Low-temperature magnetic phase of UCu_2Ge_2: A macroscopic, mesoscopic, and microscopic study

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In order to resolve the controversy over the low-temperature magnetic phase of UCu_2Ge_2 ac susceptibility, neutron-depolarization and neutron-diffraction measurements have been carried out on a well-annealed polycrystalline sample. Our measurements reveal that UCu_2Ge_2 remains ferromagnetic at all temperatures below T_c (107 K), but in the temperature range, 25–45 K, the system seems to have a randomly canted ferromagnetic phase.

I. INTRODUCTION

The 1-2-2 uranium intermetallic compounds with $ThCr_2Si_2$-type crystal structure have drawn much attention with the discovery of the coexistence of superconductivity and magnetism in the URu_2Si_2 system.[1] The magnetic behavior of various compounds belonging to the $ThCr_2Si_2$ family can be quite exotic.[2] For example, in the UT_2Ge_2 compounds (T=transition-metal atom) the magnetic moments (if present) are usually found on the $5f$ atoms, and not on the transition metals (except UMn_2Ge_2).[3] UFe_2Ge_2 and UCo_2Ge_2 do not show any ordered magnetic phase.[3,4] It is found that among all the UT_2Ge_2 compounds only UCu_2Ge_2 shows "double magnetic transition" as a function of temperature.[2–6] The unusual magnetic properties of UCu_2Ge_2, as a function of temperature, have been the subject of several investigations.[2–7] This system shows the onset of ferromagnetism (FM) at a fairly high temperature 100–110 K.[2–7] However, there are conflicting reports about the nature of magnetic ordering at low temperatures (below ~60 K). Some authors claim that the low-temperature phase is antiferromagnetic (AFM) as is inferred from their macroscopic[3,6,7] ac susceptibility, magnetization, and resistivity measurements and microscopic neutron-diffraction[2,4,5] studies. The FM-to-AFM transition temperature is, however, reported to be at variance, e.g., 25–40 K,[2] 43 K,[3] or 65 K.[6] No AFM phase was reported down to 10 K in Ref. 8. Measurements of low-field dc magnetization showed that the magnetization decreases below 60 K, but does not completely vanish even at 5 K.[7] This feature has also been seen by Dirkmaat *et al.*[3] in their magnetization measurements. The exact nature of the FM-AFM transition, which was found to be broad,[2,7] is also not known. Recent measurements of the frequency dependence of low-field complex ac susceptibility, including both linear and nonlinear responses, showed various features of a random magnetic ordering (or spin-glass-like behavior) in the FM-AFM transition temperature range of 55–80 K.[9]

In order to resolve the controversy over the low-temperature magnetic phase of the UCu_2Ge_2 system and hence to throw more light on this unusual magnetic system, we have carried out macroscopic, mesoscopic, and microscopic studies on well-annealed polycrystalline UCu_2Ge_2 samples. We seek to interpret our results of ac susceptibility (macroscopic), neutron depolarization (mesoscopic), and neutron diffraction (microscopic) in the light of some theoretical models.

II. EXPERIMENTAL DETAILS

The intermetallic compound UCu_2Ge_2 was made by repeated melting of stoichiometric amounts of the constituent elements of Cu and Ge of at least 99.99% purity and U of reactor grade in a purified argon arc furnace. The resulting ingots were annealed at 1100 K in vacuum for 6 days. Following the annealing, the buttons were crushed into fine powder and characterized by x-ray diffraction at room temperature.

The real part of the ac susceptibility (χ_{ac}) measurements were performed on this polycrystalline sample in the temperature range 12–300 K by using an APD closed-cycle helium refrigerator with Meissner coil assembly employing an EG&G PAR (model 5208) lock-in analyzer. The ac magnetic field and frequency were 5 Oe and 80 Hz, respectively.

The one-dimensional (1D) neutron-depolarization measurements were carried out using the neutron-polarization analysis spectrometer (PAS) at Dhruva reactor, Trombay (λ =1.201 Å). The detailed description of the spectrometer has been given in an earlier paper.[10] The zero-field-cooled (ZFC) and field-cooled (FC) neutron-depolarization measurements were carried out using the same procedure as described in our earlier paper.[11] A flat rectangular aluminum sample holder of effective thickness 1 mm was used for these depolarization measurements. The powder samples used were in the form of compressed pellets. The temperature of the sample was varied between 10 and 300 K in a closed-cycle

helium refrigerator and controlled to better than 0.1 K. In ZFC measurements the sample was cooled from room temperature down to 10 K in zero field. A field of 28 Oe was applied at 10 K, and then the ZFC depolarization measurements were carried out in the warming cycle after giving adequate pause at each temperature, for thermal stability. For the FC case, the sample was first cooled from room temperature down to 10 K in the presence of the same fixed field, as was applied for measurement in the ZFC case, and then measurements were carried out (keeping the field on) in the warming cycle as in the ZFC case. In all cases, the external field was applied along the $-z$ direction using an electromagnet.

Neutron-diffraction measurements were carried out over the temperature range of 10–300 K on the PAS in the two-axis unpolarized mode and with no external magnetic field on the sample. The room-temperature diffraction pattern was recorded using an ~12 g sample in a cylindrical vanadium container, whereas all low-temperature measurements were carried out using the same amount of sample with a cylindrical aluminum sample holder.

III. EXPERIMENTAL RESULTS AND DATA ANALYSIS

The x-ray-diffraction measurements exhibited the $ThCr_2Si_2$-type crystal structure with no detectable impurity phase. The room-temperature neutron-diffraction pattern (paramagnetic phase) was analyzed using the Rietveld profile refinement technique.[12] The structure was confirmed to be tetragonal, space group $I4/mmm$, with lattice constants of $a=4.058(2)$ Å and $c=10.231(5)$ Å. The fitted position parameter (z) of the germanium atom is 0.3806(4). These structural parameters are in good agreement with those published in the literature.[6,8] Refinement also shows that the composition is stoichiometric.

The temperature dependence of the ac susceptibility is shown in Fig. 1(a). Measurements show a very sharp peak at 107 K followed immediately by a steep but continuous drop at lower temperatures with a shoulder around 45 K.

The neutron-depolarization technique probes the magnetic inhomogeneity on a mesoscopic length scale.[13–15] As a result, the magnetic inhomogeneity on an atomic scale, as in a true spin-glass state, has no effect on the neutron polarization. Similarly, no depolarization is expected in a paramagnetic state because the temporal spin fluctuation is too fast (10^{-12} sec or faster) for the neutron polarization to follow the variation of the magnetic field B acting on the moving thermal neutron. In antiferromagnets there is no net magnetization: hence, no depolarization is expected. In an unsaturated ferromagnet or ferrimagnet, the magnetic domains exert a dipolar field on the neutron spins, resulting in depolarization owing to the Larmor precession of the neutron spins in the magnetic field of the domains.

In Fig. 1(b) the polarization ratio (R) (Ref. 15) (ratio of transmitted intensities for $+z$ to that of $-z$ states of incident neutron spin), which is a measure of z-z transmitted polarization, is plotted as a function of temperature. This measurement shows almost total depolarization from a few degrees below T_c down to 10 K, the lowest measured temperature. It is to be noted that at room temperature (paramagnetic phase) the measured values of R with and without samples were found to be same, which shows that there is no depolarization in the paramagnetic phase, as expected from the theory of neutron depolarization. Both ZFC and FC transmitted polarizations show a continuous drop below about 107 K and attain their constant values below about 40 K. ZFC depolarization shows a deviation from FC depolarization at $T\leqslant 70$ K.

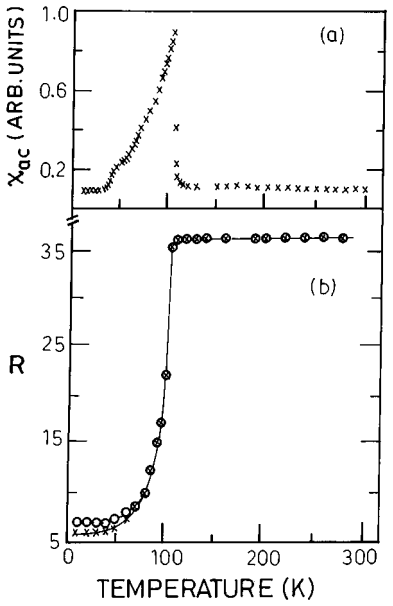

FIG. 1. (a) Temperature dependence of the real part of the ac susceptibility, measured at $\nu=80$ Hz and at $H_{ac}=5$ Oe. (b) Polarization ratio R vs temperature in the UCu_2Ge_2 compound. The data are obtained in heating cycles under zero-field-cooling (cross point) and field-cooling (open circle) conditions with a field of 28 Oe for a 1-mm-thick sample. The solid lines are just to guide the eyes.

Figure 2(a) shows the temperature dependence of the measured integrated intensity (I_{int}) of the (101) fundamental peak. I_{int} shows a sharp rise below about 107 K, clearly indicating the onset of ferromagnetic ordering. It is interesting to note that I_{int} reaches its maximum around 55 K and then decreases slightly and appears to again increase (with a small dip, around 30 K) and reaches almost to a value, observed at 55 K without any change of peak width. The same behavior has been observed for the (110) fundamental peak [Fig. 2(b)]. Neutron-diffraction patterns recorded at different temperatures ($T=10$, 30, 45, 60, and 80 K) up to the lowest Q, $\sin\theta/\lambda=0.025$ Å^{-1}, do not show any additional reflection (besides the nuclear). The magnetic contributions are manifested as increased intensities on top of all nuclear reflections except (00l). The measured ordered moment of uranium obtained from (101) and (110) reflections is found to be $(1.6\pm0.2)\mu_B$ at 10 K, which agrees well with the ordered moment observed in Ref. 5 at 4.2 K. The uranium form factor for the $5f^2$ (U^{4+}) electron configuration was adopted. The absence of a magnetic contribution to the (002) nuclear Bragg peak is clear from Fig. 2(c).

IV. DISCUSSION

Our ac susceptibility measurement on a well-annealed UCu_2Ge_2 sample [Fig. 1(a)] reveals that the transition from a

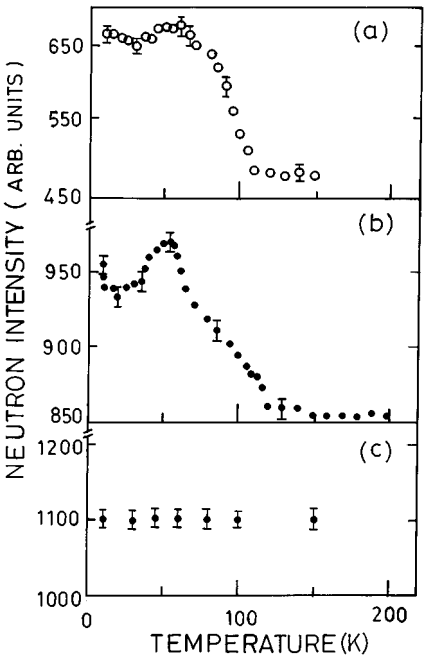

FIG. 2. (a) Integrated intensity of the (101) Bragg reflection of UCu_2Ge_2 as a function of temperature. (b) Temperature dependence of peak intensity of the (110) Bragg reflection of UCu_2Ge_2. (c) Integrated intensity of the (002) Bragg reflection of UCu_2Ge_2 as a function of temperature.

para- to a ferromagnetic state in this compound is very sharp. The appearance of a knee around 45 K seems to be interesting. Chelmicki *et al.*[2] and later on Endstral *et al.*[4] from their neutron-diffraction results on unannealed samples concluded that there is a transition from FM to AFM (IA type, $++--$) at a temperature $\sim$45 K. Roy and Coles[7] found that the magnetization decreases below 60 K, but does not completely vanish even at 5 K ($M_{5\ \mathrm{K}}/M_{\mathrm{peak}}=0.0733$). In the literature[8] it is suggested that the presence or absence of the AFM-IA-type structure at low temperature lies in the exact sample preparation procedures. But it is to be noted here that the unannealed UCu_2Ge_2 sample[7] also shows similar sharp drop in χ_{ac} behavior as our well-annealed one. In fact, magnetization studies also do not show much difference between annealed[3] and unannealed[7] samples. Hence, as far as the macroscopic measurements are concerned, there is no difference (at least qualitatively) between annealed and unannealed samples. It may be mentioned that the steep but continuous drop in χ_{ac} below the Curie point has been attributed by Roy and Coles[7] to effects arising from the temperature-dependent anisotropy in the system. The presence of temperature dependent anisotropy in UCu_2Ge_2 was also suggested by Drikmaat *et al.*[3] from their ZFC and FC magnetization measurements.

The strong depolarization of the transmitted beam observed at all temperatures from 10 K up to a few degrees below T_c [Fig. 1(b)] gives direct evidence that (i) UCu_2Ge_2 is certainly not in the pure antiferromagnetic state even at very low temperatures and (ii) that the ferromagnetic type of domain structure does exist at all temperatures below T_c. It is interesting to note that ZFC depolarization differs from FC depolarization at $T\leqslant 70$ K. This difference may be attributed to the effect of temperature-dependent anisotropies present in this system.[3]

The exact nature of ferromagneticlike correlation in UCu_2Ge_2 can be well understood from the neutron-diffraction results (Fig. 2). For all temperatures below T_c (107 K), a magnetic Bragg contribution to the nuclear peak (without any change of peak width) implies the presence of long-range ferromagnetic ordering in this intermetallic compound over all temperatures below 107 K. Hence, from these two quite independent measurements, viz., neutron depolarization and diffraction, using polarized and unpolarized neutrons, respectively, one can conclude that UCu_2Ge_2 remains ferromagnetic over the entire temperature range below 107 K (T_c). However, the observed dip in the ferromagnetic Bragg intensities of (101) and (110) reflections [Figs. 2(a) and 2(b)] remains to be explained. Roy and Coles[7] and Chakravarti *et al.*[9] have speculated on the possibility of the coexistence of ferro- and antiferromagnetic ordering in the intermediate-temperature region. It may be stressed that no antiferromagnetic-satellite peaks have been found at intermediate temperatures in our studies. The possibility of the coexistence of FM and AFM at other (low and high) temperatures, viz., 10, 60, and 80 K, can also be ruled out as no extra reflections (other than fundamental) have been observed at these temperatures also. The possibility of uniform canting relative to the tetragonal c axis (average magnetization direction) is also ruled out from the absence of any magnetic contribution to the (002) nuclear Bragg peak [Fig. 2(c)]. So it is clear from our diffraction studies that the observed loss of ferromagnetic intensity in the intermediate-temperature range 25–45 K neither appears as extra Bragg peaks (antiferromagnetic or satellite) nor as a ferromagnetic contribution to the (002) fundamental Bragg peak. This can be understood to arise from the random canting of U moments with respect to the c axis. As a result, whereas the longitudinal components (c-axis components) show long-range ferromagnetic ordering, the transverse components do not show any long-range ordering. In fact, there is no signature of short-range correlation of these transverse components of U spins in our diffraction measurements. Thus our neutron-diffraction study indicates that over the intermediate-temperature range, where the dips in the (101) and (110) ferromagnetic Bragg intensities are observed, the system seems to have a random canted ferromagnetic structure. It is to be noted that there is some strong correlation between the observed dip in the ferromagnetic Bragg intensity and the shoulder in the χ_{ac} data.

In UCu_2Ge_2, the uranium $5f$-wave functions are quite extended and hybridize substantially with the conduction band, providing both itinerant character and strong electronic correlation, and hence seem to possess essential requirements for the occurrence of such a randomly canted ferromagnetic state. Recent susceptibility[9] and magnetoresistance[16] studies on this system suggest that UCu_2Ge_2 seems to have a strongly random magnetic structure in the temperature range between 50 and 80 K. Theoretically, the coexistence of FM and AFM structure has been considered in strongly interacting itinerant-electron systems.[17,18] In this theory the coefficient of the uniaxial anisotropic term is assumed to be a positive constant so that the easy axis is parallel to the z axis, i.e., the uniaxial anisotropy direction. However, our both χ_{ac} and depolarization measurements indicate the presence of a strongly temperature-dependent anisotropy. We believe that

if one includes such a strong temperature dependence of anisotropy into the calculations the phase diagram will get modified and may provide a theoretical understanding of the random ferromagnetic phase seen in the present study.

The randomly canted ferromagnetic phase formation can also be understood within the framework of the anisotropic Ising model with competing interactions [axial next-nearest-neighbor Ising (ANNNI) model].[19,20] In this compound since the nearest-neighbor U-U separation is larger than the Hill limit of 3.5 A, it is quite likely that the oscillatory character of a RKKY-type interaction is responsible for the magnetic ordering. This being so, the interaction should show a temperature dependence. Depending upon the relative values of NN (J_1) and NNN (J_2) interactions, various magnetic orderings are expected to occur. For example, when both J_1 and J_2 are positive, only ferromagnetic order is possible. Antiferromagnetism occurs when J_1 is $-ve$ and J_2 is $+ve$. When J_2 is $-ve$, other ordered phases can occur, wherein the magnetic ordering can be complex. Thus the observation of the dip in the Bragg intensity may have an explanation within the framework of the ANNNI model.

V. CONCLUSIONS

χ_{ac}, neutron-depolarization (both ZFC and FC), and neutron-diffraction measurements are reported on well-annealed single-phase polycrystalline UCu_2Ge_2, in order to resolve the controversy over the low-temperature magnetic phase. It is concluded that (i) UCu_2Ge_2 remains ferromagnetic over the entire temperature range below 107 K (T_c) and (ii) in the intermediate-temperature range 25–45 K the system seems to have randomly canted ferromagnetic ordering, which also supports the very recent magnetoresistance results of this system. The role of observed strongly temperature-dependent anisotropy in the Moriya-Usami model, which may give rise to a randomly canted ferromagnetic phase in the intermediate-temperature range (25–45 K), has been outlined. The possibility of the occurrence of such randomly canted states within the framework of the ANNNI model has also been pointed out.

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