttons weighed ∿0.2g. Chemical analysis of the ^{243}Am metal used in this investigation (obtained from Hollifield National Laboratory) yielded the following impurities (in ppm by weight). Al 1000; B 0.5; Ca 500; Cr 30; Cu 40; Fe 300; K <0.2; Mg <1; Mn 10; Mo <0.3; Na <0.1; Ni 2; P <0.1; Pb 30; Si 50; Sr 4; Ti <1; V <0.1; Zn <0.2; Zr <0.2; Am^{241} 100; Pu^{240} 1. The remaining materials used for sample preparation were zone-refined Al (99.999% pure) and high-purity cobalt (99.99%), iron (99.99%), rhodium (99.96%) and ruthenium (99.99%). Most of the samples were arc melted twice, homogenized at 1000°C for several hours and furnace cooled. X-ray powder diffraction patterns (Straumanis-type Debye-Scherrer camera, 114.6 mm diameter) indicated that the samples were single phase, except for the $AmCo_2$ and particularly the $AmFe_2$ samples which were found to have small amounts of a second phase. The $AmFe_2$ sample was re-annealed at 1000°C for one month to insure homogenization.

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Approximately 100 mg of each compound was sealed in an aluminum capsule for magnetization measurements and a further 30 mg was sealed in a separate aluminum capsule for the NGR experiments. Magnetizations were measured between 2.5 and 300 K in fields up to 14 kOe by a force method; the experimental technique has been described in detail [2]. NGR measurements were made at 4.2 K by means of the 83.9 keV resonance in ^{243}Am.

III. RESULTS AND DISCUSSION

The crystal structures and lattice parameters of americium Laves phases are given in Table 1. The stability of Laves phases is usually discussed in terms of a hard-sphere packing model [1]. The ideal ratio of the radii of the constituent atoms R_A/R_B (A would correspond to americium) is 1.225. The fact that phases exist with ratios between 1.05 and 1.68 suggests that substantial changes occur in the size of the component atoms when the structure forms. The radius ratios of americium Laves phases (Table 1) are all greater than the ideal value. The parameters (D_A-d_A) and D_B-d_B), where D_A and D_B are the CN12 atomic diameters and d_A and d_B are the atomic diameters of the A and B atoms in the Laves phase, are usually used to indicate the degree of atomic size adjustment [1]. The values of these parameters, also given in Table 1, are consistent with the earlier results for actinide Laves phases (see Fig. 1 of ref. [1]) and indicate that when the radius ratio is greater than the ideal value (1.225) the actinide atoms contract $[(D_A - d_A)>0]$, whereas the B atoms remain unchanged in size $[(D_B - d_B) \simeq 0]$.

TABLE 1

Crystal structures and parameters of Americium Laves phases

Compound	Crystal Structure	Lattice Parameters a (Å)	c (Å)	R_A/R_B	D_A-d_A (Å)	D_B-d_B (Å)
$AmAl_2$	$MgCu_2$-type	7.861(1)[a]		1.26	0.20	0.08
$AmCo_2$	"	– [b]				
$AmFe_2$	"	7.30(1)		1.42	0.44	-0.04
$AmIr_2$[c]	"	7.550(3)		1.33	0.33	0.03
$AmNi_2$[d]	"	6.99(1)		1.45	0.57	0.01
$AmPt_2$[d]	"	7.66(1)		1.30	0.28	0.05
$AmRh_2$	"	7.51(1)		1.34	0.35	0.02
$AmOs_2$[d]	$MgZn_2$-type	5.320	8.849			
$AmRu_2$	"	5.26(1)	8.73(1)			

a. Number in parenthesis represents estimated error in last significant figure.

b. The high-angle lines were too diffuse for a lattice parameter determination.

c. B. Erdman, Kernforschungszentrum, Karlruhe, KFK 1444 (1971).

d. D. J. Lam and A. W. Mitchell, J. Nucl. Materials 44 (1972), 279.

The compounds $AmAl_2$, $AmRh_2$ and $AmRu_2$ are all paramagnetic over the entire temperature range studied. Magnetic susceptibilities χ(emu/g) were calculated by fitting the magnetization σ(emu/g) versus field H(Oe) data at different temperatures to an equation of the form

$$\sigma = \sigma_0 + \chi H. \qquad (1)$$

All the samples had significant positive values of σ_0 that are presumably associated with either ferromagnetic impurities in the ^{243}Am starting material or the ^{239}Np daughter product of the alpha decay of ^{243}Am. The molar susceptibilities of the three samples are shown as a function of temperature in Fig. 1. The rather large experimental error is associated with the presence of the σ_0 term together with the small intrinsic values of the susceptibility. The compounds show a relatively temperature-independent susceptibility and no evidence of magnetic order.

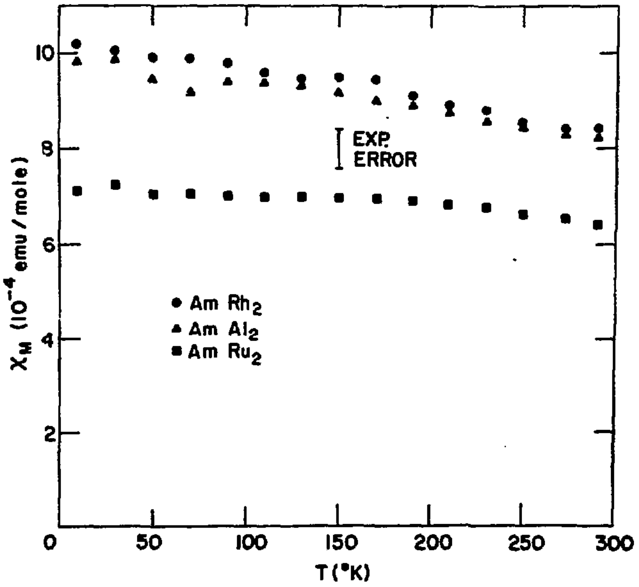

Fig. 1. Temperature dependence of the molar susceptibility of $AmAl_2$, $AmRh_2$ and $AmRu_2$.

On the other hand, $AmFe_2$ is ferromagnetic over the entire temperature range and some magnetic isotherms are given in Fig. 2. On the basis of the temperature dependence of the magnetization at constant field, we would estimate that the Curie temperature T_c is in the range 350-400 K. This temperature is substantially lower than those of $NpFe_2$ (∿500K) [3] and $PuFe_2$ (∿600K) [5]. However, the maximum magnetization value (Fig. 2) is ∿50% greater than for $NpFe_2$ and $PuFe_2$ and corresponds to a moment of $2.9\mu_B$/mole. The large, slowly-saturating field dependence is typical of actinide ferromagnets [2,3,5] and presumably reflects the presence of a large magnetocrystalline anisotropy. In the absence of single crystals, it will be necessary to use very high fields to obtain reliable bulk moments for these compounds. The decrease in the relative field dependence of the magnetization as the temperature approaches T_c (Fig. 2) again suggests the influence of anisotropy.

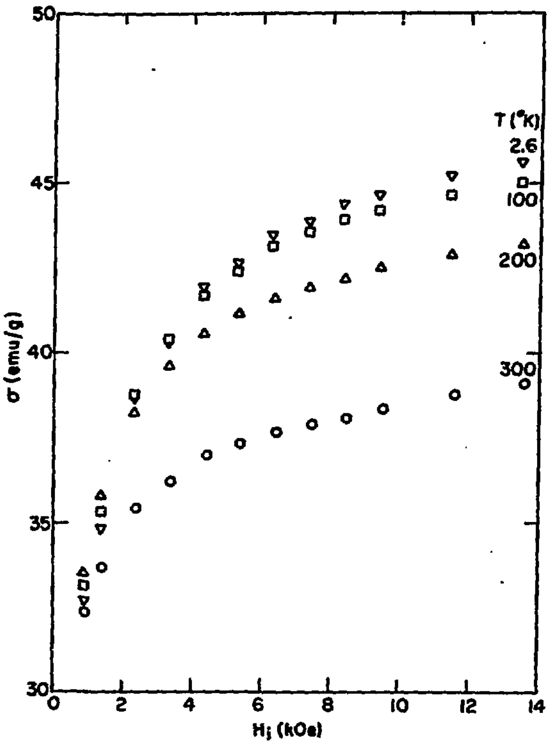

Fig. 2. Magnetization versus internal field isotherms for $AmFe_2$.

The NGR experiments showed a single resonance line for each of the samples and the results are summarized in Table 2. There is some line broadening in $AmFe_2$, which is probably due to a transferred hyperfine field, but there is no evidence of a magnetic moment at the americium site - indicating a non-magnetic ($5f^6$) ground state of the Am^{3+} ion. The moment per iron atom thus deduced for $AmFe_2$ from the magnetization results ($\sim 1.5\mu_B$) is higher than in either UFe_2 ($\sim 0.5\mu_B$) [5], $NpFe_2$ ($\sim 1\mu_B$) [3], or $PuFe_2$ ($\sim 1\mu_B$) [6]. The variation in magnetic properties among the actinide-iron Laves phases is not understood at this time.

TABLE 2

NGR results for americium Laves phases; source ^{243}Am in $PuAl_2$

Compound	Isomer Shift[a] (mm/s)	Linewidth (mm/s)
$AmAl_2$	+1.6	9.1
$AmFe_2$	-6.0	31.5
$AmRh_2$	-4.8	7.7
$AmRu_2$	-10.9	10.0
	(±0.5)	(±0.5)

[a] Relative to $PuAl_2$

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REFERENCES

1. D. J. Lam and A. W. Mitchell, J. Nucl. Materials 44 (1972) 279.
2. A. T. Aldred, B. D. Dunlap, D. J. Lam, and I. Nowik, Phys. Rev. B10 (1974) 1011.
3. A. T. Aldred, B. D. Dunlap, D. J. Lam, G. H. Lander, M. H. Mueller and I. Nowik, Phys. Rev. B11 (1975) 530.
4. A. T. Aldred, D. J. Lam, A. R. Harvey and B. D. Dunlap, Phys. Rev. B11 (1975) 1169.
5. D. J. Lam and A. T. Aldred, AIP Conf. Proc. 24 (1975) 349.
6. G. H. Lander and M. H. Mueller, private communication.