Comments on Measurements of the Magnetic Properties of Uranium Compounds Published in This Journal*

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Several experimental results describing the magnetic properties of uranium compounds (UP, UP₂, US and the UC₁₋ₓNₓ system), published recently in this journal(1)(2) have puzzled us since they are in disagreement with published data and with some unpublished results obtained at various laboratories.

Adachi & Imoto(1) found that both UP and UP₂ are antiferromagnetic, below 116° and 203°K, respectively, and have paramagnetic Curie temperatures θ of −15° and 77°K, respectively. These results as well as the paramagnetic moments agree fairly well with previous susceptibility measurements on UP and UP₂ made by Trzebiatowski & Troc(4), by Allbutt et al.(5), and by Chechernikov et al.(6). However, Adachi & Imoto(1) reported that both compounds had ferromagnetic components, below ~80°K in UP and below ~120°K in UP₂, down to liquid nitrogen temperature (~77°K). The previous susceptibility measurements(4)(5) were carried out only down to ~80°K and hence could not reveal the reported “ferromagnetic component” of UP. However, the previous measurements did not reveal the “ferromagnetic component” in UP₂ in the temperature range from ~80° to ~120°K, where it was observed by Adachi & Imoto. In addition, in previous measurements the susceptibility of UP₂ was field independent. Furthermore, neutron diffraction measurements showed(5) UP₂ to be antiferromagnetic at 77°K, with no further transition detected by specific heat measurements(5) down to 22.5°K.

Although the “ferromagnetic component” in UP₂ might be due to the presence of some U₃P₄ or UO₂ not detected by X-rays, we do not wish to speculate on this matter. However, in the case of UP the rise in susceptibility is not due to any ferromagnetic component. Recent susceptibility measurements on UP down to 4.2°K by Gulick et al.(8) show that the susceptibility falls below Tₑ and then rises from ~80°K, as found also by Adachi & Imoto(1). The susceptibility rises by ~20% down to ~27°K and then falls sharply around 22.9°K. The low temperature transition in UP, first detected by specific heat measurements(10), does not involve any change in the antiferromagnetic structure of type-I(11)(12). The low temperature transition involves only a change in ordered magnetic moment(12) which was confirmed by zero field NMR of ³¹P in the antiferromagnetic state.(13) The slight rise in the susceptibility toward the low temperature transition is related to the increase in ordered moment and not to any “ferromagnetic component”. It is unfortunate that even in their more recent paper, Adachi & Imoto(3) are not aware of many publications disproving the claim of ferromagnetic behavior in UP.

In the phase diagram of the UP₁₋ₓSₓ system(14) UP is in the type-I antiferromagnetic region while US is in the ferromagnetic region. Adachi & Imoto(3) report, in a private communication with T. Kikuchi, that US is metamagnetic. This is in disagreement with results obtained at this laboratory and also with magnetization measurements by Gardner & Smith(15) and neutron diffraction measurements by Wedgwood(16) on a single crystal of US. All these measurements and especially those on the single crystal indicate that US is a simple ferromagnet in zero and finite fields.

Ohmichi & Nasu(2) found antiferromagnetic ordering in the UC₁₋ₓNₓ system for 0.5 ≤ x ≤ 1.0, i.e., in UN, UC₀.₅N₀.₅, UC₀.₆N₀.₄, UC₀.₇N₀.₃, and UC₀.₈N₀.₂. While the ordering of UN and the Néel temperature (52°K) are in good agreement with previous results, the existence of antiferromagnetic ordering in the other com-* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
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positions is in disagreement with previous susceptibility\(^{(17)}\) and neutron diffraction\(^{(18)}\) measurements on the UC\(_{1-x}\)N\(_x\) system. de Novion & Costa\(^{(17)}\) found antiferromagnetic ordering only in UN and UC\(_{0.05}\)N\(_{0.95}\), paramagnetic behavior down to 4.2\(\degree\)K for 0.6\(\leq x\leq 0.9\), and no evidence for any magnetic moments for 0.5\(\leq x\leq 0.5\). These results were confirmed by neutron diffraction on UC\(_{0.10}\)N\(_{0.90}\) and UC\(_{0.26}\)N\(_{0.74}\), where no magnetic ordering was observed\(^{(18)}\). The "strange" feature in the results presented by Ohmichi & Nasu\(^{(2)}\) is a peak in the susceptibility of solid solutions with 0.5\(\leq x\leq 0.9\), which occurs roughly at a constant temperature of \(~43\degree\)K. This peak, which leads these authors to associate an antiferromagnetic transition with its temperature, decreases with the rise in carbon contents.

The peak in the susceptibility could arise from an impurity phase such as a U(C,N,O) composition or an oxide, or from a certain UC(N) composition, the amount of which decreases as the carbon added to UN (in the reaction UN\(+(1-x)\)C used by the authors\(^{(2)}\)) increases. This assumption implies that the samples used by Ohmichi & Nasu\(^{(2)}\) are not totally homogenized. The lattice parameters\(^{(19)}\) of UC (4.9602 Å) and UN (4.8892 Å) are close together and it is difficult to distinguish between the X-ray powder photographs taken from close compositions; therefore, a pattern of a single phase might constitute several close compositions. Leitnaker et al.\(^{(18)}\) found a significant positive deviation of the lattice parameters of the UC-UN solid solutions from Vegard's law. This fact lowers the carbon contents of solid solutions in which the lattice parameters equals the value expected from the nominal composition and linear interpolation, as was the case of the samples of Ohmichi & Nasu\(^{(2)}\). For example, the sample designated by them as UC\(_{0.1}\)N\(_{0.9}\) corresponds to \(x>0.95\). It is probably the UC(N) composition which remains to some extent in successive non-homogenized solid solutions and gives rise to the strange feature observed. Such an explanation is only tentative due to lack of better documentation by Ohmichi & Nasu of their samples.

Finally, Adachi & Imoto\(^{(6)}\), dealing with a model to account for the magnetic parameters of UN, UP and UAs, somehow neglected the fact that UAs undergoes a transition from the type-I antiferromagnetic structure (+-+-) at high temperatures to the type-IA (++++) at low temperature\(^{(20)}\). The type-IA structure is the one found in the UP\(_{1-x}\)S\(_x\) system\(^{(21)}\). It should be recognized that any proposed model should use the correct properties of the materials for which it is aimed.

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Counter Comment to Dr. Kuznietz for his Comments

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For the rise in susceptibility of antiferromagnetic UP and UP₅ at lower temperatures (~80° and 110°K, respectively), Kuznietz agrees with our result for UP, being supported by the recent data by Gulick et al., but he does not agree with our observation for UP₅ on the ground that the anomaly was not revealed in other previous measurements. For UP₅, we have certainly examined whether it could be due to the presence of UP₀, which naturally suggested itself as the most possible contamination. Measurements of susceptibility were carried out on various UP₅ samples prepared under various conditions—including 100 hr annealing of UP₀ samples in phosphor vapor at 500°C—, but no discrepant results in susceptibility were observed. It was on the basis of this finding that we considered that the anomaly would not be due to the presence of UP₀.

For UP, Kuznietz attributes the anomaly at ~80°K to the change of the ordered magnetic moment whose transition occurs at 22.8°~9°K, but it would not appear suitable to associate the rise in susceptibility of UP at ~80°K to the very sharp transition observed at 22.8°~9°K.

In applying the term “ferromagnetic components” to UP and UP₅, we referred only to the magnetic behavior revealed by susceptibility and its hysteresis, which are characteristic of many ferromagnetic substances. It may not be really justified to restrict the meaning of this term to the magnetic behavior characterized by the magnetic transition detected by neutron diffraction and specific heat measurements etc.

Next, we shall reply to the comment on the paper, we have made a calculation on other types of ordering structures in NaCl type compounds along the line carried out on the type-I structure. The result indicated that the type-IA ordering is less stable than the ordering of the first or second kind, but there may possibly be a reversal of stability in the narrow range around 2kₗ=11 which roughly corresponds to UAs in our model, if more exact account is taken of the effect of certain other interactions. Moreover, if the valence electron number of UP₁₋₅S₅, which is different from that of UP, largely affects the stability, there may be the same possibility as described above for UP₁₋₅S₅ of suitable composition.

According to the communication from T. Kikuchi on the magnetic behavior of US, the specimen was prepared through a solid-gas reaction of uranium and sulfur, and was heat treated at 1900°C to homogenize the specimen, which was confirmed to be of single phase as a result of X-ray diffractometry. Measurements of magnetization against temperature at low magnetic fields revealed the presence of a maximum point of magnetization. This maximum point shifted downward from 164° to 140°K with increasing field strength from 0.2 to 1.2 kOe, and vanished.

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