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LETTER TO THE EDITOR

The onset of quadrupole ordering at the structural phase transition in DyB_2C_2

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Abstract

X-ray diffraction and heat capacity data for DyB_2C_2 are used to derive quantitative information about the structural phase transition at 24.7 K. A successful interpretation is achieved in terms of a continuous transition to a crystal structure belonging to the space group $P4_2/mnm$ (No 136) that supports a motif of Dy 4f quadrupoles which belong to the A_g representation of the point group C_{2h} for the Dy site in the distorted structure. There is evidence in favour of the Ising universality class for the transition, including a critical exponent $\beta = 0.30 \pm 0.02$ and a near-logarithmic divergence of the heat capacity.

Awareness of the significance of orbital degrees of freedom in determining material properties has grown in recent years, particularly in relation to 3d transition compounds where charge, orbital, and spin degrees of freedom can appear on an equal footing. Rare-earth ions are essentially different from 3d ions because orbital and spin degrees of freedom are indissolubly bound and the ion's environment exerts a strong influence (with the $4f^7$ ion the general exception). By and large, to date orbital properties have been inferred from experimental data. Now, the availability of synchrotron sources of x-rays makes it possible to routinely exploit the direct coupling of photons with orbital degrees of freedom.

Dysprosium borocarbide, DyB_2C_2, is a fascinating material which undergoes a structural phase transition at $T_Q = 24.7$ K and a magnetic phase transition at $T_N = 15.3$ K. Pioneer work on the material was carried out by Yamauchi and co-workers [1]. The magnetic phase transition has been extensively studied by means of neutron diffraction and it is thought to be well understood [1, 2]. Evidence for the nature of the structural transition came from the

use by Tanaka *et al* [3] of the newer technique of resonant x-ray Bragg diffraction applied at the Dy L_{III} absorption edge. Resonant intensity at $(0, 0, l)$ with $l = n/2$ develops below T_Q through a distortion of the lattice occupied by B and C atoms, which reduces the Dy site symmetry to $2/m$ from $4/m$. Diffraction at space-group-forbidden reflections $(0, 0, l)$ below T_Q is an example of Templeton and Templeton scattering [4] caused by spatial anisotropy in the Dy charge distribution, and the anisotropy mirrors the site symmetry (Neumann's principle). Hirota *et al* [5] have confirmed diffraction at $(0, 0, l)$.

A displacement of the B and C ions and a reduction of the Dy site symmetry are inseparable signatures of the structural phase transition at T_Q, where the space group changes to No 136 from No 127 [3, 6, 7]. Both signatures are in evidence at our chosen Bragg reflections (h, k, l) with $h + k$ odd and $l = n/2$. Change in the Dy site symmetry induces Thomson scattering associated with a structure factor [7, 8],

$$F_c \propto (k_a^2 - k_b^2)\{\langle j_2\rangle\langle Q_{aa} - Q_{bb}\rangle + \cdots\}, \tag{1}$$

where $\boldsymbol{k}$ is the scattering wavevector (h, k, l) and lattice vectors are denoted by a, b, and c (the c-axis coincides with the axis of twofold rotation symmetry). The remaining quantities in equation (1) are properties of the Dy 4f valence shell; $\langle Q_{\alpha\beta}\rangle$ is the quadrupole moment, and $\langle j_m\rangle$ is the spherical Bessel function transform of the 4f radial distribution, and with $m > 0$, $\langle j_m\rangle$ vanishes for $h = k = l = 0$. The dots in equation (1) stand for 4f multipoles of rank 4 (hexadecapole) and 6 (hexacontatetrapole). A fractional displacement of B or C along the c-axis has associated with it a structure factor which is proportional to

$$\sin(\pi l)\sin(2\pi l\delta)\sin\left[\frac{\pi}{2}(h + k\xi)\right]\sin\left[\frac{\pi}{2}(k - h\xi)\right], \tag{2}$$

where ξ is related to the position parameter in space group No 127. As expected, near T_Q, intensity from B and C ions is directly related to the distortion δ that comes with the structural phase transition. Lastly, when the primary energy of the x-ray beam is tuned to the Dy L_{III} edge, there is Templeton and Templeton scattering that is also a signature of the structural phase transition at T_Q, exactly as previously described for Bragg reflections $(0, 0, l)$.

The description of the distorted structure below T_Q, which is given here in terms of space group No 136 together with an ordering of 4f quadrupole moments, is disputed by Matsumura *et al* [9] on the grounds that the space group appears to allow strong non-resonant (Thomson) reflections that are not observed. However, the intensity estimates quoted by Matsumura *et al* for reflections (h, h, l) with l a half-integer arise from questionable assumptions. First, a 10% displacement at the phase transition in B and C positions and, secondly, a uniform sign of the displacements; in contrast to this, realistic displacements are likely to be less than 1% in magnitude (on passing through T_Q, crystals of DyB_2C_2 do not shatter, which is what might be anticipated from a 10% displacement) and B and C displacements of opposite sign have to be considered. Taking both these factors into account dramatically reduces calculated intensities and, most importantly, revised values are in accord with recent observations [10]. Additionally, the distorted structure proposed by Matsumura *et al*, which invokes a periodic displacement of Dy ions, is found to be consistent with Dy ions at sites 4(e) in space group No 128 ($P4/mnc$) that do not support non-zero off-diagonal quadrupole moments, e.g. $\langle Q_{ab}\rangle$ and $\langle Q_{aa} - Q_{bb}\rangle$, because the Dy sites have C_4 symmetry. In consequence, a periodic displacement of Dy ions proposed by Matsumura *et al* does not fulfil the necessary condition for ordered Dy quadrupoles.

Resonant x-ray diffraction measurements were made at the undulator beamline BL29XU at SPring-8. Incident x-rays were monochromatized using a Si(1, 1, 1) double-crystal monochromator. The primary beam was reflected by a Si mirror with an angle of 0.188° in order to eliminate higher harmonics. The energy of the incident x-rays was tuned close to

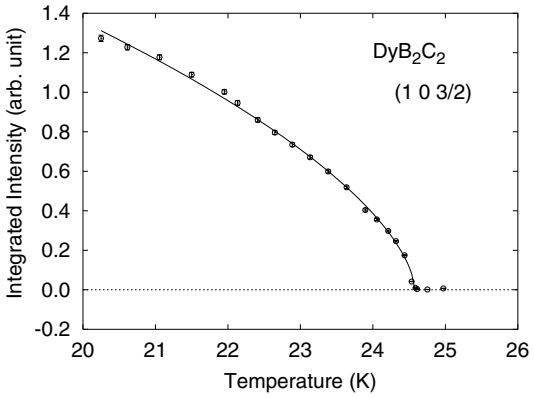

Figure 1. The temperature dependence of the integrated intensity of the $(1, 0, \frac{3}{2})$ Bragg reflection. The curve is drawn as a guide to the eye. Uncertainties in the data are no larger than the drawn data points.

the Dy L_{III} absorption edge ($E = 7.790$ keV) with an accuracy of $\sim$1.1 eV. A platelet sample with the size of about 5 mm $\times$ 3 mm $\times$ 0.3 mm was mounted with beeswax in a closed-cycle ^{4}He refrigerator, with the c-axis almost parallel to the ϕ-axis of the diffractometer. The mosaic spread of the single crystal used in this work was about 0.04° at the full width at half-maximum measured at the (0, 0, 2) reflection. The slit aperture was limited to 0.5 mm $\times$ 0.5 mm in size.

Heat capacity measurements on the same sample were performed with a MagLab^{HC} microcalorimeter (Oxford Instruments, UK). This microcalorimeter consists of a small sapphire chip on which a thermometer and a heater are evaporated. For a measurement, the heater power was first increased stepwise and maintained for a period of 3τ to ensure that equilibrium was closely approached, where τ is the relaxation time. Then the power was stepped back to its original value. The variation of the chip temperature with time was fitted with an exponential function from which τ, and thus the heat capacity, was obtained.

The integrated intensity at the $(1, 0, \frac{3}{2})$ Bragg reflection was measured as a function of temperature and data are shown in figure 1. Almost no hysteresis is seen in the vicinity of T_Q between the measurements performed with increasing and decreasing temperature runs. This observation is consistent with the theoretical prediction that the structural phase transition, between space groups Nos 127 and 136, is continuous [11]. The Bragg intensity, I, has been fitted to

$$I = I_0[1 - T/T_Q]^{2\beta}, \tag{3}$$

where, I_0 is a constant. We see in figure 2 a very good fit to data over a few decades in the reduced temperature, $1 - T/T_Q$. Using all our data we find $T_Q = 24.58 \pm 0.03$ K and $\beta = 0.30 \pm 0.02$, and fitting to data within 10% of T_Q gives the same value for β. Bragg intensities at $(0, 0, \frac{5}{2})$ have been studied by another group of researchers [5, 9]. In [5], they reported the values $T_Q = 24.7 \pm 0.9$ K and $\beta = 0.18 \pm 0.06$. Later, the value of β was changed to $\beta = 0.35 \pm 0.01$ [9], for the reason that the previous measurement did not have enough accuracy. The value of $T_Q = 25.52 \pm 0.009$ K reported in [9] is higher than that obtained in this work and in [1].

Let us proceed to the heat capacity measurement. Figure 3 shows the temperature dependence of the heat capacity in the vicinity of T_Q, after subtracting that of LaB_2C_2 [1] from the measured heat capacity, and thereby removing from our data the lattice part of the heat capacity. Measurements performed with increasing and decreasing temperatures across T_Q showed no hysteresis, which is additional evidence that the transition at T_Q is continuous.

We analysed our data in terms of two functions of the temperature, namely, a power law ($\alpha \neq 0$) and a logarithmic divergence ($\alpha = 0$) [12]. The logarithmic divergence gave a

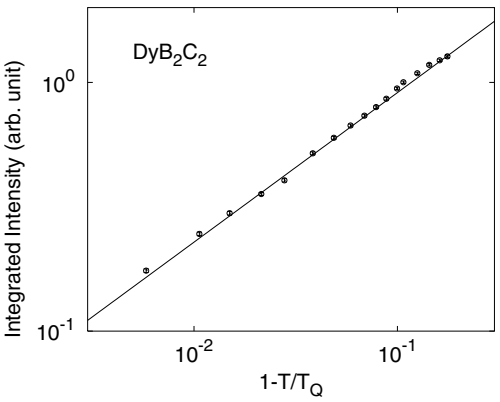

Figure 2. The integrated intensity of the $(1, 0, \frac{3}{2})$ Bragg reflection is plotted versus the reduced temperature, $1 - T/T_Q$.

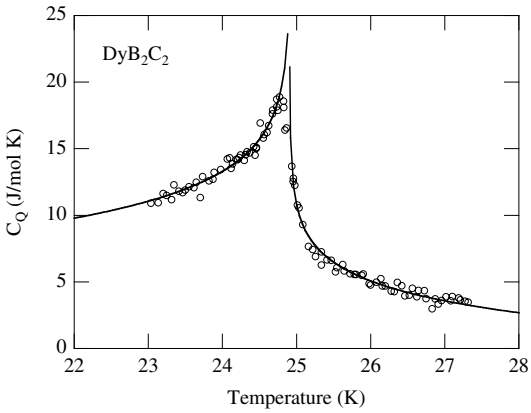

Figure 3. The temperature dependence of the heat capacity of DyB_2C_2 after subtracting the heat capacity of diamagnetic LaB_2C_2.

superior fit, and in figure 4 our data are shown with

$$C_Q = -A^{\pm} \ln |1 - T/T_Q| + B^{\pm}, \tag{4}$$

where $A^{\pm}$ and $B^{\pm}$ are constants, and $\pm$ means the corresponding quantity above (+) and below (−) T_Q. We find $T_Q = 24.91 \pm 0.01$ K, $A^+ = 2.30 \pm 0.05$, $A^- = 3.02 \pm 0.08$, $B^+ = -2.11 \pm 0.17$, and $B^- = 3.29 \pm 0.31$. The good quality of the fit strongly suggests that a Landau theory of the structural phase transition at T_Q is not appropriate. The value of T_Q determined from the x-ray diffraction and heat capacity measurements is slightly different even if we consider the error bar. We believe that the difference comes from the absolute accuracy of the calibration of the thermometers.

An immediately plausible model for all our experimental data belongs to the Ising universality class. Our value for the exponent $\beta = 0.30 \pm 0.02$ is certainly compatible with calculations performed on the three-dimensional (3D) Ising model with nearest-neighbour interactions that give $0.303 \leqslant \beta \leqslant 0.318$ [13] and also with the exponent obtained from an $N = 1$ field theoretical model ($\beta = 0.3258 \pm 0.0014$ [14]). Note that theoretical studies show that β is independent of the spin value, $\mathcal{S}$, for the Ising model [13]. It was shown rigorously that the heat capacity of a two-dimensional Ising model showed a logarithmic divergence at the critical point [15]. Although there are no rigorous results on the heat capacity of a three-dimensional Ising model, we expect that the heat capacities in two- and three-dimensional Ising models will behave similarly. Additionally, a standard model for structural phase transitions belongs to the Ising universality class. In discussing the critical properties we have to identify

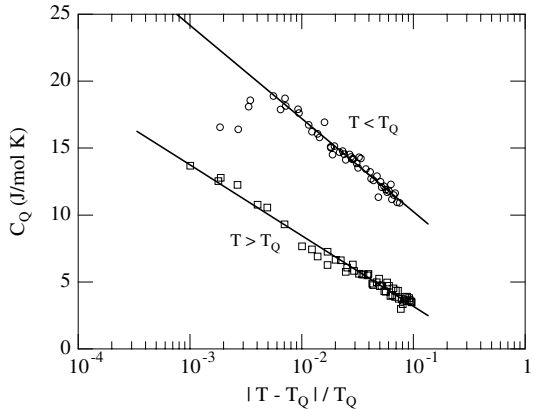

Figure 4. The anomalous part of the heat capacity in DyB_2C_2 is plotted versus the reduced temperature, $|T - T_Q|/T_Q$.

the range of interaction between the quadrupole moments; is it short ranged [16, 17] or long ranged [18, 19]? For a large value of $\mathcal{S}$ ($\gg\frac{1}{2}$), one may use a spherical model [20]. A spherical model with an infinite-ranged interaction predicts critical phenomena similar to those given by a mean field approximation. It is evident that the value of β and the behaviour of C_Q are not consistent with what a mean field theory predicts.

Now we discuss the Ising criticality found in this compound from an atomic level. Usually, rare-earth atoms in a compound are in the trivalent state, and the ground state electronic configuration of $Dy^{3+}(4f^9)$ is ^6H with total orbital moment $L = 5$ and total spin $S = \frac{5}{2}$. Of the six manifolds, the one with $J = \frac{15}{2}$ is the lowest, where $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$. The $J = \frac{15}{2}$ state is constituted of eight Kramers doublets. From recent inelastic neutron spectroscopy performed on a sample with Dy diluted by Y [21], the Dy crystal potential has states at approximately 17 and 48 K ($\sim 2T_Q$) above the ground state. The above information gives substance to the conjecture by Yamauchi *et al* [1], based on heat capacity measurements, that just two Kramers doublets are essential in determining structural and magnetic properties, namely, the ground and first excited Kramers doublets. Such an energy level scheme immediately accounts for an entropy $R \ln 2$ released at T_Q and T_N. Let us suppose that the ground state is spanned by $|\Psi\rangle$ and its time-reversed partner $|\overline{\Psi}\rangle$, with

$$|\Psi\rangle = \mathrm{i}\sin\theta\sin\phi|M\rangle + \cos\theta|M-2\rangle + \mathrm{i}\sin\theta\cos\phi|M-4\rangle, \tag{5}$$

where $|M\rangle \equiv |J = \frac{15}{2}, M\rangle$ and the axis of quantization is parallel to the crystal c-axis. The linear combination of states respects the Dy site symmetry $2/m$, and the relative phases are chosen to make $\langle\Psi|Q_{xy}|\Psi\rangle = \langle\overline{\Psi}|Q_{xy}|\overline{\Psi}\rangle$ different from zero, in the light of the finding from x-ray diffraction at $(0, 0, l)$ about the nature of the ordering of quadrupoles in DyB_2C_2.

One condition on the mixing angles can be derived by considering a state that is suitable for the first excited level at around 17 K. The state $|\Psi_2\rangle = \cos\theta\sin\phi|M\rangle + \mathrm{i}\sin\theta|M-2\rangle + \cos\theta\cos\phi|M-4\rangle$ automatically satisfies $\langle\Psi|\Psi_2\rangle = 0$ and $\langle\Psi|Q_{xy}|\Psi\rangle = -\langle\Psi_2|Q_{xy}|\Psi_2\rangle$. For a second condition on θ and ϕ, one can take $\langle\Psi|Q_{xy}|\Psi_2\rangle = 0$, in which case $|\Psi\rangle$ and $|\Psi_2\rangle$ span a space where Q_{xy} behaves like an Ising spin-$\frac{1}{2}$ variable.

Lastly we consider the saturation magnetic moment developed in a ground state $|G\rangle$ which is a linear combination of $|\Psi\rangle$ and $|\overline{\Psi}\rangle$. Since $\langle\Psi|J_z|\overline{\Psi}\rangle = 0$ and $\langle\Psi|J_z|\Psi\rangle = -\langle\overline{\Psi}|J_z|\overline{\Psi}\rangle$, one finds $\langle G|J_z|G\rangle = 0$ and the moment does indeed lie in the basal plane [1]. With respect to the x-axis the canting angle $= \tan^{-1}\{\langle G|J_y|G\rangle/\langle G|J_x|G\rangle\}$ and the saturation moment

$$\mu_0 = \tfrac{4}{3}\{\langle G|J_x|G\rangle^2 + \langle G|J_y|G\rangle^2\}^{\frac{1}{2}}. \tag{6}$$

On taking $M = \frac{5}{2}$, we find that μ_0 is in the range 7.2–8.8 μ_B for a canting angle $= 23°$, and these values are completely consistent with neutron diffraction data [1, 2].

To conclude, we have put forward a full interpretation of resonant x-ray Bragg diffraction data at the $(1, 0, \frac{3}{2})$ reflection of DyB_2C_2, arguing that contributions to scattering faithfully represent the structural phase transition at $T_Q = 24.7$ K. The diffraction data and heat capacity data are consistent with the Ising universality class of phase transitions. Absence of hysteresis in our data sets indicates that the transition is continuous, which is a feature shared by the preferred model, in which the distorted phase belongs to space group No 136 and the Dy site symmetry drops to $2/m$ from $4/m$ at the transition. The observed order parameter belongs to the A_g representation of $2/m$ (C_{2h}). A reduction in site symmetry is a necessary condition for the motif of ordered quadrupoles seen in x-ray diffraction data at $(0, 0, l)$ gathered below T_Q. Striction exists in DyB_2C_2 [5], so an accurate description of our findings is that the structural phase transition is of the first kind and very close to being continuous.

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