Experimental report

05/07/2016

Proposal: **7-01-418** **Council:** 10/2014

Title: Spin-lattice coupling in magnetoelastic 4d and 5d oxides

Research area: Physics

This proposal is a resubmission of 4-01-1384

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Samples: Ba3BiIr2O9
Ba3BiRu2O9
Ba4BiIr3O12

Instrument	Requested days	Allocated days	From	To
IN4	7	7	19/06/2015	26/06/2015

Abstract:

We wish to investigate the giant magnetoelastic transition of Ba3BiIr2O9, which shows an extremely rapid, large (1%) and anisotropic volume increase on cooling through a critical temperature T* = 72 K, and isostructural Ba3BiRu2O9. The volume increase is driven by a 5% increase in the Ir-Ir bond length at T*, and is accompanied by a sharp drop in magnetic susceptibility. We believe the most likely explanation is the opening of a spin-gap, where the observed rapid decrease in susceptibility is related to the formation of local spin singlets (dimers). We previously collected TOF INS data for Ba3BiIr2O9 and Ba3BiRu2O9 on IN4, observing a spin-gap signal for the Ru compound at 33 meV. We now wish to explore this feature in greater detail and search for the gap in Ba3BiIr2O9, which ab initio calculations indicate should have approximately half the energy. We also wish to search for evidence of a magnetoelastic wave associated with the phase transition.

Inelastic neutron scattering (INS) measurements were carried out on the direct-geometry, thermal-neutron time-of-flight spectrometer IN4C at the Institut Laue Langevin (Grenoble, France). An incident wavelength $\lambda_i = 1.11$ $\AA$ (E_i=66.4 meV) was selected using a pyrolitic graphite monochromator. 20 g of polycrystalline $Ba_3BiRu_2O_9$ was sealed into a thin aluminium foil that was fixed to the cold tip of the sample stick of a standard orange cryostat. Measurements were performed at 100 K and 200 K, below and above $T^* = 176$ K respectively. The scattering function $S(Q, E)$ was measured in the neutron energy loss mode, in which the setting used in the down-scattering regime leads to a momentum transfer (Q) and energy transfer (E) extending up to 10 $\AA^{-1}$ and 60 meV, respectively. Standard corrections including detector efficiency calibration and background subtraction were performed. The data analysis was done using ILL software tools.

Fig. 1 shows the color-coded Bose-factor corrected $S(Q, E)$ maps of the scattering intensity obtained on IN4C for $Ba_3BiRu_2O_9$ above, and at three temperatures below, $T^* = 176$ K. A spin-gap excitation peak is clearly seen to emerge at low Q below T^*. Fig. 2 shows scans taken through the peak at $E_f = 14.87$ meV and $S_2 = 15.5$ $°2\theta$ ($|\ Q\ | = 2.60$ $\AA^{-1}$ at $E = 36$ meV) at 3 and 200 K. The spin-gap peak was fitted to a Gaussian with respect to energy transfer to yield a spin-gap value $E_{exp} = 36 \pm 1$ meV. Fig. 2(b) shows the temperature dependence of this peak intensity, fit to an order parameter $((T_c - T)/T_c)^{2\beta}$, yielding $T_c = 175$ K and $\beta = 0.204$, perfectly consistent with $T^* = 176$ K. An analogous spin-gap excitation was not observed for $Ba_3BiIr_2O_9$; however, this is unsurprising given the very high neutron absorption cross-section of Ir and the extremely rapid fall-off of the Ir^{4+} magnetic form-factor, both of which obscure magnetic scattering intensity.

From previous experiments, no magnetic Bragg peaks were observed in neutron powder diffraction data for $Ba_3BiRu_2O_9$ [8] below T^*, indicating a lack of (observable) long range magnetic ordering. A model for diffuse scattering for liquids/gases etc., which is generally used for dimer systems, was therefore used to fit the INS data. Assuming the dimer state can be described by the wavefunctions $|s_1, s_2, M\rangle$ at the energy transfer corresponding to the spin gap, the intensity of scattered neutrons is given by [25]:

$$I \propto \exp(-\frac{\Delta_0}{k_B T}) \exp(-2W) f^2(Q) \mathbf{M} (1 - \frac{\sin(QR)}{QR}) \quad (1)$$

where Δ_0 is the spin gap, $\exp(-2W)$ is the Debye-Waller factor, $f(Q)$ the magnetic form factor and $\mathbf{M}$ is the matrix element describing the transition, and R is the metal-metal distance. In this case, we wish to study whether the effect is due to intra-dimer of inter-dimer alignment. The last term describes interference effect as a result of the metal-metal distance in the dimer.

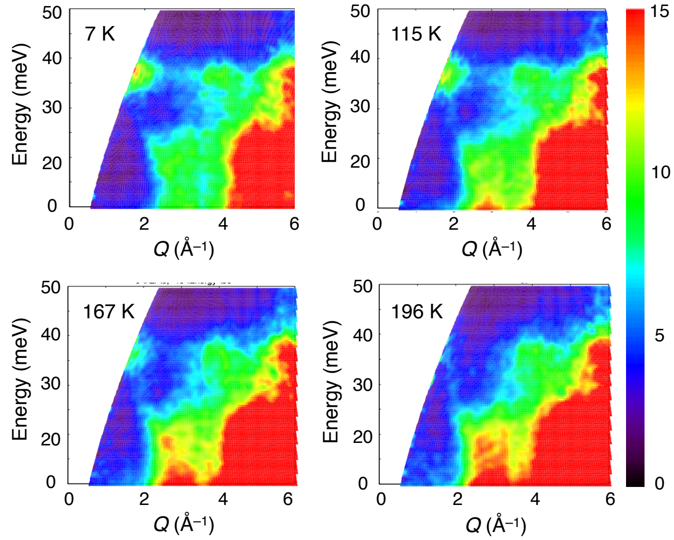

FIG. 1. Color-coded Bose-factor corrected SQ, E maps of the inelastic neutron scattering of $Ba_3BiRu_2O_9$ taken on Merlin at ISIS above, and at three temperatures below, $T^* = 176$ K. A magnetic excitation emerges below T^* at low-Q and an energy transfer of 36 meV. The color scale at right shows intensity (arbitrary units).

An integrated intensity slice was taken over the energy transfer range 32-42 meV at 7 K and fitted to Equation (1) from $Q = 1.6$ to $Q = 2.4$. Larger Q values were excluded because the phonon background became significant. The form factor for Ru^{5+} [26] was used to perform the analysis, as there is no available experimental form factor for Ru^{4+}, and a phonon background was modeled of the form $xQ^2 + y$. Two alternative fits to determine the Ru-Ru distance were performed: one starting from the experimental intra-dimer Ru-Ru distance of 2.6 Å; and another starting from the (average) experimental inter-dimer distance of 5.9 Å[8]. The former converged to an intra-dimer distance of R $= 2.61 \pm 0.01$ Å, and the latter to R $= 5.5 \pm 0.2$ Å. Note that the second discrete peak near $Q = 4$ is a phonon peak due to the aluminum sample holder. The intra-dimer model, shown in Fig. 3, produced the better fit to the low Q intensity. However, it should be acknowledged that without very low Q data, the inter-dimer model cannot be conclusively ruled out.

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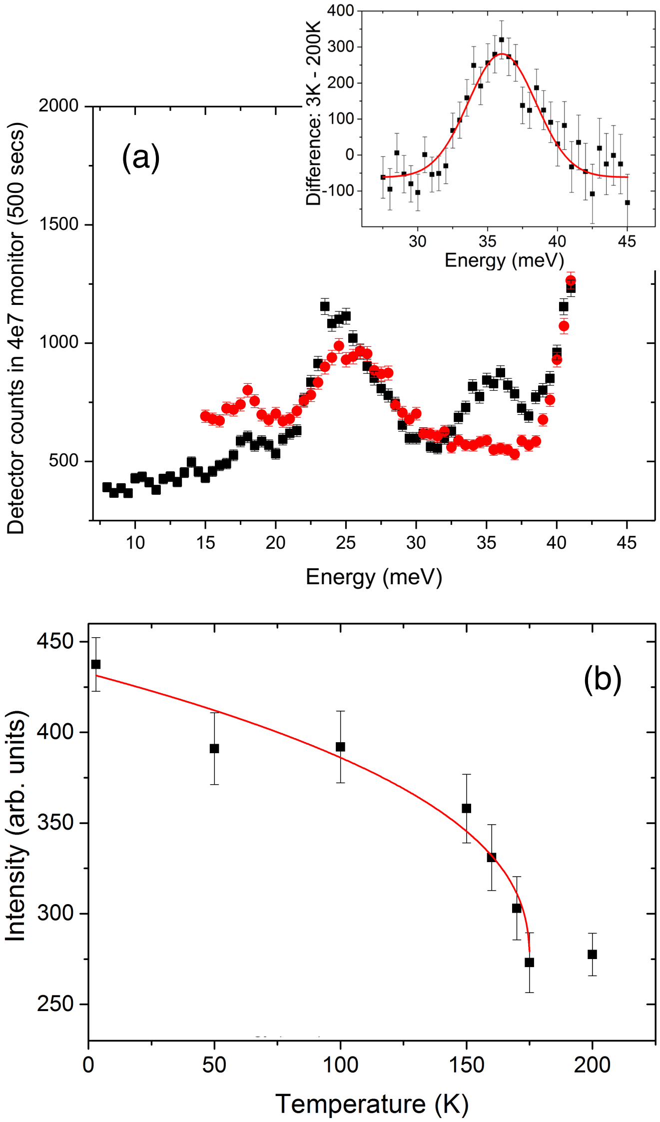

FIG. 2. Inelastic neutron scattering from $Ba_3BiRu_2O_9$, measured on Taipan at ANSTO. (a) Shows low-Q scans above (200 K, red) and below (3 K, black) $T^* = 176$ K. The inset shows the difference (3 K - 200 K) fit to a Gaussian centred at $E_{exp} = 36.03 \pm 0.14$ meV. (b) The intensity of this peak as a function of temperature, fit to an order parameter (see text for details).

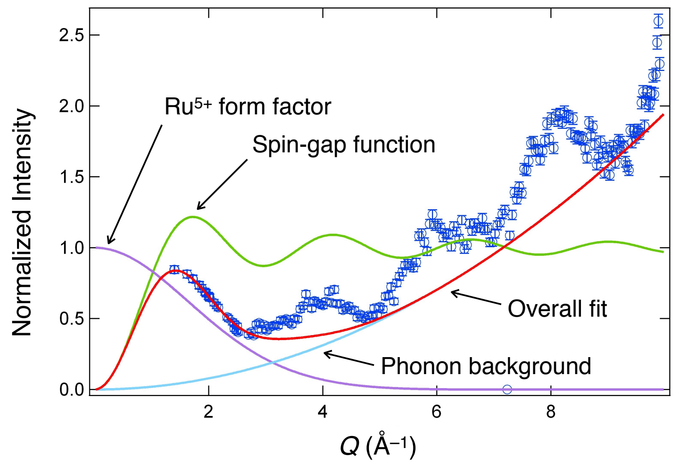

FIG. 3. Integrated intensity over the energy transfer range 32-42 meV of the Merlin data at 7 K, fit to equation (1). Components of the fit are labelled (see text for details). The oscillations at higher Q in the experimental data (blue circles) are non-magnetic (phonon) peaks due partly to the aluminum sample holder.

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