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CRYSTALLINE STRUCTURE AND PHYSICAL PROPERTIES OF UCo_2Al_3

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Some intermetallic compounds which contain uranium or cerium present heavy fermion characteristics. Take, for example, in the UM_2Al_3 (M = Pd, Ni) family, superconductivity and magnetism coexist and present heavy fermion behavior. This work presents the crystallographic characteristics and physical properties of a new compound of this family; the intermetallic compound UCo_2Al_3. Our initial crystallographic studies performed in a small single crystal show that the structure is hexagonal and similar to the UNi_2Al_3 and UPd_2Al_3 parent compounds. The space group is P6/mmm with $a = 5.125$ Å and $c = 4.167$ Å crystalline parameters. Measurements of resistivity and magnetization performed on the single crystal reveal that the compound is not superconducting when measured at about 1.8 K. The compound is highly anisotropic and features related to Kondo-like behavior are observed. A weak ferromagnetic transition is observed at a temperature of about 20 K.

Keywords: Magnetism; superconductivity; heavy fermions; intermetallic compounds.

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1. Introduction

Actinides, particularly uranium atoms, form intermetallic compounds with transition metals that present many interesting characteristics and electronic properties. Some of these compounds, for example, UPd_2Al_3 (Ref. 1) and UNi_2Al_3 (Ref. 2), are heavy fermions systems with superconducting and magnetic characteristics. The magnetic ordering in the two compounds is of antiferromagnetic type, and occurs at temperature below 20 K. The superconductivity appears at much lower temperatures. Recently, it has been discovered that both phenomena, superconductivity and magnetisms coexist in the two compounds.[3,4]

Among other characteristics of the heavy fermion behavior is that the superconducting condensate is of different symmetry to the *s*-wave wave function, thus, it may be different from the normal BCS. In superconductors with *s*-wave symmetry, ferromagnetism and superconductivity are antagonist phenomena. However, if the pairing symmetry is d or f, these two processes may be compatible as it is believed to occur in heavy fermions and in high temperature superconducting materials.[4]

From the viewpoint of the crystallographic characteristics, the two mentioned intermetallic systems have the hexagonal $PrNi_2Al_3$-type crystalline structure, and the magnetic ordering of antiferromagnetic type presents a Néel temperature, at $T_N = 14.2$ and 4.6 K, for UPd_2Al_3 and UNi_2Al_3, respectively. On the other hand, the superconducting transition temperatures for UPd_2Al_3 and UNi_2Al_3 occur below, at about $T_c \sim 2.0$ and $\sim$1.0 K, respectively.[1–8] Other alloys with uranium and transition metals also present superconductivity or magnetism, but both phenomena are independent. One interesting case is the UFe_x family of compounds. This presents superconductivity at temperatures higher than U alone, when Fe is introduced. The transition temperature reaches a maximum of about the limit of segregation of Fe in U. The maximum T_c measured by Verdin and Escudero was about 2.78 K.[9] That behavior is different from pure uranium as the transition temperature only reaches 0.68 K. In this compound, the magnetism of iron does not suppress superconductivity; in fact, it increases it. Two possible scenarios have been proposed in order to explain the increase in the superconducting temperature.[9] In the first one, it may be assumed that the pairing mechanism is different from s-wave wavefunction symmetry, in that case paramagnetic impurities do not suppress superconductivity. The second assumption is much more simple and reliable, and it implies that the wave symmetry is an s-wave, and the only effect of Fe atoms is to increase the electronic density of states at the Fermi level. Then, according to BCS, this will enhance superconductivity because T_c, as is well known, depends exponentially on the density of states at the Fermi level. Many other uranium-transition metal alloys exist, and some show superconductivity and/or magnetism, but in general, the behavior may be explained because they obey the Hill radius criteria for the absence of superconductivity or presence of magnetism.[10] However, in intermetallics alloys with heavy fermion characteristics, superconductivity and magnetism exist when the distance between U atoms is bigger that the Hill radius.[10]

In this work, we present the study of the intermetallic compound UCo_2Al_3 synthesized for the first time. Our studies indicate that the crystalline structure of the compound is hexagonal, with $PrNi_2Al_3$ type structure, similar to the other members of this family shown in Table 1. In addition, we study the magnetic and transport characteristics of this new compound from room temperature to about 1.8 K. The compound is not superconducting in the temperature range studied.

2. Synthesis and Crystal Structure Determination

The Al and Co starting elements for the sample preparation were with purities 99.999% and 99.9%, respectively. The Uranium depleted was purified by remelting several times at high temperature under an argon atmosphere.[11,12] The alloy was prepared using a radiofrequency induction furnace with water-cooled cooper crucibles. Three steps were used to produce the final alloy. Initially, Co-U was melted several times under an argon atmosphere. In a second step, aluminum metal was added to fulfill the 1:2:3 stoichiometry. In a third final step, we performed an annealing process at temperature of about 600°C. It is important to note that higher temperatures tend to decrease the correct 1:2:3 stoichiometry. For the annealing procedure, the button-alloy was wrapped in tantalum foil and enclosed in an evacuated quartz tube, for a period of about 24 hours.

Electron-backscattering analysis was performed on a polished surface of the button; this shows different regions with different compositions. The regions have different coloration spots: metallurgical analysis shows that the regions with gray-dark color spots are very close to the UCo_2Al_3 stoichiometry.

In order to perform the X-ray analysis, and the magneto-transport measurements, the obtained buttons of UCo_2Al_3 were crushed. The regular prismatic-like crystals of small size (gray-dark zone) were mechanically selected from the polycrystalline mass. Selected samples with appearance of prismatic single crystals show the correct stoichiometry. In Fig. 1, we show a photography of a single crystal extracted from the polycrystalline mass.

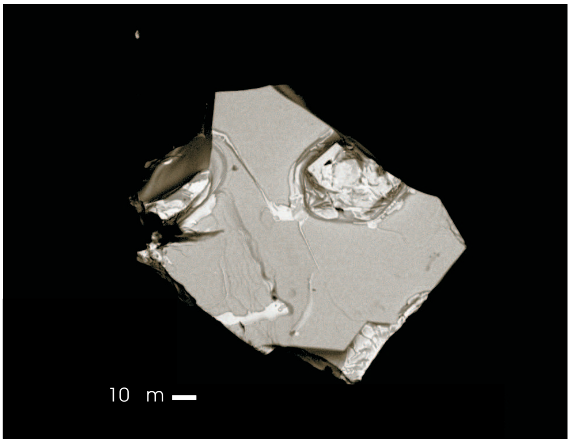

Fig. 1. Photograph of a typical UCo_2Al_3 single crystal.

Single crystals were studied at room temperature by X-ray diffraction using a Bruker P4 diffractometer with graphite monochromatic Mo-K_α radiation. Figure 2 shows a long-time exposure photograph of the diffraction studies on the single crystal. No secondary phases were detected; each reflection was measured between 12 and 18 times. We observed that the diffraction peaks are symmetrical, with low background on a complete diffraction sphere of up to 0.50 Å resolutions. The set of spots indexed yields the cell parameters; $a = 5.1252(2)$ Å and $c = 4.1667(2)$ Å, volume $V = 94.786$ Å^3, and with 13% independent reflections (R_{int}), which is quite correct, considering the redundancy of the diffraction patterns (additional studies

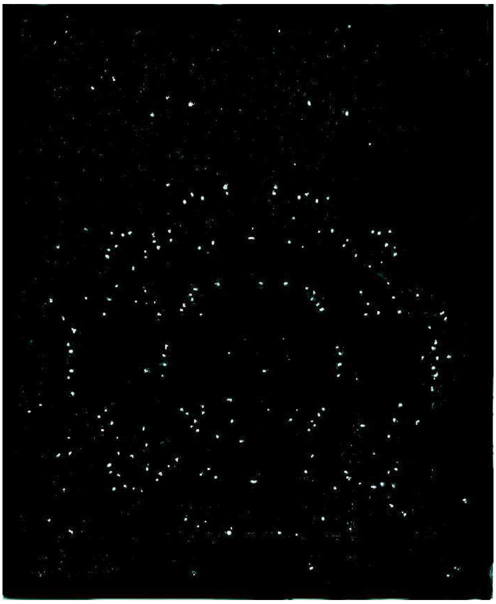

Fig. 2. X-ray Laue diffraction pattern of UCo_2Al_3 crystal.

to produce more single samples are under way). The atomic U–U separation of 4.1667 Å is consistent with one of the prerequisites to heavy fermion behavior. On the base of the obtained data, we estimate that the single crystal under consideration is a pure crystalline sample of the UCo_2Al_3 phase, compatible with a hexagonal system and space group P6/mmm.

3. Transport and Magnetic Measurements

Electrical resistivity measurements were determined by the standard four terminal dc method. Four gold wires, with diameters 10 μm, were glued to the single crystal of dimensions $0.12 \times 0.10 \times 0.05$ mm^3. Magneto-transport measurements were performed at different magnetic fields; the maximum field was 1 Tesla, from 1.8 to 300 K. Magnetic measurements were performed in a MPMS Quantum Design magnetometer decreasing the temperature from 300 K to about 1.8 K, with and without applied magnetic field. These were performed at Zero Field Cooling (ZFC) and Field Cooling (FC) cycles, using low magnetic fields (maximum 0.010 T).

4. Results and Discussion

We studied the transport and magnetic properties of the new compound and also investigated if the material presents superconducting behavior. From this point of view, the substitution of nickel by cobalt in the type of hexagonal crystalline structure mentioned is quite interesting because of the high ferromagnetic characteristics of cobalt. Our initial studies performed in this compound indicate that this is not superconducting, but presents a magnetic order that in principle is of weak ferromagnetic type at a temperature close to 20 K, as we will show in the next few paragraphs.

Measurements performed in this compound show that in one crystallographic direction of the single crystal, the behavior is metallic. However, at low temperatures, there is an upturn in the resistance-temperature characteristic. This upturn might be attributed to a Kondo-scattering effect. Moreover, if the interaction is due to Kondo-scattering, this will require an antiferromagnetic interaction between magnetic atoms and the conduction electrons. Thus, it will be possible to assume that the magnetic interaction at 12 K is a weak ferromagnetic ordering with canted spins, that at lower temperatures, turns into an antiferromagnetic order. The magnetic features were observed only in one crystallographic direction of the single crystal, according with our magnetic measurements. Magnetic characteristics in the UPd_2Al_3 and UNi_2Al_3 compounds have also been observed in only one direction.[5] We also observed that the resistivity measurements show anisotropy in the two directions of the crystal. The studies of magnetoresistance indicate a negative magneto resistive effect only in one direction of the crystal.

In Table 1, we show some structural and electronic characteristics of members of this family. Our electrical resistivity measurements, ρ(T) are shown in Fig. 3. It seems that the behavior of the curves is clearly different in the two directions of the single crystal (current j in directions: a, b plane and parallel to c direction). The differences are in magnitude (one order of magnitude different for both directions) and in the temperature dependence. It is interesting to mention that ρ(T) with injected current in the c direction, and with the applied field in the ab plane, is reminiscent of a heavy fermion behavior. We noted a clear maximum at around 100 K, similar to the observed in UPd_2Al_3 compound.[17] In contrast, the behavior of ρ(T) with the current injected in the a, b plane, and applied field parallel to the c direction, shows a pronounced decrease in temperature. This is the typical

Table 1. Crystallographic data and summary of properties of the family of compounds with chemical formula RT_2M_3; R = Ce or T = Ni or Pd, and M = Al or Ga.

Compound	T_C (K)	T_N (K)	a (Å)	c (Å)	Volume (Å^3)
UNi_2Al_3[a]	~ 1.0	~4.6	5.207	4.018	94.31
UPd_2Al_3[b]	~ 2.0	~ 14.4	5.365	4.186	104.31
$CeNi_2Al_3$[c]	NR	NR	5.309	4.045	98.70
$CePd_2Al_3$[d]	NR	2.7	5.467	4.214	109.10
UNi_2Ga_3[e]	NR	9.6	5.168	4.028	93.13
UPd_2Ga_3[f]	NR	13.4	5.301	8.511	207.17
UCo_2Al_3[g]	NR	12.0	5.125	4.167	94.79

[a]Refs. 2 and 8, [b]Ref. 1, [c]Ref. 13, [d]Refs. 14, [e]Ref. 15, [f]Ref. 16, [g]Present work, NR (not reported).

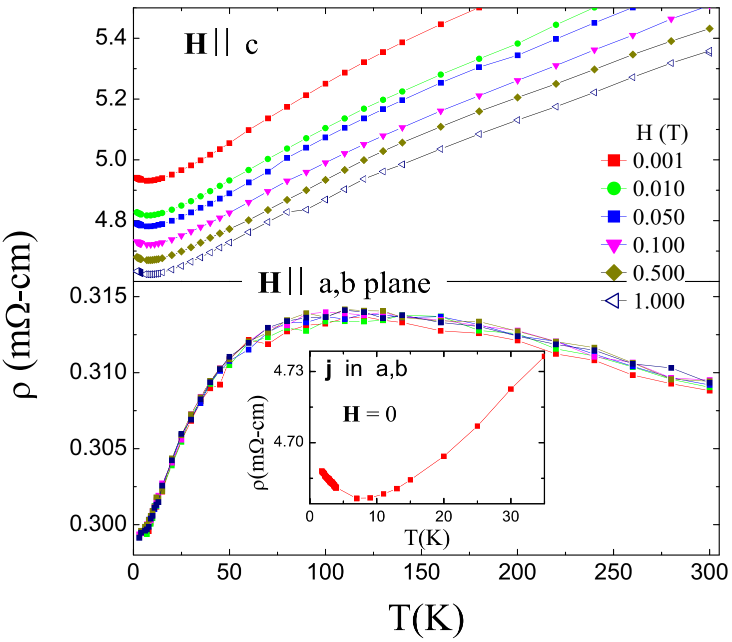

Fig. 3. R(T) dependence with applied magnetic fields. The current is in a, b plane and c direction, H is perpendicular to them. The inset shows the curves for H = 0. Note the minimum below 10 K attributed to a Kondo anomaly.

characteristic of a well-behaved metallic alloy. However, we also note that at low temperatures (see inset of Fig. 3) a clear anomaly is presented with respect to a normal metal; ρ(T) characteristic presents a minimum below 10 K (7.4 K) that can be fitted quite well to a $\rho(\mathrm{T}) \sim -\log \mathrm{T}$ function. Interestingly, this upturn in ρ(T) is the characteristic feature of a Kondo anomaly.[18] This anomaly does not exist, in the other two superconducting members of this family, and it may be explained as a many-body effect due to the interaction of magnetic atoms which affects the scattering rate of the conduction electrons via interacting with localized moments, and must be attributed to Co atoms interacting in an antiferromagnetic ordering. [For explanation of the type of many-body effects, see J. Kondo, *Solid State Physics* **23** (1969), eds. D. S. Turnbull and H. Ehrenreich (Academic Press, New York, 1969), p. 184.] The main frame of Fig. 3 shows ρ(T) versus applied magnetic field, in two directions of the single crystal. The injected current is in the perpendicular direction to the applied magnetic field. With magnetic field parallel to the c direction, the shape of the entire ρ(T) curves is not affected by the field, but ρ(T) decreases in magnitude from about 4.9 to 4.6 mΩ-cm. In contrast, when magnetic field is applied in the perpendicular direction to c, the entire ρ(T) curves is not affected. The inset of Fig. 3 presents the low temperature behavior of the resistivity in c direction. Clearly, we see the upturn of the resistivity, showing the "Kondo anomaly".

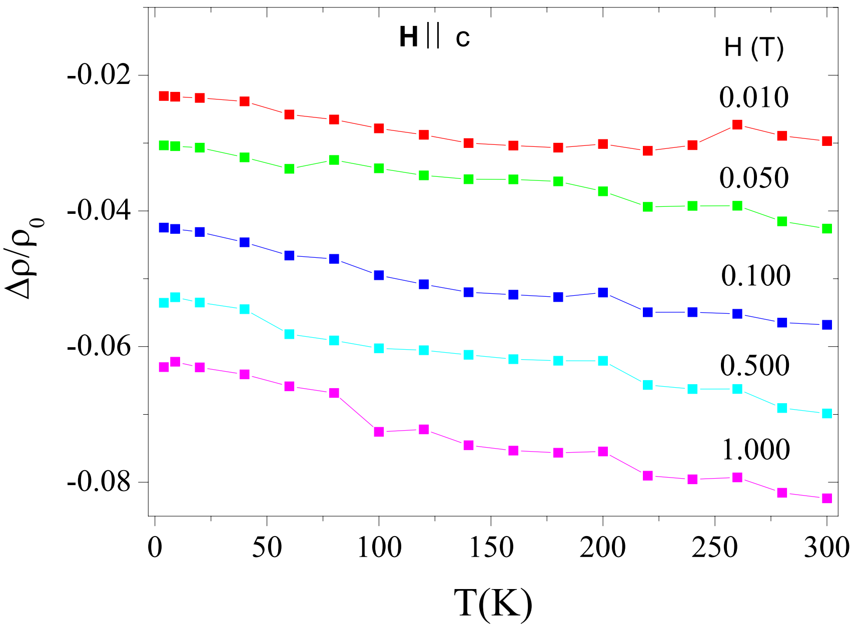

Fig. 4. Normalized magnetoresistance versus temperature with applied fields. The current is on *a*, *b* plane. H is perpendicular to it.

In Fig. 4, we present magnetoresistance measurements, in the form as $\Delta\rho/\rho_0 = [\rho(\mathrm{H}, \mathrm{T}) - \rho(0, \mathrm{T})]/\rho(0, \mathrm{T})$ versus temperature at different magnetic fields from 0.01 to 1 Tesla. Magnetoresistance changes are observed only in one direction of the crystal. The values are negative and the magnetoresistance data increase with negative slope as the magnetic field increases. It is important to note that we did not find evidence of magnetic ordering on the *c* direction (according to the magnetic measurements). However, it seems that more studies are necessary in order to complete characterizing and understanding this unexpected behavior. It is important to emphasize that the negative value for the magnetoresistance implies that the rate of scattering is due to spins which are decreasing by the orienting magnetic field.

Figure 5 shows data on magnetization-temperature characteristics, performed under zero field cooling (ZFC) and field cooling (FC) magnetization cycles, in low DC field of 0.005 T. A ferromagnetic transition occurs at 20 K. However, a big irreversibility in ZFC and FC magnetization occurs for T below 20 K with a clear cusp at 12 K in the ZFC magnetization, which can be indicative of a spin glass freezing for $\mathrm{T} < \mathrm{T}_{\mathrm{cusp}}$.[19] Nevertheless, another possibility is that a weak ferromagnetic ordering is presented, indicative of canted spins in this compound, which eventually, at low temperatures, may give antiferromagnetic-type ordering. In this case, the initial assumption of the observed Kondo anomaly will be reinforced.

Thus, two possible explanations for the absence of superconductivity in this compound may be relevant: one could be the weak ferromagnetism presented at

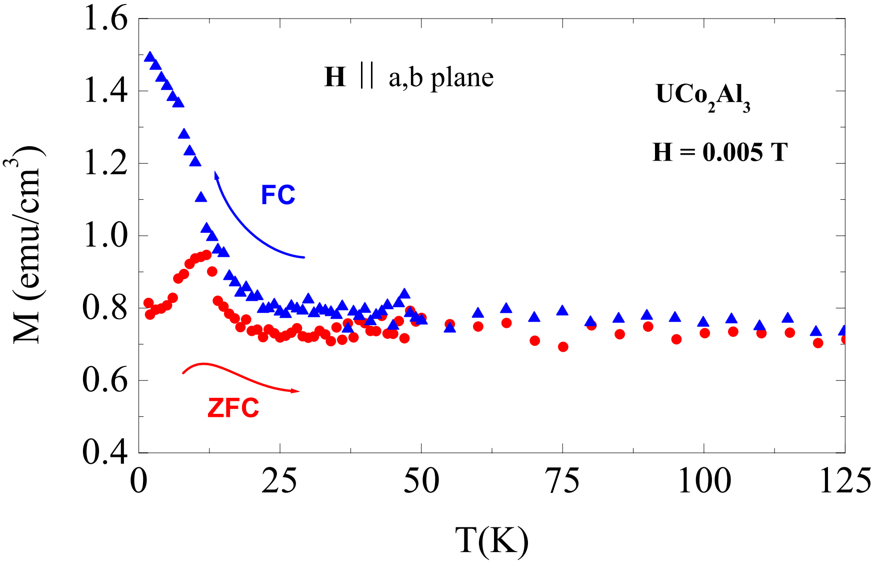

Fig. 5. Magnetization versus temperature for H parallel to the *a*, *b* plane. In zero field cooling (ZFC) and field cooling (FC) mode. The weak ferromagnetic transition maximum is at about 20 K. At 12 K, a cusp is clearly observed in ZFC measurements.

20 K, and the other, the Kondo anomaly at low temperatures. It is important to mention that in the two other superconducting UNi$_2$Al$_3$ and UPd$_2$Al$_3$ parent compounds, a correlation exist between the antiferromagnetic ordering and the superconducting transition temperature. Take, for instance, in this Co compound, T_N may be well below 3 K, quite below respect to both Pd (14.2 K) and Ni (4.6 K) based compounds. The magnetic transition temperatures are very dependent of the transition metal atomic radius. Take, for instance, we see that the Néel temperatures follow a trend of decreasing similar to the atomic radius, that is, Pd (1.37 Å), Ni (1.25 Å), and Co (1.24 Å), whereas the Néel temperature decreases as 14.2, 4.6 and perhaps below 2 K, respectively. At this point, it is tempting to imply that at least the chemical internal pressure must be playing an active role for the physical characteristics on this family as well.

5. Conclusions

A new uranium intermetallic compound, UCo$_2$Al$_3$, was synthesized and its structure was studied by X-ray diffraction. The compound crystallizes in the hexagonal PrNi$_2$Al$_3$-type structure, similar to a variety of ternary intermetallic alloys that contain U or Ce.

We found anisotropic behavior in the ρ(T) measurements. In the *c* direction, the characteristic is typical of a heavy fermion material. Our initial measurements show that at the minimum measured temperature, about 1.8 K, there is not superconducting behavior. However, more studies at low temperatures are necessary in order to determine if the compound is superconducting or not. In the other direction of the crystal, the T-dependence of the resistivity shows a metallic behavior. Moreover, at about 10 K, we observed a minimum characteristic of a Kondo-like effect which is due to Co atoms. Magnetic measurements shows a weak ferromagnetic transition at about 20 K. However, at 12 K, a irreversibility is observed in ZFC measurements, implying weak ferromagnetism or/and spin glass behavior. More studies are in progress in order to clarify the physical characteristics of this new compound.

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