The fifty years it has taken to understand the dynamics of UO$_2$ in its ordered state

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Abstract

In 1966 Roger Cowley (together with Gerald Dolling) reported the first neutron inelastic scattering from the magnetic excitations from UO$_2$ below its antiferromagnetic ordering temperature of 30 K. They showed the strong magnon–phonon coupling in this material and that the excitations appeared to contain an additional mode that was not anticipated. Cowley never returned to UO$_2$, but showed a keen interest in the developments. Forty years after this pioneering work, unambiguous evidence was found (using resonance x-ray techniques) for the ordering below $T_N$ of the electric quadrupoles involving the anisotropy of the 5f charge distribution around the uranium nuclei. A further 10 years later, now armed with a full theory for the excitation spectrum expected for phonons, magnons, and quadrupoles, we can identify the latter as the source of the ‘extra’ mode reported first in 1966. The story is a long winding one, with the expected serendipity and dead ends, but is now (almost) completed.

Keywords: magnetoelastic interactions, electric quadrupole order, noncollinear magnetic order, uranium dioxide, quadrupole modes

(Some figures may appear in colour only in the online journal)
many other important experiments were published on UO$_2$ in the 1960s, the understanding of excitations in systems with large orbital moments was still largely unexplored. What they knew at that time about UO$_2$ was the magnetic structure (or at least its ordering wave-vector) and the fact that the ordering was first-order at $T_N = 31$ K [7, 8]. Moreover, there existed two competing theories for the ground state, which did not agree on the energetic ordering of the crystal-field states [9, 10]. There had been no attempt to measure the energy of these states at that time.

We show in figure 1 (central panel) the experimental points measured by Cowley and Dolling [6] and their theory, compared (left-hand side) with results obtained later by polarization analysis measurements [11, 12], and on the right-hand side, the current theoretical model for the low-energy excitations in UO$_2$ [12, 13]. It can be seen immediately that the observations made at Chalk River 50 years ago have stood the test of time and have not been bettered – polarization analysis, however, has helped a great deal in understanding the origin of these modes, first in 1999 [11] and again in 2011 [12]. The second aspect of figure 1 that is noticeable is that the model proposed by Cowley and Dolling has only two modes, one spin acoustic wave (SA) that has a gap at the $X$ point and then rises to be degenerate at the $\Gamma$ point with the spin optic (SO) mode, which has a minimum at the $\mathrm{X}$ point of ~10 meV. This model with two magnetic excitations is to be expected given the high symmetry of UO$_2$, and cannot explain the presence of the two modes at $\Gamma$ and $X$ between 10 and 13 meV. Although the *Phys. Rev. Lett.* article [5] was mainly about the mixing of the spin wave and the transverse acoustic phonon, a considerable effort was made in the long paper [6] to explain the extra mode in terms of effects arising because of the domains in the ordered antiferromagnetic. Some measure of agreement was obtained (see figure 8 in [6]), but it was never fully satisfactory.

Roger then left UO$_2$ and in 1970 left Chalk River (and presumably access to the UO$_2$ crystals) for a professorship (at 31 years old!) at Edinburgh University. He never returned to UO$_2$, but always expressed a great interest in its progress.

2. Early experiments aimed at understanding UO$_2$

During the 1960s there were many studies of UO$_2$, perhaps the most important, apart from the neutron papers above, being the experimental and theory work of Allen [14, 15] and of Brandt and Walker [16, 17]. Allen measured the infra-red spectrum and noted that the indirect quadrupole–quadrupole interaction caused by the virtual exchange of an optical phonon is as large as the exchange coupling (~30 K), and significantly modifies the spin-wave energies and wave functions. Brandt and Walker [16, 17] measured the elastic constants and showed that there is a strong reduction in the $c_{44}$ elastic constant as a function of temperature, with these effects beginning at ~$100 \text{ K}$ (i.e. more than three times $T_N$). This can be modeled based on strain effects and a strong coupling between the magnetic and lattice degrees of freedom. Brandt and Walker also make the following remark [17]: ‘one might almost say that the more the material (UO$_2$) is studied the more confusing the picture becomes’. Both Allen and Brandt and Walker invoke quadrupolar interactions, although they did not anticipate that the quadrupoles themselves might order below $T_N$. However, by the end of the 1960s most experimental studies agreed that the $\Gamma_5$ triplet was the ground state [9], although the size of the crystal-field potential, and hence the separation to the first excited level, was still unknown.

Two important studies were published in the 1970s. Sasaki and Obata [18] showed that the susceptibility does not fit a Curie–Weiss type relationship and the deviation from this linear relationship may be explained by a reduction factor due to the presence of a dynamical Jahn–Teller mechanism, which will also reduce the ordered moment anticipated from the $\Gamma_5$ triplet ground state. Faber and colleagues [19, 20] showed that below $T_N$ an internal distortion of the oxygen atoms appears in UO$_2$. A difficulty in interpreting the observed oxygen distortions was that no external distortions (which would reduce the symmetry from cubic to a lower symmetry) had been found either with low-temperature x-ray studies [21] or in the measurements of the elastic constants [17]. In fact, the symmetry of the antiferromagnetic structure of UO$_2$ was incorrectly assumed at that time to be orthorhombic based on the assumption of a 1-k AF structure.

The 1980s saw two further key developments. The first was the realization that the AF structure was not a 1-k one, but a 3-k structure [22], which preserves cubic symmetry and does not require an external distortion. It also removes the question of domains in the AF structure. With a 3-k structure (which is a superposition of the 3 individual 1-k structures in the cubic unit cell) there are no spatial domains, only so-called ‘phase domains’. This result also highlighted (again) the puzzle of the ‘extra’ excitation found by Cowley and Dolling in the excitation spectrum [6]. The second major achievement in this decade was the measurement of the crystal-field energy levels with neutron inelastic scattering at the new (at that time) spallation neutron sources, which have access to higher incident energy neutrons than usually available at a reactor. Initial experiments at Argonne National Laboratory [23] were followed by a more complete study published by Amoretti et al [24] in 1989 using the ISIS source. These measurements proved beyond doubt that the ground state of UO$_2$ was the $\Gamma_5$ triplet, but the magnitude of the crystal-field splitting was some 4 times smaller than predicted in [9]. Still, the first excited state is ~150 meV above the ground-state $\Gamma_5$ triplet, so the latter is the only state of interest in defining the low-temperature properties. The resolution of these two problems allowed theory to now play a role in trying to solve the puzzles still remaining in the dynamics of UO$_2$.

In the 1990s there was progress on the theory together with a realization that understanding the higher multipolar interactions would be important in capturing the physics of UO$_2$—a follow up of the earlier work of Allen [14, 15] and the interpretation of the elastic constant measurements of Brandt and Walker [17]. Earlier theoretical work [25] was examined in more detail. Advances in instrumentation at the Institut Laue Langevin (Grenoble) meant that it now was possible to
examine the excitation spectra in UO$_2$ with polarization analysis. This technique is able to separate effects due to the lattice vibrations from those arising from electronic (magnetic) excitations. The new experiments [11] showed that all the three excitations found by Cowley and Dolling [6] below $T_N$ were magnetic in character, as they had assumed. The work by Caciuffo et al [11] also showed that significant magnetic scattering was present in the paramagnetic state. Two broad, but dispersive, peaks were observed at low energy and interpreted as showing that the correlations corresponded to those from dynamic 1-k domains, with the assumption that these coalesced into a static 3-k structure below $T_N$.

The 2000s were to see an important breakthrough with resonant x-rays rather than neutrons. However, one key experiment was performed with neutrons with full polarization analysis at the ILL. This experiment explored the interaction of the dynamic spectrum with the full 3D polarization tensor, and, in addition to setting some markers for future theory, the experiment showed unambiguously the 3-k nature of the UO$_2$ magnetic structure below $T_N$ [26].

3. Higher multipolar effects as observed in resonant x-ray diffraction

The importance of quadrupolar (and higher) multipolar interactions in condensed matter physics, especially of f-electron systems, has been known for some time. The direct observation of such effects, on the other hand, is complicated, and there were only a few examples up to ~1995. Perhaps the most outstanding experiment in this regard is that reported by Keating [27] working in 1969 with the element Ho. At low temperature in the magnetic spiral phase of Ho the periodicity of the anisotropic charge density of the 4f shells gives new satellites at $\pm nq$ (where the strongest term, the quadrupole contribution is with $n=2$, and the magnetic spiral wave-vector is defined as $q$). These satellites were observed using a conventional x-ray laboratory source, representing an experimental tour de force. Some years later a similar experiment was performed with neutrons [28] to observe the anisotropy of the magnetic moment density; in this case the magnetic quadrupolar satellites are based on the magnetic wave-vector ($q$) so now appear at $\pm (q + 2q) = \pm 3q$. These satellites could be observed because of the spiral nature of the magnetic ordering, but this is a special condition. The charge and magnetic quadrupoles have a different propagation vector than the dipole signals, and this allows them to be seen by x-ray and neutron scattering, respectively. However, how is one able to do this in a normal material in which the ordering is not a spiral?

Already in the 1990s such effects were receiving attention, see, for example Morin and Schmitt [29]. However, it was the development of resonant x-ray scattering (RXS) at synchrotron sources that really opened the way for direct observations of these effects [30]. Since these experiments are complicated, requiring both the polarization analysis, as well as a scattering geometry that allows the azimuthal dependence of the intensity about the scattering vector to be measured, we shall not explain this in great detail in this short article. It is sufficient to reference Hill and McMorrow [30], as well as the long review article by Santini et al in 2009 [31]. The first such unambiguous identification of orbital ordering was in RXS experiments in 1998 on LaMnO$_3$ [32], where the Mn K transition ($1s \rightarrow 4p$) was used and suggests that the orbital ordering of the Mn 3$d$ states gives rise to a energy splitting of the Mn 4$p$ levels.

It was soon realized that the key ingredient for characterizing any orbital order was the exact nature of the transition examined. The resonant process occurs at absorption edges in the x-ray spectrum, and these are not only element sensitive, but also shell specific. For example, in the 3$d$ systems the K-edge couples ($1s \rightarrow 4p$) states, so to be sensitive to the orbital order (at least in the dipole transition channel) there must be ordering involving the metal 4$p$ states, as in [32]. But
this is not a very common type of ordering, and it would be best to examine the low-energy L edges that are below 1 keV, which couple 2p → 3d states and would be more likely to observe such effects as it is within the unfilled 3d shell that orbital order certainly occurs predominantly. In fact, such an observation occurred once a so-called ‘soft x-ray diffractometer’ was constructed [33] and orbital ordering in 3d materials observed. For 4f systems the appropriate resonant edges are the M edges (3d → 4f) at again slightly less than 1 keV in energy, but work can also be done at the L edges as the 6d states (especially in Ce systems) are hybridized with the 4f states, although some careful modeling is also needed [34].

For actinides the important resonances are those involving 5f final states, e.g. M4,5 (which correspond to 3d → 5f transitions) with the M4 = 3.73 keV for U. Such x-rays (often called ‘tender’) do not require a full vacuum for all the beamlines so may be examined with conventional diffractometers at synchrotron sources. One of the first experiments in 2001 to show orbital ordering [35] was on UPd3, a localized system with 5f electrons, in which many transitions had been observed at low temperatures with bulk techniques. An early experiment (1999) on NpO2 [36] gave tantalizing results, but at that time neither polarization analysis nor full azimuthal scattering capability were available at the ID20 beamline at the European Synchrotron Radiation Facility (ESRF), Genoble, France. A new experiment in 2002 with these capabilities gave beautiful results showing that the quadruple ordering in NpO2 clearly condenses at $T_f = 25$ K, as shown by the very strong signal at the Np M4,5 edges [37]. This result led to understanding the electronic structure of NpO2 after 50 years of effort [38].

Meanwhile, experiments had searched for indication of the orbital ordering in UO2, but none was found. The clue as to why the initial experiments failed lay in understanding the exact terms in the cross section. In the E1 (dipole) resonance there are three terms in the scattering amplitude:

$$f_{\text{RXS}}(E1) = f_0 + j f_1 + f_2$$

where

$$f_0 = (\epsilon_r \cdot \epsilon_l)[F_{10} + F_{1-1}];$$

$$f_1 = (\epsilon_r \times \epsilon_l) \cdot z[F_{11} - F_{1-1}];$$

and

$$f_2 = (\epsilon_r \cdot T \cdot \epsilon_l)[2F_{10} - F_{11} - F_{1-1}],$$

where $F_{1q}$ are the resonant energy factors [30], $z$ is the direction of the magnetic moment, and $\epsilon_r$, $\epsilon_l$ are the initial and final polarization states of the x-ray beam. The term in $f_0$ does not depend on multipolar moments so can be neglected, for $\sigma$ incident polarization the term $f_1$ performs a rotation of the polarization of the beam, and probes a term with odd time-reversal symmetry and is normally associated with the magnetic resonant term. The resulting intensity is not necessarily proportional to the magnetic moment, but is sensitive to the overall magnetic features. In contrast, $f_2$ probes a tensor ($T$) of rank 2, even in time-reversal symmetry. This can arise from an asymmetry intrinsic to the crystal lattice (Templeton [39] or anisotropic tensor susceptibility scattering) or it can be due to the antiferro-order of electric quadrupole moments.

Although the quadrupole scattering had been found in NpO2 at reflections such as (003), the type of such ordering is different in UO2 than that found in NpO2. Figure 2 shows the types of quadrupolar ordering that can occur in the 3-k structure with a wave-vector of $q \equiv (001)$. There is a subtle difference between the longitudinal (as found in NpO2) and...
transverse (as found in UO$_2$) arrangements. In particular, evaluating the $T$ matrix for the transverse structure in $f_2$ above showed that no intensity would appear at the (001) type reflections, unlike in the case of NpO$_2$ [37, 38]. This explains why these effects were not found in the early 1990s when UO$_2$ was first examined with resonant x-rays. To succeed an off-specular reflection, such as (1 1 2), had to be chosen [40]—see figure 3. This reflection also has a contribution from $f_1$ coming from the dipole magnetic moments, which arise from the 5$f$ electrons, but (with the incident photon beam polarized as $\sigma$) this magnetic contribution is totally rotated $\sigma \rightarrow \pi$, so that the $\sigma \rightarrow \sigma$ channel of the intensity can be identified as arising from the electric quadrupole ordering. As one can see from the $T$–dependence of the intensities in figure 3, it is the magnetic dipole interaction ($f_1$) that drives the first-order phase transition at $T_N$, but the three phenomena are clearly coupled.

4. Influence of ordered quadrupolar moments on the dynamics of UO$_2$

Once the presence of the quadrupolar ordering was proven, the question was raised what effect it would have on the dynamics of UO$_2$ in the ordered state? We should emphasize that such quadrupolar effects are very difficult to observe (one reason the understanding of UO$_2$ has taken so long!). Unless they give rise to a new periodicity in the system (such as for holmium [27]) they cannot be observed by either conventional x-ray scattering and never by neutron scattering (the term observed in the neutron experiments on holmium [28] corresponds to the magnetic quadrupolar signal, a third-order effect odd in time-reversal symmetry). X-rays can be used to perform inelastic scattering to observe excitations at the meV level, but the back-reflection condition for Si analyzers determines the energies, and they cannot be tuned to certain resonances. The way they can be observed is thus through matrix elements for other allowed processes and a coupling of quadrupolar effects through other more conventional excitations, which can be observed by either (or both) neutrons and x-rays [13]. Figure 5 shows an artist impression of how the quadrupolar waves “surf” on the magnetic or phonon excitations and, as long as their energies are not too different, can be observed. Carretta et al [13] pointed out that the high-energy mode in UO$_2$ seen at about 12 meV in UO$_2$ (see figure 1) is indeed a quadrupolar optic excitation (QO), which is close (about 2 meV different) in energy to the SO mode centered at ~10
meV at the $\Gamma$ point in figure 1, and is observable because these two modes mix with one another. This resolves, in an elegant way, the dilemma that Roger Cowley faced in 1965, when an ‘additional mode’ was first observed in the dynamic spectrum of UO$_2$ [5, 6]. Carretta et al [13] went on to extract values for the superexchange and magneto-elastic couplings that could be deduced from both the dispersion and polarization (as measured by Blackburn et al [26]) of the excitations. In particular, the model shows that the effects of quadrupole-quadrupole and magneto-elastic interactions are roughly comparable (a point suggested by Allen in his pioneering work of 50 years ago [14, 15]) and that their interplay is at the basis of the very rich physics observed in UO$_2$.

Searching for positive evidence of the existence of the quadrupolar acoustic wave (QA) (see figure 1) still continues. Calculations of the intensity show that this mode will be hard to observe and has an intensity much smaller than the corresponding QO mode. We show some evidence (figure 6) from neutron scattering at the IN14 cold-source triple-axis spectrometer at the ILL for a weak signal at an energy transfer of ~6.5 meV in the [0 0 $\xi$] direction with $\xi = 0.6$ as published in 2011 in [12]. Efforts are now also being made with inelastic x-ray scattering. This technique is not sensitive to the magnetism, and could observe the quadrupole modes through their coupling to the phonons.

5. Conclusions

Uranium dioxide has the simple cubic CaF$_2$ structure. Since the 1950s it has been the nuclear fuel of choice for the majority of power reactors around the world. Given the huge investment

Figure 6. Dispersion along the [00 $\xi$] direction of the mixed magnon–phonon modes in UO$_2$ at 2 K, near the anticrossing position at $q = (0,0,0.45)$ as measured with neutrons. The diagrams show detector counts normalized to monitor as a function of the energy transfer measured with IN14 (at the ILL) at $Q = (1,1,−1+\xi)$. A sloping background has been subtracted from the raw data. The top inset shows calculated intensity maps in the energy–momentum transfer space. For $\xi = 0.6$, a small peak is visible at 6.5 meV, which might be the quadrupolar acoustic mode (QA) and the details shown in the lower inset. Note that the shapes of the peaks at low values of $\xi$ are affected by the resolution function of the instrument. Adapted from Caciuffo et al [12]. Reprinted figure with permission from [12], © 2011 American Physical Society.
in this material, one would have thought that all was known long ago about its properties. Still, a quantitative ab initio description of the electronic properties of UO$_2$ remains a difficult task requiring advanced theoretical and computational techniques. Examples are given by recent studies that used the dynamical-mean-field theory scheme in combination with a linear-response method for evaluating superexchange interactions [41], or a non-collinear density functional theory approximation accounting for Anderson’s superexchange, spin–orbit interaction, and strong 5f correlations [42]. These studies are in agreement with a large part of the experimental evidence and confirm that the non-collinear 3k order in UO$_2$ is driven by a purely electronic superexchange mechanism acting in the undistorted cubic lattice structure [13].

Although the properties of UO$_2$ below 30 K would appear to have little impact on its performance as a nuclear fuel, operating at ~1000 K, it is strange that it has taken physicists so long to understand the properties at a basic level. These physical properties are fundamental to understanding the complete behavior of UO$_2$, and there have been a number of unusual properties measured in UO$_2$ that have been attributed, albeit indirectly, to the low-temperature interactions we have studied. Examples are the apparent anisotropy in the thermal conductivity [43] and the possible disorder in the oxygen atoms at high temperature [44]. Both of these measurements need further confirmation before they can be addressed theoretically, but both have possible impacts on our understanding of the practical side of this material.

Acknowledgments

Roger Cowley’s original work was the inspiration for much of our own. We deeply regret that he is no longer with us and able to enjoy the sense of satisfaction in solving (if not yet fully) the complex physics of this fascinating material. We thank many colleagues for their help over this long period, and especially the theorists at University of Parma, Italy, who played such a prominent role.

When this article was completed we learned, with deep regret, of the death of Gerald Dolling. Both pioneers have now left us.

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