Low-Temperature X-Ray Diffraction Studies of Near-Equiatomic VRu Alloys

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A crystallographic transition of the ordered near-equiatomic VRu alloys has been observed between 360 and 110 K. This cubic-to-tetragonal distortion occurs over a temperature interval commensurate with the observed anomalies in electrical resistivity, magnetic susceptibility, and the Knight shift. The transition involves a 1.4% expansion in volume for $V_{0.50}Ru_{0.50}$. This expansion is very nearly temperature independent between 300 and 110 K. The volume change for $V_{0.51}Ru_{0.49}$ at 110 K is 1.5%. For both compounds the CsCl-type ordering is approximately 100%.

I. INTRODUCTION

Recently Chu *et al.* reported the results of a study of electrical resistivity, magnetic susceptibility, and the Knight shift of V^{51} as a function of temperature of the near-equiatomic VRu alloys.[1] In contrast to previous results, it was observed that the resistivity increased, the magnetic susceptibility decreased, and an increase of the Knight shift K_V occurred over a narrow temperature range during cooling. It was suspected that the tetragonal-to-cubic crystallographic transition was associated with these changes in properties.[2,3] In order to confirm this phase change, low-temperature diffraction studies were performed on several alloys.

II. EXPERIMENTAL

The samples used for these experiments are the same as those described in Ref. 1. Each powdered VRu sample was mounted on a copper disc in intimate contact with a Chromel-Alumel thermocouple and the entire assembly was fitted to a Philips - Norelco spectrometer. The sample temperature was varied by blowing cold N_2 gas directly on the sample surface. A Varian temperature controller was used to monitor the flow of N_2 gas. The x-ray radiation used was Cu $K\alpha$ with a 1-deg beam divergence and $\frac{1}{4}$-deg/min scanning speed.

Two unannealed powdered samples $V_{0.55}Ru_{0.45}$ and $V_{0.50}Ru_{0.50}$ were each mounted on a glass fiber and placed in a General Electric x-ray powder camera. Long exposures, ~16 h, were taken with Mo $K\alpha$ radiation at room temperatures and at approximately 110 °K. The low-temperature exposures were obtained by use of the Varian controlled N_2-gas probe.

III. RESULTS

In the case of the unannealed powder samples no crystallographic phase change was observed either in the wet-film exposures or in the diffractometer tracings. These x-ray patterns were those of a cubic CsCl structure, $B2$. A calculation of CsCl-

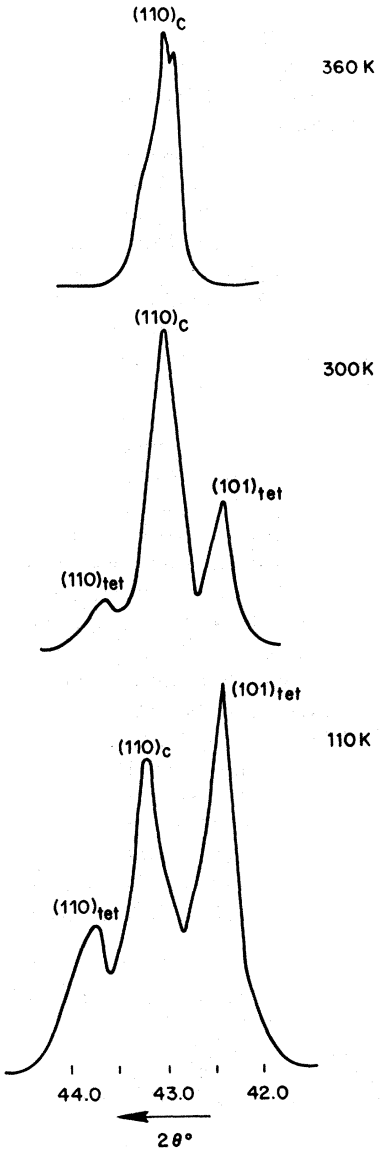

FIG. 1. X-ray diffractometer tracings of the cubic $(110)_c$ reflection and the tetragonal $(101)_{tet}$ and $(110)_{tet}$ reflections at three temperatures.

TABLE I. Lattice parameters for the annealed $V_{0.50}Ru_{0.50}$ and $V_{0.51}Ru_{0.49}$ samples in Å.

$V_{0.50}Ru_{0.50}$		$V_{0.51}Ru_{0.49}$	
300 K			
Cubic	Tetragonal	Cubic	Tetragonal
$a = 2.986(2)$	$a = 2.939(10)$ $c = 3.125(10)$	$a = 2.990(4)$	
110 K			
$a = 2.977(3)$	$a = 2.927(6)$ $c = 3.123(6)$	$a = 2.975(9)$	$a = 2.928(8)$ $c = 3.118(9)$

type ordering for the unannealed $V_{0.55}Ru_{0.45}$ sample revealed no more than 36% ordering. All of the reflection peaks were broad and diffuse and remained so at low temperature.

In contrast to these results the annealed $V_{0.51}Ru_{0.49}$ and $V_{0.50}Ru_{0.50}$ samples each had sharp reflection peaks and a well-defined cubic-to-tetragonal temperature-induced phase transition. This $B2$ cubic-to-tetragonal transition was reported previously by several authors[4,5] as a function of composition. They found that it occurs in nearly equiatomic VRu alloys as the Ru concentration increases. Both of the $V_{0.51}Ru_{0.49}$ and $V_{0.50}Ru_{0.50}$ annealed alloys were approximately 100% ordered. In the case of $V_{0.50}Ru_{0.50}$ at room temperature, approximately one-third of the material was $B2$ tetragonal, while in the case of the $V_{0.51}Ru_{0.49}$ sample, 100% of the material was $B2$ cubic. As the temperature of the ordered $V_{0.50}Ru_{0.50}$ sample was lowered, the tetragonal reflections grew in intensity while the cubic reflections diminished. This effect was also observed for the ordered $V_{0.51}Ru_{0.49}$ powder. At elevated temperatures, ~360 K, nearly all of the annealed $V_{0.50}Ru_{0.50}$ sample transformed to the cubic $B2$ phase. Figure 1 shows the diffractometer tracings of the (110) reflection for this sample at various temperatures. One can see that at the experimental limits of temperature, 360 and 110 K, there still remains a residual amount of the tetragonal and cubic phases, respectively. It should be noted that at high temperature the tetragonal distortion is very small, resulting in the barely discernible shoulders on the (110) cubic peak. Chu *et al.*[1] report that the transition temperature increases with increasing Ru concentration and our data are in agreement with this. The lattice parameters for the annealed $V_{0.50}Ru_{0.50}$ and $V_{0.51}Ru_{0.49}$ samples are indicated in Table I.

IV. DISCUSSION

It is important to note that the cubic-to-tetragonal transitions of the ordered VRu alloys involve an increase of unit-cell volume. For the equiatomic sample this was a 1.4% increase in volume at 300 K and a nearly identical increase, within experimental limits, at 110 K. However, between 300 and 360 K the ΔV of transition for this sample was definitely temperature dependent since the appearance of tetragonal shoulders on the $(110)_c$ peak at 360 K indicated that the ΔV of transition was gradually approaching zero. This effect was not observed in the case of the $V_{0.51}Ru_{0.49}$ alloy. The percent volume change appears to be composition independent since this change for the $V_{0.51}Ru_{0.49}$ sample was found to be 1.5% at 110 K. The rather broad temperature range for the transition can be interpreted as a characteristic of a martensitic-type transition. The microstructure of these phases strongly suggests a martensitic origin.[3] In the case of $V_{0.50}Ru_{0.50}$ the cubic-to-tetragonal transition involves a 1.7% contraction in the V-V interatomic distances along the [100] and [010] directions from 2.99 to 2.94 Å. A simultaneous 4.7% expansion occurs in V-V distances along the [001] direction from 2.99 to 3.13 Å. In addition to these changes, the V-Ru distances along the unit-cell body diagonals increase 2.4% from 2.54 to 2.60 Å. It appears that the near-equiatomic VRu alloys have an increase in volume over a temperature interval which is commensurate with the anomalies in electrical resistivity, magnetic susceptibility, and Knight shift.

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