FRAGILE THERMODYNAMIC ORDER*

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An asymmetric shift in the position of the magnetic Bragg peak with respect to the fiducial lattice has been observed by resonant X-ray scattering in a diverse series of antiferromagnetic compounds. This apparent violation of Bragg's law is interpreted in terms of a dynamically phased order parameter. We demonstrate the use of this effect as a novel probe of fragile or dynamic thermodynamic order in strongly correlated electronic systems. In particular, fresh light is shed on the paradoxical situation encountered in URu_2Si_2 where the measured entropy gain on passing through $T_{\text{Néel}}$ is incompatible with the ground state moment estimated by neutron diffraction. The intrinsic space-time averaging of the probe used to characterise the thermodynamic macroscopic state may play a crucial and previously neglected role. In turn, this suggests the further use of resonant X-ray scattering in investigations of systems dominated by quantum fluctuations.

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1. Introduction and summary

The underlying complexities of macroscopic states may be subsumed by construction of phenomenologies based on conserved, or thermodynamic, variables. A primary concept has been the introduction of an order parameter (OP) to describe the changes in macroscopic state, induced by variation of thermodynamic or mechanical constraints, at a phase transition. A classic example is the attribution of a spontaneous magnetisation $\boldsymbol{M}$

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(macroscopic moment density) to the ferromagnetic state. As an inferential tool, bridging our thinking between macro- and microscopic states (hereafter written as macrostate and microstate respectively), the OP has proven of immense value even if an *a priori* rigorous definition in terms of underlying microscopic theory is difficult. Symmetry arguments, in combination with sophisticated mean field models have lead to powerful free energy density functionals based on the OP, which, construed as the summation over independent mesoscopic volumes may be written: $\boldsymbol{M} = \int d^3\boldsymbol{r}\boldsymbol{m}(\boldsymbol{r})$ where $\boldsymbol{m}(\boldsymbol{r})$ is the thermodynamic time expectation of the magnetisation. With the advent of neutron scattering techniques not only has it proven possible to measure the distribution $\boldsymbol{m}(\boldsymbol{r})$ compatible with ferromagnetic long range order (LRO) but new, oscillatory, antiferromagnetic densities have been discovered [1]. Such macrostates are assigned a new phase variable, $\phi = i\boldsymbol{Q_0} \cdot \boldsymbol{r}$, thereby extending the notion of an OP to spatially modulated states, $\boldsymbol{M}(\boldsymbol{r}) = \boldsymbol{M}\mathrm{e}^{i\boldsymbol{Q_0}\cdot\boldsymbol{r}}$; a development which has become the integral basis for describing the Néel state of static LRO [2]. The generalised OP now carries a (vectorial) magnitude together with an ordering wave vector, $\boldsymbol{Q_0}$, constructed to give the relative phase accumulated between two points of separation $\boldsymbol{r}$. The question we address is whether, *on departure from LRO*, such a static phase variable is sufficient to capture the dominant phase correlations of the macrostate. And, if not, how can the additional (dynamic) phase correlations be accounted for, and what inferences may be drawn for the corresponding thermodynamic states?

As noted below, the observed shift of the phasing variable ϕ from its thermodynamic value, $\phi = i\boldsymbol{Q_0} \cdot \boldsymbol{r}$, may provide a sensitive probe of the departure from LRO and the build up of a dynamically ordered state. From this perspective recent, high resolution, resonant X-ray diffraction experiments (by us and others) in a diverse series of compounds with antiferromagnetic ground states which have revealed an anomalous, *asymmetric*, displacement of the magnetic ordering wave vector with respect to the fiducial lattice suggest that essential details of the phase correlations in such dynamic macrostates may lie outside the current framework. To date this apparent violation of Bragg's law has remained unexplained [3,4]. We propose that such effects may be captured most simply by extension of the OP to incorporate a dynamic phase, ϕ_d, giving the total phase as, $\phi = i(\boldsymbol{Q_0} \cdot \boldsymbol{r} - \phi_d)$ where ϕ_d, on leaving the thermodynamic LRO state realised at $\phi_d = 0$, (re)-installs the missing phase accumulated in the 2-site decorrelation function. For a given diffraction peak this leads to an asymmetric displacement, Dq, to smaller wave vectors proportional to the inverse spatial correlation length of the diffracting volume, *i.e.* the q-width, Δq. This monotonic shift and the approximate linear relationship, $Dq \sim \Delta q$, has been found for all systems studied so far.

In the following we discuss first, the displacement, Dq, its observation using resonant X-ray scattering (RXS) techniques and rationalisation in terms of a dynamical phase. Then, as a direct application of this idea, we use it to examine a controversial aspect of the physics of strongly correlated electron systems. Namely to understand, in general terms, how certain materials form an antiferromagnetic state with a very small polarisation (moment $\sim 0.05\ \mu_{\rm B}$) having, at the same time, an entropy change at the phase transition, $T_{\rm N}$, defined from the divergence of the heat capacity compatible with a much larger sublattice polarisation ($\sim 1\ \mu_{\rm B}$). A prime example is the antiferromagnetic heavy fermion superconductor URu_2Si_2 where the saturated magnetic moment determined by neutron diffraction is $\sim 0.03\ \mu_{\rm B}$ and the entropy change at $T_{\rm N}$ is $\sim 15\%$ of $k_{\rm B}\ln[2]$. In this material displacements, Dq, in diffraction peaks of finite width are observed at all measured temperatures below $T_{\rm N}$. These observations lead us to a novel physical interpretation of the unusual low moment in URu_2Si_2 and a resolution of the low temperature entropy balance in terms of a dynamically phased OP.

2. The dynamical phase

To gain insight into the formation of antiferromagnetic macrostates RXS has been used to measure the thermal evolution of positions and widths of magnetic reflections in the following materials: *(i)* UO_2 an archetypal antiferromagnetic ionic compound [5,6], *(ii)* UPd_2Al_3 a large moment heavy fermion superconductor [7] and *(iii)* URu_2Si_2 a small moment heavy fermion superconductor [8]. The key observations are shown in Fig. 1 where the anomalous displacement, the heat capacity and the sublattice moment for each material are displayed as a function of temperature. The effects in Dq are small; the displacements from the nominal Bragg positions are at most a few parts per thousand and the observations exploit the high q-space resolution available at modern synchrotrons. The feasibility to extend these studies into a significant region above $T_{\rm N}$ depends on the high intensity source together with the enhanced resonant cross section [9]; presented data were taken at the uranium M_4 absorption edge sampling spatial correlations associated with the $5f$ shell polarisation. In Fig. 1 Dq is seen to be an order of magnitude greater, and in the opposite sense to, the thermal dilation of the lattice. Parity eliminates both a developing incommensurate order at $\boldsymbol{Q}_{\rm afm} \pm q_i$ between the magnetic and chemical lattice since there is no appearance of the mandatory, second, symmetry related peak and inelastic or diffuse scattering. The anomalous displacements appear irrespective of the size of the low temperature thermodynamic moment; for example, in UPd_2Al_3, where $\mu \sim 1\ \mu_{\rm B}$, the shifts are similar in sign and magnitude to URu_2Si_2, $\mu \sim 0.02\ \mu_{\rm B}$. Moreover, the occurrence depends neither on

the material being metallic nor on the degree of the transition as shown by the occurrence in the ionic compound UO_2, which exhibits a discontinuous, first order transition. Finally, the report [4] of a similar effect in HoB_2Ni_2C suggests that the phenomenon is not a peculiarity of actinide compounds or the experimental method; an important issue on account of the limited X-ray sample penetration at the actinide M_4 resonance.

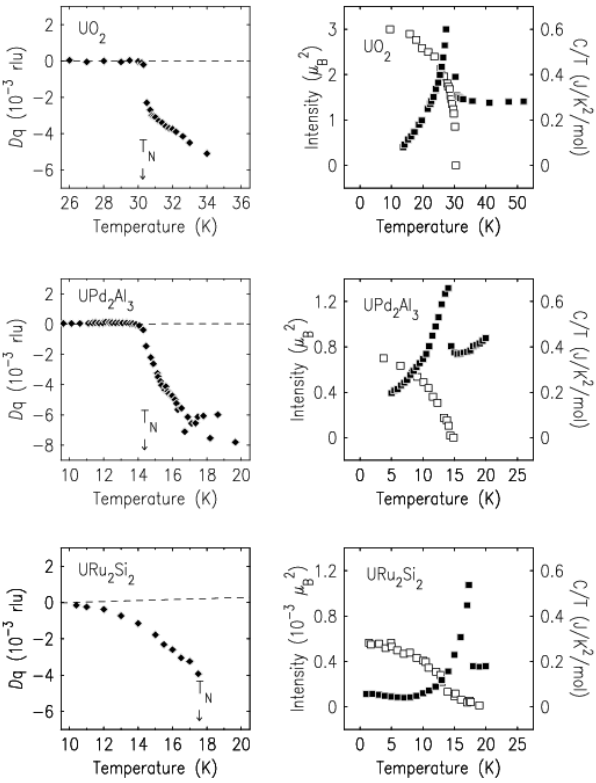

Fig. 1. Left hand side: Shift, Dq, in the reciprocal lattice position of the magnetic Bragg reflection as a function of temperature recorded in UO_2 [3], UPd_2Al_3 (taken at X22C, NSLS, BNL), and URu_2Si_2 (taken at ID20, ESRF), by RXS at the uranium M_4 edge at 3.728 keV. The change in the lattice parameter, as measured in the same experiment at the charge Bragg reflection, is indicated by the broken line. In URu_2Si_2 the presence of a shift below T_N signals the dynamic nature of the fragile thermodynamic state. Note that the assignment of $Dq = 0$ at the base temperature of 10 K is arbitrary. A measurement of the absolute value of Dq is difficult; all measurements are relative to the base temperature. Right hand side: Specific heat capacity (open squares) and normalised temperature dependence of the OP as measured by neutron diffraction (closed squares) [5–8,12].

A degree of reality may be given to a chosen OP in instances where an available probe couples to the dominant symmetry breaking variable of the macrostate [10]. In general this requires a measurement time compatible with the thermodynamic nature of the OP. For example, the alternative use of neutron or X-ray Bragg scattering to assess the expectation of $\boldsymbol{m(r)}$ is limited by the probe space-time coherence volume, a constraint to be respected when refining such an inferential probability density functional by comparison with experimental data [10,11]. The Bragg diffraction condition is itself limited by the accumulated phase lag between 2 points of separation $\boldsymbol{r}$. The dynamic contribution to which, written in terms of its average value $\langle \phi_d / r \rangle = Dq$, leads to loss of coherence beyond the spatial decorrelation length, $r_{\max}$, where $Dq \cdot r_{\max} = \pi$. This implies a wave vector displacement in proportion to the width of the diffraction peak, $Dq \sim \pi r_{\max} \sim \Delta q$, a linear relationship substantiated in Fig. 2. Moreover, since antiferromagnetic order

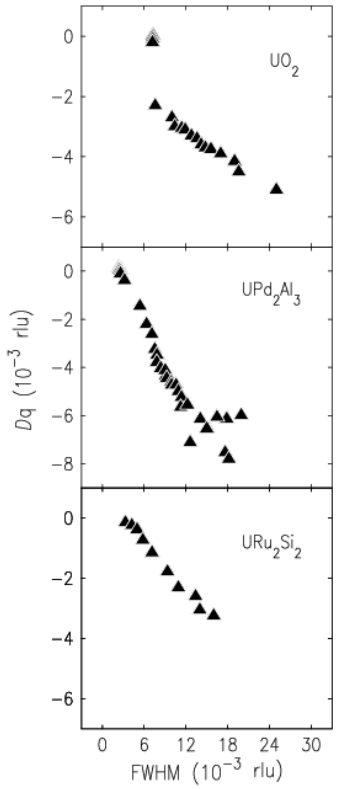

Fig. 2. The anomalous displacement, Dq, of the antiferromagnetic wave vector as a function of fwhm in URu_2Si_2, UPd_2Al_3, and UO_2, with temperature as an implicit parameter. As explained in the text both the negative shift and monotonic dependence may be rationalised with the concept of a dynamical phase.

corresponds with maximal intersite phase difference, all departures lead to a reduction of phase and hence a systematic fall in the value of the resonant $\boldsymbol{Q}$-vector.

3. Fragile macrostates revealed through Dq

We now turn to the second key problem raised by the observations in Fig. 1 and with it open the discussion to the use of the anomalous displacement as a probe of the intrinsic properties in strongly correlated electron systems. Corresponding with the anomalous displacements, Fig. 1 also gives the temperature dependencies of the specific heat and OP as determined by neutron diffraction [5-8,12]. As with Dq the heat capacity anomalies are strikingly similar. Conventional OP mean field theory then faces the paradoxical situation of URu_2Si_2 and UPd_2Al_3, with a moment ratio $\sim$50, having comparable, $\sim k_B \ln[2]$ discontinuities in C/T at T_N.

The focus of the discussion is then URu_2Si_2 where the microscopic nature of the low moment antiferromagnetic state has been surrounded by interest and controversy since its discovery. The transition to an antiferromagnetic ground state below $T_N \sim 17.5$ K was anticipated in the wake of thermodynamic and transport measurements, which indicated large jumps in the heat capacity, bulk susceptibility and resistivity. However, despite the significant change in entropy recorded at T_N, no signature of a (quasi-)static moment was detected by NMR techniques [13] whilst neutron diffraction yielded only a very weak moment estimated to be in the region of 0.02–0.03 μ_B per U ion [12], a value apparently incompatible with existing thermodynamic data [8].

There is an extreme sensitivity of physical properties in URu_2Si_2 to sample quality [12-14], even in the most meticulously prepared samples at least two marked anomalies remain. First, the estimated maximum range of magnetic correlations, parallel to and perpendicular to the ferromagnetic a–b basal plane sheets, is in the region of 200–600Å [12,14]. Second, the transition temperature of antiferromagnetic order recorded by neutron scattering is some $2 \sim 3$ K below and smeared when compared with the sharp jump recorded in the heat capacity, typical data being reproduced in Fig. 1. Interpretation of physical properties based on mean field models have been motivated by the sharp λ transition in the heat capacity, such approximations are however enigmatic in view of the relatively short correlation lengths, which persist to the lowest temperature. The discord between diffraction and thermodynamic observations noted in URu_2Si_2 stands in contrast to the stable moment system UPd_2Al_3 where the collapse of long range magnetic order is signalled by the concomitant rapid change of neutron diffracted intensity and the rise in the specific heat on approaching T_N as shown in Fig. 1.

In view of the controversial evidence on the range and stability of magnetic order in URu_2Si_2, the discussion of which has included amongst others various suggestions of a 'hidden' primary OP [15], we undertook to examine the RXS response in some detail. Building on the pioneering work of Isaacs *et al.* [14] we have measured the position, line width and intensity of RXS in pure, annealed samples of URu_2Si_2 as a function of temperature. The data are shown in Fig. 3. The longitudinal shift of the peak to smaller

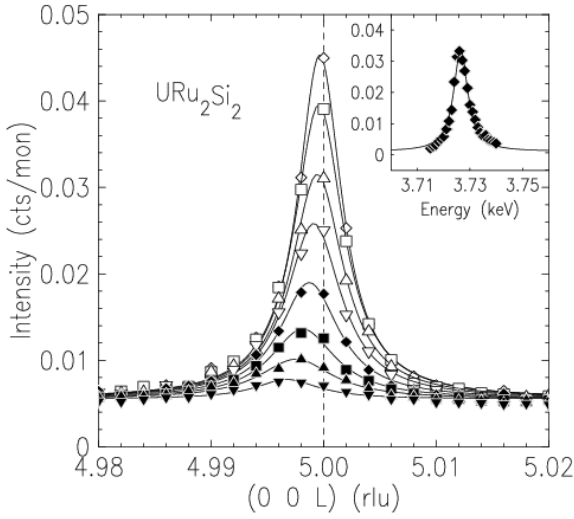

Fig. 3. Longitudinal scans through the (005) magnetic specular reflection in URu_2Si_2 showing the shift and broadening of the peak as the temperature increases. Insert: Incident photon energy dependence of the (005) peak. This wide Lorentzian profile is independent of temperature and signifies a substantial intermediate state matrix element associated with a strong $5f$ polarisation [11] whilst the broad q-vector peak (main frame) gives a measure of the short range (dynamical) magnetic order.

wave vector and the broadening are clearly observable, there is no (symmetry precluded) measurable change in the transverse co-ordinate. Mössbauer data taken on dilute (10 and 50%) Np doped URu_2Si_2 [16] using the ^{237}Np nuclear recoil have shown that above 10% Np concentrations the hyperfine field corresponds to a static (within the Mössbauer window of $\sim 10^{-8}$s) Np magnetic moment of 1.5(1) μ_B. Recent Mössbauer experiments confirmed this order of magnitude of the Np moment in the 5% Np sample where RXS measurements were used to determine the ratio of the uranium and neptunium signals [17]. Across the U-Np substitution series the uranium signal amplitude is remarkably stable (after normalization for the concentration) and corresponds to $\sim 20\%$ of that from the neptunium. Changing (under the

same experimental conditions) from the Np sample of lowest dopage to pure URu_2Si_2 gave a similar signal at the U M_4 resonance, pointing to a stable dipole-like $5f$ shell polarisation both in URu_2Si_2 and its Np substitutional alloys of $\sim 0.3\ \mu_B$ as measured on the time scale of the RXS probe. A detailed study of the azimuthal dependence of the (005) magnetic reflection in URu_2Si_2 gave an angular dependence consistent with the dipole (E1) nature of the magnetic scattering and discriminating against primary OP models involving a large quadrupole moment in the a–b basal plane, as suggested recently [18].

In striking contrast with the other compounds, where the wave vector shifts take place only in the dynamic, paramagnetic state above T_N, in URu_2Si_2 they occur below the thermodynamically determined T_N (Fig. 1). This suggests that the OP remains in a dynamic state even in the nominal antiferromagnetic phase. A plausible origin to the small moment in URu_2Si_2 as deduced from neutron diffraction experiments is then available since the local OP can appear in one of the two time reversed Néel states. Temporal averaging over these states (lifetime τ_ϕ) on the neutron coherence time ($\tau_n \sim 10^{-11}$–10^{-10} s) yields a reduced norm as correlated volumes spontaneously form and dissolve in the (weak) time-average mean field. From the ratio of moments estimated by RXS ($\sim 0.3\mu_B$) and neutron diffraction ($\sim 0.03\ \mu_B$), probing on the electronic hopping (10^{-15}–10^{-14} s) and slow quasi-thermodynamic time scales respectively, one extracts the ratio $m_n/m_0 \sim 0.1$ where m_0 is the moment on time scale $\leq \tau_\phi$ sensed, for example, by RXS.

The dynamic OP also enables the accumulated entropy change at T_N to be reconciled with the magnetic moment estimated by neutron diffraction. The entropy, *i.e.* our lack of knowledge, of the paramagnetic state is reduced at low temperature with increasing magnetic order. The fractional decrease in number of states, g, accessed over τ_n is estimated for a weak polarisation, p, as $g_{low}/g_{high} \sim \exp(-p^2/2\sigma^2)$[19] producing the entropy decrement, $\Delta S/k_B = -(\tau_n/\tau_\phi)p^2/2$. Equating this with the measured change yields $p \sim [2(\tau_\phi/\tau_n)0.15\ln[2]]^{1/2}$ and hence $m_n \sim 0.04\ \mu_B$.

A fragile or pseudo-thermodynamic state, identified by an anomalous displacement, Dq, in the OP Bragg wave vector, thus provides a framework within which the different, slow and fast time scale, response in URu_2Si_2 may be rationalised. It enables an interpretation of the thermodynamic entropy balance and low temperature sublattice moment as estimated by neutron diffraction. In a similar manner, μSR results which have been variously interpreted as implying a weak homogeneous moment [20] or antiferromagnetic order in $\sim$10% of a paramagnetic host [21] may also be understood. On longer time scales, as explored, for example, by NMR, an even weaker effective moment is anticipated. In this light, the inference from NMR studies [13]

that URu_2Si_2 comprises of only $\sim$1% inhomogeneously distributed volumes of moment $\sim 0.3\mu_B$ in a paramagnetic host, may rather be seen in the light of extended time averaging; an alternative that simultaneously resolves the order of magnitude discrepancy in volume (10% to 1%) of distributed moment with that previously attributed by μSR and neutron scattering techniques.

4. Conclusions

Motivated by the discovery of superconducting-magnetic phases, high T_c and CMR amongst others, major efforts are being made in the search for unconventional macrostates. Fundamental to our understanding will be a comprehensive description of the weakly interacting quasiparticle (pseudo-eigenstates) out of which they evolve [10]. The anomalous displacement, Dq, initially appearing as an apparent violation of Bragg's law, may turn into a novel tool providing a first caliper on dynamically stabilised macrostates. In addition to the case of antiferromagnetism treated here, where introduction of a dynamical phase, ϕ_d, permits one to (re-)insert the fundamental Néel state temporal degeneracy, the concept of temporal (as opposed to, or indeed as a resolution of, geometric) frustration broadens our perspective on other exotic, *e.g.* non-Fermi liquid, and quantum critical states [22]. In such cases the quasi-instantaneous nature of the resonant X-ray process may enable unique information, which is otherwise lost in the intrinsic temporal averaging of the measurement, to be accessed. Following this line of attack, and given the availability of suitable X-ray resonance edges, further exploratory experiments would appear eminently worthwhile.

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