Interesting magnetic response of the nuclear fuel material \( \text{UO}_2 \)

Sudip Pal\(^a\), L. S. Sharath Chandra\(^b\), Maulindu Kumar Chattopadhyay\(^b,c\) and S. B. Roy\(^a\)

\(^a\)UGC DAE Consortium for Scientific Research, Indore, India; \(^b\)Free Electron Laser Utilization Laboratory, Raja Ramanna Centre for Advanced Technology, Indore, India; \(^c\)Homi Bhabha National Institute, Mumbai, India

**ABSTRACT**

We report results of dc magnetization measurements on \( \text{UO}_2 \). Our study reveals a deviation from standard Curie-Weiss (CW) paramagnetic behavior below 280 K, and that is followed by a transition to antiferromagnetic state with marked thermomagnetic irreversibility below \( T_N = 30.6 \) K. The zero field cooled (ZFC) magnetization exhibits distinct structures not usually observed in the antiferromagnets, whereas field cooled (FC) magnetization looks more like a ferromagnet. The thermomagnetic irreversibility continues to exist in a subtle way even in the paramagnetic regime well above \( T_N \). This behavior along with the deviation from CW law highlight non-standard nature of the paramagnetic state. Magnetic response below \( T_N \) changes significantly with the increase in the applied magnetic field. In the isothermal magnetic field variation of magnetization, a subtle signature of a magnetic field-induced phase transition is observed. All these experimental results highlight the non-trivial nature of the magnetic state in \( \text{UO}_2 \).

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**1. Introduction**

Uranium dioxide (\( \text{UO}_2 \)) is a well-known nuclear fuel material and is used worldwide in nuclear reactors for electrical power generation and research. \( \text{UO}_2 \) is also recognized as a Mott–Hubbard insulator [1, 2], and it promises other technological applications apart from a nuclear fuel [3, 4]. Thermal conductivity is very important for the removal of heat produced in a nuclear reactor by fission in the nuclear fuel materials. As a result thermal properties of \( \text{UO}_2 \) particularly have drawn much attention over the years [1, 5–8]. \( \text{UO}_2 \) crystalizes in face centered cubic (fcc) calcium fluorite structure (\( Fm\overline{3}m \)), in which \( \text{U}^{4+} \) ions are surrounded by eight \( \text{O}^{2−} \) ions forming a cube [9]. Therefore, the anisotropic thermal conductivity reported in this compound is rather unexpected and emphasizes the relevance of spin-phonon coupling, which is associated with the magnetic state of the system [8]. The Mott insulating state in \( \text{UO}_2 \) further highlights the importance of strong electron–electron correlation in the system [2, 4]. Various techniques, including neutron scattering and nuclear magnetic resonance (NMR) have revealed a complex 3k-non-collinear antiferromagnetic (AFM) spin ordering below \( T_N = 30.6 \) K. The transition is first order in nature and is accompanied by a small lattice distortion, predominantly in the oxygen cage [10–12]. In cubic crystal field, the nine-fold degenerate (5\( f^2 \), \( J=4 \)) state splits up with a 3-fold degenerate ground state, resulting in Jahn–Teller (JT) instability [13].

Spin-orbit coupling, Coulomb interaction, antiferromagnetic exchange interaction and JT distortion are of comparable strength in \( \text{UO}_2 \). Below \( T_N \), a quadrupolar ordering is established together with AFM spin ordering, facilitated by the interaction between cooperative JT distortion,
antiferromagnetic exchange interaction and 5f quadrupoles [14–17]. While there is some understanding of the physical properties of UO₂ in the antiferromagnetic state below \( T_N \), characteristics of the high-temperature state are not quite clear. The nature of the high-temperature state, although considered to be paramagnetic, is not so straightforward. Temperature dependence of thermal conductivity exhibits a minimum at \( T_N \) and a maximum around \( T=220 \) K, which clearly highlights the unusual physical state above \( T_N \). Moreover, significant magnetostriction has been observed both above and below \( T_N \) which further indicates spin-lattice coupling even in the paramagnetic phase. Neutron scattering has provided evidence for dynamic JT distortion of the oxygen sublattice above \( T_N \)[18–21]. Temperature dependence of elastic constant above \( T_N \) also exhibits unconventional behavior [11]. UO₂ has been reported to be showing some other interesting physical properties, such as piezomagnetism and magnetoelastic memory driven by spin-lattice interaction [9].

Here we present a detailed study of the temperature (\( T \)) and magnetic field (\( H \)) dependence of magnetization (\( M \)) in UO₂. The results of our study highlight various hitherto unknown interesting aspects of the magnetic response of UO₂. We show that below \( T=280 \) K the low field magnetization or susceptibility deviates from standard Curie–Weiss paramagnetic behavior. Abrupt changes in both the zero field cooled (ZFC) and field cooled (FC) magnetization are observed at \( T_N = 30.6 \) K where UO₂ undergoes a phase transition to antiferromagnetic state along with distinct thermomagnetic irreversibility i.e. \( M_{ZFC}(T) \neq M_{FC}(T) \) inside the antiferromagnetic state. The magnetic response in the antiferromagnetic state changes considerably with the increase in the applied magnetic field. The observed behavior may be correlated to a magnetic-field-induced phase transition. The thermomagnetic irreversibility in the antiferromagnetic state continues to exist in the temperature range above \( T_N \) and below \( T = 150 \) K, but it gets suppressed completely at higher applied magnetic fields.

2. Experimental details

A powder sample of UO₂ has been prepared by reducing UO₃ in the hydrogen atmosphere at 700°C at Bhabha Atomic Research Centre, Trombay. Room-temperature X-ray diffraction data have been recorded at the wavelength of \( \lambda = 0.7121 \) Å in the beamline-BL12 in Indus-2 synchrotron radiation source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. Magnetic measurements have been carried out in an MPMS-3 SQUID-VSM magnetometer (M/S Quantum Design, USA). Temperature dependence measurements of magnetization have been performed in temperature sweep mode of measurement at 0.5 K/min cooling and heating rate.

3. Results and discussion

Figure 1 shows the X-ray diffraction data of UO₂ measured at room temperature in \( \theta - 2\theta \) geometry. In the inset, we have shown a magnified view of the data around (111) peak, which is the most intense peak in this case. Sharp diffraction peaks and flat background reveal the good crystalline nature of the sample. The data have been analyzed by the Rietveld refinement method using the Fullprof software package. All the peaks can be indexed in cubic fcc structure (space group \( Fm\overline{3}m \)), which rules out the presence of any secondary phase in the sample. The optimized lattice parameter obtained from fitting is, \( a=5.4594 \) Å. The lattice parameter of UO₂ is sensitive to oxygen stoichiometry of the sample, which crucially depends on the oxygen partial pressure during synthesis and it is a very important feature of this compound. It follows an empirical law given by, \( a=5.4705-0.132x \), where \( x \) is defined as UO₂₊ₓ [22]. It means the unit cell contracts upon increasing oxygen content. In our case, the obtained lattice parameter corresponds to, \( x=0.08 \).

The role of oxygen defect in controlling the local structure as well as physical properties of UO₂₊ₓ continue to be a subject of considerable interest [23–25]. It has been proposed that excess oxygen enters into the interstitial position and may form oxygen clusters. Around \( x=0.08 \) concentration of oxygen, the additional oxygen ions occupy the interstitial positions in the lattice as small
defects such as mono and di-interstitials \[26, 27\]. On the other hand, investigation of X-ray absorp-
tion spectra of the oxygen excess samples \(0 \leq x \leq 0.20\) reveals that adventitious O atoms are
incorporated as oxo groups, which causes structural modi-
cfications in the form of diminished order arising due to displacements of the U and O atoms from their lattice sites. X-ray absorption near-edge spectra indicates towards an increase in the valance of some of the U to give rise to a
mixture of \(U^{4+}\) and \(U^{6+}\) charge states \[23\].

Figure 2(a) shows the temperature dependence of magnetization \(M\) in \(\text{UO}_2\) measured at an
applied field of \(H=100\ Oe\) in the zero field cooled (ZFC) warming, field cooled cooling (FCC) and
field cooled warming (FCW) protocols. In ZFC protocol, the measuring field \(H = 100\ Oe\) is
applied after cooling the sample to the lowest temperature (here 2 K) of measurement in zero exter-
nal field. ZFC magnetization \(M_{ZFC}\) is then measured while warming the sample. After reaching the
highest temperature (room temperature) of measurement, the sample is subsequently cooled back
to 2 K in the same field while measuring the FCC magnetization \(M_{FCC}\). After FCC measurements,
the FCW magnetization \(M_{FCW}\) is measured while by warming the sample again gradually to room
temperature in the same field. Temperature variation of magnetization in the high-temperature
regime in all the protocols (ZFC, FCC and FCW) indicates the presence of magnetic moment in
\(\text{UO}_2\), which is in line with the Mott insulator status of the sample. Below \(T=50\ K\), \(M\) tends to
flatten while the temperature is further reduced and then \(M\) changes abruptly around \(T_N = 30.6\ K\).
Note that, this temperature matches well with the reported temperature for stoichiometric \(\text{UO}_2\),
where it is supposedly undergoing a phase transition to a complex antiferromagnetic state \[12\].

Figure 2(a) shows the presence of a very distinct thermomagnetic irreversibility i.e. \(M_{ZFC}(T) \neq M_{FC}(T)\) in the antiferromagnetic state. Such thermomagnetic irreversibility is not
expected in any standard antiferromagnet \[28\], and to the best of our knowledge has not been
reported earlier for \(\text{UO}_2\). \(M_{FCC}(T)\) and \(M_{FCW}(T)\) curves overlap at all temperatures of measurement
and now onward, we will designate the field cooled magnetization as \(M_{FC}\). Interestingly, in an
expanded scale (see the inset of Figure 2(a)), one can see that the \(M_{ZFC}(T)\) and \(M_{FC}(T)\) curves actu-
ally start to bifurcate below \(T=150\ K\), which is well over \(T_N\) and nearly equal to \(5T_N\); the bifurcation

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Figure 1. X-ray diffraction pattern of \(\text{UO}_2\) powder sample recorded at room temperature using wavelength, \(\lambda = 0.7121\ \text{Å}\). The data have been fitted using the Rietveld refinement method. Indexes of the most intense planes are also mentioned. The allowed Bragg peaks are shown by the vertical bar symbol. The blue line at the bottom shows the difference between experimental data and fitted curve. X-ray diffraction pattern of the powder sample of \(\text{UO}_2\), which is a plot of scattered intensity of X-ray and the angle between incident and scattered X-ray. It shows multiple sharp peaks at different angles.
gradually increases with a decrease in temperature. The bifurcation between the $M_{ZFC}(T)$ and $M_{FC}(T)$ curves below the antiferromagnetic transition temperature $T_N$ is much larger than the bifurcation above $T_N$. The bifurcation also persists above $T_N$ at least up to 150 K in the applied field of 100 Oe. The inset in Figure (a) shows the magnified view of ZFC and FCW curve above $T_N$ in an applied field of 100 Oe. The inset in Figure (b) shows $\Delta M = M_{FC} - M_{ZFC}$ in fields of $H=100$ Oe and 1 kOe. In applied fields of 50 kOe and 70 kOe $M_{ZFC}(T)$ and $M_{FC}(T)$ curves show a sudden and discontinuous fall in magnetization at $T_N$, $M_{ZFC}(T)$ and $M_{FC}(T)$ bifurcate below temperature $T_N < T_d$ (see Figures (c) and (d)). It shows temperature variation of magnetization data at four different magnetic fields. This figure highlights how the magnetic behavior of UO$_2$ evolves with an increase in the applied magnetic field.

Various experimental techniques revealed that the antiferromagnetic transition in UO$_2$ is first order in nature [12, 33–36]. In neutron scattering measurements, the antiferromagnetic transition was found to be very sharp and no critical scattering peak was observed [33, 34]. NMR and heat capacity measurements have further revealed strong spin-lattice coupling across the transition [12, 35, 36]. A conventional first-order transition shows thermal hysteresis in the cooling and
heating cycles due to supercooling and superheating respectively. However, such thermal hysteresis has not been observed across the first-order antiferromagnetic transition in the studied single crystal sample of UO$_2$ in a neutron scattering experiment [33]. In line with this observation, the $M_{FCC}(T)$ and $M_{FCW}(T)$ curves do not show any thermal hysteresis across $T_N$ in our present study. This means that the supercooling and superheating phenomena, which are usually observed across a first-order phase transition in many systems [37, 38], are absent across the antiferromagnetic transition in UO$_2$. In a pioneering work, Imry and Wortis [39] showed that static, quenched-in, purely statistical compositional disorder could introduce a landscape of transition temperatures in a system undergoing first-order phase transition, which in macroscopic scale gave the impression of a disorder broadened first-order phase transition. This effect in turn may smear out the associated supercooling and superheating and hence the absence of distinct thermal hysteresis across the first-order phase transition.

Figure 2(b) presents the results of the magnetization measurements as a function of temperature carried out in an applied magnetic field of $H=1$ kOe. $M_{ZFC}$, $M_{FCC}$ and $M_{FCW}$ curves appear to be qualitatively similar to those obtained at $H=100$ Oe. However, there are important differences, which are noted below:

1. The difference between $M_{ZFC}$ and $M_{FC}$ curves i.e. the thermomagnetic irreversibility above $T_N$ is completely erased.
2. The thermomagnetic irreversibility below $T_N$ increases by a large extent than that at $H=100$ Oe. The value of $\Delta M = M_{FCW} - M_{ZFC}$ at $H=100$ and 1 kOe is shown in the inset of Figure 2(b).
3. Bifurcation of $M_{ZFC}$ and $M_{FC}$ curves starts just below $T_N$ and this temperature does not seem to change with an increase in applied magnetic field from 100 Oe to 1 kOe.
4. The low-temperature increase in $M_{ZFC}$ is more pronounced.

Thermomagnetic irreversibility is a characteristic feature of spin glass or cluster glass systems, where it arises due to freezing of spins or magnetic moments originating from the competing magnetic interactions and associated frustration [40, 41]. Thermomagnetic irreversibility is also observed in ferromagnets, which is associated with domain wall pinning [42]. Even some antiferromagnets with ThCr$_2$Si$_2$ structure exhibits thermomagnetic irreversibility, which was attributed to the stacking faults in those compounds with layered structures [43, 44]. Strong anisotropy can also play a role here, which may cause hindrance to the domain walls motion. In UO$_2$, spin-orbit interaction is a possible source of the magnetocrystalline anisotropy. However, in all these magnetic systems, the thermomagnetic irreversibility gets suppressed with an increase in the applied magnetic field. This is in contrast with the observed increase in thermomagnetic irreversibility in UO$_2$ with the increase in applied fields from 100 Oe to 1 kOe. Such behavior in UO$_2$, however, changes in the region of high applied fields. Figure 2(c,d) presents the temperature dependence of magnetization at $H=50$ and 70 kOe measured in ZFC, FCC and FCW protocols. Note that, the bifurcation between $M_{ZFC}(T)$ and $M_{FC}(T)$ curves appears only below a temperature $T_{irr}$ (see Figure 2(c,d)), which is lower than the transition temperature $T_N$. The thermomagnetic irreversibility as well as $T_{irr}$ get reduced as the applied magnetic field is increased from 50 to 70 kOe, whereas the antiferromagnetic transition temperature $T_N$ remains largely unaffected. It may also be noted that the thermomagnetic irreversibility in the paramagnetic regime is totally absent in this high applied field regime.

From the results discussed above it is clear that magnetic response in low applied magnetic fields in both ZFC and FC states below $T_N$ in UO$_2$ is distinctly different from that at high applied magnetic fields. More evidences in this direction emerge if one looks carefully to the temperature dependence of high field magnetization. As the UO$_2$ sample is cooled from high temperature, magnetization increases and tends to saturate around 35 K. However, just above $T_N$, magnetization decreases by a small amount, resulting in a small hump prior to $T_N$. The magnetic response at $T_N$, and also at low temperatures, change drastically both in the ZFC and FC states, as compared to
magnetic behavior at low fields, shown in Figure 2(a,b). At $H = 50$ kOe, both the $M_{ZFC}(T)$ and $M_{FC}(T)$ curves undergo an abrupt and discontinuous fall at $T_N$, which is immediately followed by a small rise in magnetization with a decrease in temperature. Then, they show a relatively flat region over a temperature region of 28–22 K. In the lower temperature region, the $M_{ZFC}$ and $M_{FC}$ curves bifurcate: the $M_{ZFC}$ curve starts to decrease, whereas the $M_{FC}$ curve slowly increases. Note that, the $M_{ZFC}$ also shows an additional shallow dip around $T_d = 15$ K. At $H=70$ kOe, magnetization shows a larger drop at $T_N$ and all the three curves gradually decrease with a further decrease in temperature (see Figure 2(d)). Below $T_{irr}$, the $M_{ZFC}$ curve continues to decrease, whereas the $M_{FC}/M_{FCW}$ curve increases. This is in clear contrast to the temperature dependence of magnetization obtained in applied magnetic fields of 100 Oe and 1 kOe (see Figure 2(a,b)).

To investigate further on the antiferromagnetic state in UO$_2$, we present in Figure 3 the isothermal $M$–$H$ curves at $T=29$ and 2 K measured starting from the ZFC state. Here, the sample is initially cooled to the temperature of measurement in the absence of any external field. Then $M$ is measured while increasing $H$ isothermally to 70 kOe to record initial (virgin) $M$–$H$ curve, which is shown in Figure 3(a,b) for $T=29$ and 2 K, respectively. After recording the virgin $M$–$H$ curve, $M$ is measured while varying $H$ between ±70 kOe to record the envelope $M$–$H$ curves, which are shown in Figure 3(c,d). The virgin $M$–$H$ curves at both temperatures lie within the envelope $M$–$H$ curves. Note that, at $T=29$ K, the $M$–$H$ curve shows a small change in the slope above $H_d = 1.2$ kOe and continues to increase at a higher field up to the highest applied field of $H=70$ kOe. Whereas, the virgin $M$–$H$ curve at $T=2$ K deviates from linearity above $H_d = 15$ kOe. The envelope $M$–$H$ curve at $T=29$ K shows a small hysteresis with a coercive field of around $H_C = 2.2$ kOe, which increases to 4.5 kOe at 2 K. The $M$–$H$ curves do not show any tendency of saturation till $H=70$ kOe. The non-saturating $M$–$H$ curve highlights the antiferromagnetic state but the presence of hysteresis is rather unexpected in the AFM state. At further lower temperature, both coercive field and remnant magnetization further increase as evident from the $M$–$H$ curve at $T=2$ K. This change in the slope of $M$–$H$ curves above $H = H_d$, may indicate some sort of field-induced transition of the zero field cooled AFM state.

The increase in the difference between $M_{ZFC}(T)$ and $M_{FC}(T)$ with the applied magnetic field is one of the important signatures of kinetically arrested first-order phase transitions [38, 45–48]. In this case, the dynamics of a first-order phase transition get arrested in a $H$–$T$ window. The difference between $M_{ZFC}(T)$ and $M_{FC}(T)$ increases because cooling in different magnetic fields produces different volume fractions of the high- and low-temperature magnetic phases. As stated earlier, the antiferromagnetic transition in UO$_2$ is first order in nature, and like a kinetically arrested system thermomagnetic irreversibility in the low field regime increases with the applied magnetic field. In this context, the $M$–$H$ curves shown in Figure 3, can be rationalized in the following manner: the ZFC state undergoes a field-induced transition above a critical field $H_d$, as observed from the change in slope. However, in the field decreasing cycle, the reverse transition is not observed, so that the magnetic state induced by the applied magnetic field persists during the entire envelope curve and gives rise to the hysteresis loop. Such behavior has been reported in the literature in the cases of kinetic arrest of first-order phase transition in various magnetic systems, where the zero field cooled state may be either equilibrium low-$T$ phase, or the kinetically arrested high-$T$ phase, depending on the nature of the ground state [48, 49]. Now, after zero field cooling, in the first case, when a magnetic field is increased, above a certain field, the equilibrium phase undergoes a field-induced transition to the high-$T$ phase as the superheating band is crossed [46, 48, 49]. On the other hand, in the second case, the kinetically arrested state devitrify into the equilibrium low-$T$ phase while increasing the field. In either case, the envelope curve does not show the reverse transition.

The unusual dependence of magnetization on temperature and the finite difference between $M_{ZFC}(T)$ and $M_{FC}(T)$ curves much above $T_N$ clearly highlight an unconventional paramagnetic state at high temperatures. Besides the concomitant structural changes due to excess oxygen and the charge state of some of the U$^{4+}$ ions have to increase to preserve the electrical neutrality of
the system, which also should affect the magnetic behavior, such as effective moment, Curie temperature extrapolated from the paramagnetic state at high temperatures. Therefore, to further understand the magnetic property of UO$_2$ at high temperatures, inverse susceptibility $\chi^{-1}$ versus $T$ at $H=100$ Oe measured in ZFC protocol is plotted in Figure 4. The $\chi^{-1}$ versus $T$ data appears to be grossly linear in the temperature range from $T=300$ K to 70 K. We tried to fit the results in this temperature regime by using Curie–Weiss (CW) law, given by $\chi = \frac{C}{T+T_0}$, where $C = \frac{N g^2 \mu_B^2}{3 k_B} = \frac{N g^2 J(2J+1)}{3 k_B}$. However, when looked carefully, the CW law does not fit the experimental data in the entire temperature regime. In fact, it deviates from linearity below around $T=280$ K (see the inset of Figure 4). The effective magnetic moment $\mu_{\text{eff}}$ obtained to be 2.82 $\mu_B$/f.u., which is smaller than the expected value of 3.57 $\mu_B$/f.u. for $J=4$ ($L=5$ and $S=1$). However, it matches well with the value of effective moment expected for UO$_2$ in a cubic crystal field [12, 50]. $T_0$ is obtained to be around 171 K, which is around 5.6 times higher than the transition temperature. The deviation of the susceptibility from CW law, the presence of irreversibility much above $T_N$, higher value of $T_0$ than $T_N$ are interesting. In UO$_2$’s fluorite structure, the crystalline electric field partially lifts the degeneracy of the free ion electronic configuration, and the nine-fold degenerate 3H$_4$ configuration is split into the ground-state triplet, the excited doublet, triplet, and singlet states. The ground state is separated from the first excited state by approximately 0.15 eV [13], and thereby puts limitations on the applicability of the Curie–Weiss law at low temperatures. However,
it should be mentioned that there exist some earlier reports of the unusual characteristics above \( T_N \) [8]. In inelastic neutron scattering experiments, the magnetic inelastic response has been observed above \( T_N \) up to as high as \( T = 200 \) K [20]. It has been suggested that the coherent motion of the neighboring oxygen cages produces uncorrelated 1-k type dynamical JT distortion in the paramagnetic state of UO\(_2\) [20]. With the lowering in temperature correlation builds up and a static 3-k type distortion condenses at \( T_N \) [20]. The tendency of \( M \) to saturate as \( T_N \) is approached during cooling, the deviation from the CW law, existence of bifurcation between the ZFC and FC curves highlight the unusual paramagnetic state at high temperature, therefore may arise due to short-range 1-k type dynamic JT distortion.

Our present sample of UO\(_2\) is slightly hyperstoichiometric. The role of oxygen stoichiometry in controlling the magnetic state of UO\(_{2+x}\) was raised earlier by Arrot [51, 52], but there was a lack of knowledge of the actual composition of the samples. It is interesting that all the samples studied with excess oxygen (\( x = 0.1, 0.25, 0.3 \)) were found to show a sharp peak around \( T = 6.4 \) K [52]. In spite of these earlier reports, a thorough investigation is lacking till date. The excess oxygen leads to structural distortion as well as change in the valance state of some of the U ions to preserve electrical neutrality and therefore expected to affect the indirect exchange interaction in the system [51, 53, 54]. It may, however, be noted that the \( T_N = 30.6 \) K obtained in our sample closely matches with the transition temperature of 30.8 K expected for the stoichiometric compound. This indicates that the underlying exchange interaction is not affected significantly. There is another interesting possibility of a phase separation between UO\(_2\) and U\(_4\)O\(_9\) (UO\(_2.25\)) depending on the sample preparation condition [25, 55, 56]. It can influence the overall magnetic response of the material. Such possibility can be disregarded in our sample, where the amount of excess oxygen ions is relatively small and which has been prepared at \( 700^\circ \)C. In addition, our XRD data also do not reveal any obvious signature of such phase separation (see Figure 1).

There can be other sources of ferromagnetism. To begin with, in some oxides with antiferromagnetic ground state, a weak ferromagnetic response may arise due to surface spin disorder, which is produced by broken bonds and structural modification at the surface [57, 58]. It should be mentioned that this effect is more dominant in nanoparticles where surface to volume ratio is considerable and where the surface magnetism will contribute significantly. This scenario may not be

![Figure 4. \( \chi^{-1} \) versus \( T \) data measured at \( H = 100 \) Oe in the ZFC protocol. The inset shows the CW law fitting above 280 K. It is a plot of \( \chi^{-1} \) and \( T \) along \( y \) and \( x \) axis respectively. It is obtained from the ZFC curve measured at \( H = 100 \) Oe.](image-url)
applicable in our case of bulk UO₂ sample. On the other hand, a ferromagnetic response due to non-stoichiometric surface, where ferromagnetism is attributed to O surface electronic states cannot be ruled out [59] and needs further investigations.

4. Conclusion

Summarizing, we can say from the results of temperature- and magnetic-field-dependent studies of dc magnetization that UO₂ undergoes an antiferromagnetic transition at \( T_N = 30.6 \) K. The transition is reported to be of first-order nature from neutron diffraction, NMR, specific heat measurements, but the temperature-dependent magnetization does not show any thermal hysteresis across the transition. The low-temperature antiferromagnetic state in UO₂ is non-trivial in nature and is accompanied with large thermomagnetic irreversibility. The field cooled magnetization \( M_{FC}(T) \) measured in low fields of 100 Oe and 1 kOe indicates the presence of ferromagnetic character in UO₂. This inference is further corroborated by the presence of hysteresis in isothermal field variation of magnetization along with the appreciable coercive field. The ferromagnetic response may appear due to the non-collinear antiferromagnetic nature of the ground state and slight oxygen off-stoichiometry in the sample. The other intriguing possibility of ferromagnetic response is a field-induced first-order transition which gives rise to a few other non-trivial signatures in the temperature- and field-dependent magnetization at high fields. The nature of the thermomagnetic irreversibility changes in the presence of high applied magnetic field. In the low magnetic field region, the thermomagnetic irreversibility increases with the increase in applied field, which can be rationalized in terms of the kinetic arrest of magnetic-field-induced first-order phase transition. The thermomagnetic irreversibility in the high magnetic field regime decreases with the increase in applied field. Prima facie this behavior is quite similar to that observed in some ferro and antiferromagnets, where it can be attributed to the hindrance in domain wall motion. Furthermore, the paramagnetic state in UO₂ is also unusual with a deviation of Curie–Weiss law and the presence of thermomagnetic irreversibility in the temperature region much above \( T_N \). These results indicate the existence of some short-range magnetic correlations well inside the paramagnetic region of UO₂. Overall the results of our present study are expected to stimulate further microscopic measurements involving neutron scattering and muon spin rotation (\( \mu \)SR) measurements to find out the exact microscopic nature of magnetic states in various magnetic field \((H) – temperature (T) \) regime of UO₂.

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Disclosure statement

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