Magnetic properties of a LuVO₃ single crystal studied by magnetometry, heat capacity and neutron diffraction

L.D. Tung a, *, J. Schefer b, M.R. Lees c, G. Balakrishnan c, D.McK. Paul c

a Department of Physics, University College London, Gower Street, London WC1E 6BT, United Kingdom
b Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
c Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

1. Introduction

The interplay between spin-orbital interaction and phase transitions has attracted much interest recently in strongly correlated electron systems, particularly in the transition metal (TM) oxides. Coupling to the lattice further enriches the interplay through lattice distortions, phonons, and cooperative effects such as Jahn-Teller (JT) distortions [1]. Cuprate superconductors and Manganites with colossal magnetoresistance belong to the TM oxides with 3d e_g bands at the Fermi level. Perovskite Vanadates RVO₃ (R = rare earth and Y) belong to the same type but with 3d t_2g bands and show very different behaviour.

The crystal structure of RVO₃ is distorted from cubic to orthorhombic Pbnm symmetry by a cooperative rotation of the VO₆ octahedra [2]. A long-range magnetic ordering of the V sublattice has been observed at low temperatures for different RVO₃ compounds with the magnetic structures being either being C-type with the spins parallel along the c-axis but antiparallel in the ab-plane or G-type with the spins antiparallel along all directions [3]. In RVO₃ it was found that, with decreasing Lanthanide ionic radii, the onset temperature for the orbital ordering (OO) T_{OO} increases (137 K for LaVO₃ and 179 K for LuVO₃) while the spin ordering (SO) temperature T_{SO} decreases monotonically (139 K for LaVO₃ and 107 K for LuVO₃). The crossover of T_{OO} and T_{SO} is between R = La and Ce. Recent Hartree-Fock studies [4] have shown that the C- and G-phases are energetically close, consequently, the interplay between different factors such as JT distortions, orbital quantum fluctuations, and the Dzyaloshinsky–Moriya interaction have led to very interesting properties.

In the perovskite-type RVO₃ compounds, the OO phenomenon investigated for LaVO₃ and YVO₃ indicated an orbitally induced-structural phase transition from orthorhombic to monoclinic when cooling through T_{OO}. In LaVO₃, the SO temperature T_{SO} is 139 K which is slightly above T_{OO} of 137 K [5], whereas it is equal to 116 K and so well below the 200 K of T_{OO} for YVO₃. When cooling down further, interestingly, an additional first-order phase transition appears at transition at T_{S} = 77 K for YVO₃ below which the orthorhombic phase is recovered and the magnetic structure becomes G-type [6,7]. Concerning the high temperature phase at T_{S} < T < T_{SO} in YVO₃, a magnetic neutron scattering study [8] has revealed some unusual features: i) the magnetic structure is non-collinear, and just more complex than previously assumed for the simple C-type; ii) The magnon band width as derived from inelastic neutron scattering along the ferromagnetic c-axis is larger than that in the antiferromagnetic ab-plane. This violates the standard Goodenough–Kanamori rules according to which ferromagnetic superexchange interactions are generally substantially weaker than...
the antiferromagnetic interactions; iii) The spectrum is split into optical and acoustic magnons with a gap of 5 meV. To explain the latter feature, C. Ulrich et al. [8] proposed two different ferromagnetic exchange bonds $J_e$ along the c-axis (i.e. dimerisation) which can be made possible by an orbital Peierls state due to the formation of an orbital singlet. However, Z. Fang et al. [9] argued that the splitting should be accounted for by the two different exchange interaction $J_{ab}$ of inequivalent VO$_2$ layers which have different amounts of JT distortion.

For LuVO$_3$, an earlier powder neutron diffraction (PND) study by Zubkov et al. [3] indicated that the compound has a G-type magnetic structure at low temperature. Munoz et al. [10], also using PND, studied the structural and magnetic structure in the temperature range from 2 to 300 K. They pointed out that LuVO$_3$ has G-type magnetic ordering below $T_{SO} = 107$ K and this magnetic structure remains stable down to 2 K. The material also has an OO temperature of 190 K, but without any structural phase transition at this temperature. The change in the crystallographic structure from orthorhombic to monoclinic symmetry occurs instead between −82 and 94 K, which is below the SO temperature. Recently, we have studied this compound in detail using high quality single crystals combining a variety of experimental methods including neutron and synchrotron studies [11]. In this work, a canted C-type magnetic structure was observed that transforms to a collinear G-type at lower temperature. It has also been shown that the features of orbital-Peierls state (i.e. orbital-singlet similar to spin-singlet dimers) attributed previously in YVO$_3$ [8] are in fact a consequence of the static OO and corresponding JT distortion.

In this contribution, we report on the magnetic, heat capacity, and neutron diffraction studies of single crystal LuVO$_3$. The compound appears to be an antiferromagnet and its observed magnetic properties are consistent with the inhomogeneous nature of the compound.

2. Experimental details

Single crystal LuVO$_3$ was grown by means of the floating zone technique using a high temperature Xenon arc-furnace. At first, LuVO$_3$ was prepared by mixing stoichiometric quantities of Lu$_2$O$_3$ and V$_2$O$_5$ (with purity of 99.9%), followed by annealing at 1100 °C for 48 h. The product was then reduced at 1000 °C in flowing H$_2$ for 10 h to produce the LuVO$_3$ powder phase. The LuVO$_3$ feed and seed rods used for the single crystal growth were made by pressing the powder under hydrostatic pressure and then annealing these rods at 1500 °C under a flow of Ar. A similar procedure for single crystal growth is described elsewhere [12].

Measurements of the zero-field-cooled (ZFC) [13] and field-cooled (FC) magnetisation and the magnetic isotherms were carried out in a Quantum Design SQUID magnetometer. Here we use zero and ZFC in italics to indicate that we neglect the small trapped field in the superconducting solenoid of the magnetometer. For the FC measurements, the sample was cooled from the paramagnetic region to 1.8 K in an applied field, e.g. 0.1 kOe, with the data collected (FCC), then it was warming during the measurements (FCW). For the ZFC measurements, the sample was cooled in zero field to 1.8 K before the magnetic field was applied. The data were then taken on warming. Heat capacity measurements of the sample were carried out in a Quantum Design Physical Property Measurement System (PPMS) with a heat capacity option using a relaxation technique. The magnetic structure of the compound was determined from single crystal neutron diffraction measurements on the TriCS instrument at the Paul Scherrer Institute, Switzerland using a wavelength of 1.1807 Å [13].

3. Results and discussion

In Fig. 1, we present the results of the heat capacity measurements on the LuVO$_3$ single crystal; C vs. T (left scale) and C/T vs. T (right scale). Three transitions are detected and defined as the orbital ordering (OO) $T_{OO} = 179$ K, the spin ordering (SO) $T_{SO} = 107$ K, and $T_e = 82.5$ K manifested as a drop in the heat capacity with decreasing temperature. The values of these transition temperatures are in good agreement with those obtained for the polycrystalline sample [10].

To determine the magnetic structure, the results of the neutron diffraction studies with some selected reflections as a function of temperature are presented in Fig. 2. Below $T_e = 82.5$ K, we observed the magnetic contribution on top of the (h k l) reflections with h zero or even, k odd and vice versa, l odd (e.g. (0 3 1) (0 1 1) reflections as seen in Fig. 2) indicating the collinear G-type magnetic structure [8]. Between $T_e$ and $T_{SO}$, a magnetic contribution is seen to develop on a different set of (h k l) with h zero or even (odd), k odd (zero or even) and l zero or even characteristic of the C-type magnetic structure (see Fig. 2 for (100) and (012) reflections). The magnetic structure is, however, canted since the magnetic contribution due to a G-type magnetic structure is seen not to diminish completely which is also in accordance with that reported in Ref. [11].

To explore further, the results of the FCC and FCW M(T) measured in two different magnetic fields of 0.1 kOe and 0.4 kOe along the principal axes are displayed in Fig. 3. There is an upturn in the magnetisation with decreasing the temperature at $T_{SO} = 107$ K. In the SO regime, there is an additional first order transition at $T_e$ of about 82.5 K, consistent with the observation of magnetic hysteresis between FCC and FCW data. Earlier, we reported M(T) measurements for some different RVO$_3$ compounds [12], and showed that the form of the ZFC curves are very much dependent on the very small value of the trapped field (TF) in the superconducting magnet of the SQUID magnetometer. We have examined this TF carefully. Before each measurement, we ran a degauss sequence to minimise the TF; its absolute value was estimated to be less than 2 Oe. We can “generate” a TF with opposite sign by reversing the sign of the magnetic fields in the de gauss sequence [12]. In Fig. 4, it can be seen that the ZFC magnetisation measured in an applied field of 0.1 kOe observed after cooling in a positive TF (ZFC_PTF) is mirrored with that of the negative TF (ZFC_NTF) even though the TF is about two orders of magnitude smaller than the applied field used for the measurement. It is well known that for conventional magnetic materials, domain translation is reversible at (very) low magnetic

![Image](image_url)
fields [14] and so the TF of the order of a few oersteds does not have any influence on the nominal ZFC results. However, this is clearly not the case for LuVO₃. It is surprising that a TF of less than 2 Oe can create the irreversible magnetisation at low temperature for this compound.

In Fig. 5, we present the results of the reciprocal of the magnetic susceptibility as a function of temperature. Since there is a OO transition at a temperature $T_{OO} = 179$ K accompanying a change in the crystallographic structure from a $Pbnm$ orthorhombic space group to a monoclinic $P2_1/b$ space group [11], there is a change in the slope in the $\chi^{-1}(T)$ as well. We have tried to fit for the Curie–Weiss behaviour in the paramagnetic regime in two different temperature ranges, namely between 120–175 K and 185–300 K. The values of the effective moments $\mu_{eff}$ and the Weiss temperatures $\theta_p$ along different principal crystallographic axes as derived from the fitting are listed in Table 1. The values of $\mu_{eff}$ ranged from 2.16 to 2.61 $\mu_B$/f.u. which is somewhat lower than the value of 2.83 $\mu_B$ for a free ion $V^{3+}$ (spin only, $S = 1$). The Weiss temperatures $\theta_p$ are all negative in the range from $-108.8$ K to $-265$ K, indicating the presence of strong antiferromagnetic correlations in the compound.

In Fig. 6, we present the magnetic isotherms measured at 1.8 K along different principal crystallographic axes. Despite the fact that the compound has a simple collinear G-type antiferromagnetic structure, at 1.8 K we observe open hysteresis loops along all directions with coercivities $H_c$ being 1.7 kOe, 3 kOe, 0.2 kOe and remanent magnetisation $M_r$ of 0.012$\mu_B$, 0.0011$\mu_B$, 0.0002$\mu_B$ along the $a$-, $b$-, and $c$-axes, respectively. This anomalous feature is indeed consistent with the inhomogeneous nature due to the defects in the compound.

Fig. 2. Integrated intensity of some selected Bragg reflections as indicated, for a LuVO₃ single crystal as a function of temperature.

Fig. 3. FCC (solid symbols) and FCW (open symbols) magnetisation versus temperature curves measured along the main axes of a LuVO₃ single crystal in an applied field of 0.1 kOe (left panels) and 4 kOe (right panels).
spin orbital system as has been proposed recently for the RVO$_3$ compounds \[12,15\). In this model, LuVO$_3$ can be considered as an inhomogeneous antiferromagnet in which a fraction of the spins interact via weak local fields and thus they can turn easily to lie along the direction of the applied field. The remaining spins are strongly antiferromagnetically coupled (i.e. are hardly affected by the applied field) and are responsible for the observed SO temperature $T_{SO}$ and the negative Weiss temperatures. In addition, we would like to note that the weak local fields of the former spins also imply that the crystal field effects can lead to the reduced magnetic moment as well as the anisotropy in the magnetisation along different directions. In order to estimate the number of spins with weak local fields we consider the ratio between $M_r/M_s$ where $M_s$ is the saturation magnetisation which we assume to be $2\mu_B$ of the full moment expected for V$^{3+}$. At 1.8 K, the ratio $M_r/M_s$ measured along the $a$-$b$-$c$-directions is 0.6%, 0.055% and 0.01%, respectively. From these, we derive the number of spins with weak local fields in respect to the applied field of 0.3% which is determined as a half of the largest value obtained along the $a$-axis. This percentage of spins with weak local field is very small and can hardly be detected using experimental techniques like neutron diffraction, but as they are embedded in a strong antiferromagnetic matrix, their effect is strong and visible on the observed magnetic properties.

4. Conclusions

In summary, we have studied the magnetic properties of a LuVO$_3$ single crystal using magnetometry, heat capacity and neutron diffraction measurements. The compound undergoes an OO transition at $T_{OO} = 179$ K, followed by SO with a canted C-type magnetic structure at $T_{SO} = 109$ K. In the SO regime, with lowering temperature there is the change in magnetic structure from C-type to G-type at $T_G = 82.5$ K. The open hysteresis loops observed in the collinear G-type magnetic structure are attributed to the small inhomogeneity from spins with weak local fields embedded in the majority strongly antiferromagnetic matrix.

Acknowledgements

LD Tung would like to thank AFOSR for funding. The work at the University of Warwick was supported by EPSRC, UK, Grant EP/M028771/1. Part of the work is based on experiments performed on the single crystal neutron diffraction Instrument TriCS at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute, Switzerland. LD. Tung would like to dedicate this paper to Dr. P.E. Brommer.

References

[1] M. Imada, A. Fujimori, Y. Tokura, Metal-insulator transitions, Rev. Mod. Phys. 70 (1998) 1039.
[2] J.B. Goodenough, J.M. Longo, in: K.H. Hellwege (Ed.), Crystallographic and Magnetic Properties of Perovskite and Related Compounds, 1970, p. 126.
[3] V.G. Zubkov, G.V. Bazuev, G.P. Shevekin, Low temperature neutron and X-ray topographic studies of rare earth othovanadates, Sov. Phys. Solid State 18 (1976) 1163.
[4] T. Mizokawa, D.I. Khomskii, G.A. Sawatzky, Interplay between orbital order and lattice distortions in LaMnO$_3$, YVO$_3$ and YTiO$_3$, Phys. Rev. B 60 (1999) 7308.

[5] L.D. Tung, A. Ivanov, J. Schefer, M.R. Lees, G. Balakrishnan, D.McK. Paul, Spin, orbital ordering, and magnetic dynamics of LaVO$_3$: magnetization, heat capacity, and neutron scattering studies, Phys. Rev. B 78 (2008) 054416.

[6] G.B. Blake, T.T.M. Palstra, Y. Ren, A.A. Nugroho, A.A. Menovsky, Transition between orbital orderings in YVO$_3$, Phys. Rev. Lett. 87 (2001) 245501.

[7] Y. Ren, T.T.M. Palstra, D.I. Khomskii, E. Pellegrin, A.A. Nugroho, A.A. Menovsky, G.A. Sawatzky, Temperature-induced magnetization reversal in a YVO$_3$ single crystal, Nature 396 (1998) 441.

[8] C. Ulrich, G. Khaliullin, J. Sirker, M. Reehuis, M. Ohl, S. Miyasaka, Y. Tokura, B. Keimer, Magnetic neutron scattering study of YVO$_3$: evidence for an orbital Peierls state, Phys. Rev. Lett. 91 (2003) 257202.

[9] Z. Fang, N. Nagaosa, Quantum versus John-Teller orbital physics in YVO$_3$ and LaVO$_3$, Phys. Rev. Lett. 93 (2004) 176404.

[10] A. Muñoz, J.A. Alonso, M.T. Casais, M.J. Martínez-Lope, J.L. Martínez, M.T. Fernández-Díaz, Thermal evolution of the crystallographic and magnetic structure in LuVO$_3$: a neutron diffraction study, Chem. Mater. 16 (2004) 1544.

[11] M. Skoulatos, S. Toth, B. Roessli, M. Enderle, K. Habicht, D. Sheptyakov, A. Cervellino, P.G. Freeman, M. Reehuis, A. Stunault, G.J. McIntyre, L.D. Tung, C. Marjerrison, E. Ponomarev, P.J. Brown, D.I. Khomskii, Ch. Rüegg, A. Kreyssig, A.I. Goldman, J.P. Goff, John-Teller versus quantum effects in the spin-orbital material LuVO$_3$, Phys. Rev. B 91 (2015) 161104(R).

[12] L.D. Tung, M.R. Lees, G. Balakrishnan, D.McK. Paul, Magnetization reversal in orthovanadate RVO$_3$ compounds (R=La, Nd, Sm, Gd, Er, and Y): inhomogeneities caused by defects in the orbital sector of quasi-one-dimensional orbital systems, Phys. Rev. B 75 (2007) 104404.

[13] J. Schefer, M. Könnecke, A. Murasik, A. Czopnik, T. Strässle, P. Keller, N. Schlamp, Single-crystal diffraction instrument TriCS at SINQ, Phys. B 276–278 (2000) 168.

[14] P. Boutron, Anisotropie magnétique au-dessus du point d'ordre et paramètres d'environnement cristallin, J. Phys. 30 (1969) 413.

[15] L.D. Tung, P.rVO$_3$: an inhomogeneous antiferromagnetic material with random fields, Phys. Rev. B 72 (2005) 054414.

[16] L.D. Tung, Tunable temperature-induced magnetization jump in a GdVO$_3$ single crystal, Phys. Rev. B 73 (2006) 024428.

[17] L.D. Tung, M.R. Lees, G. Balakrishnan, D.McK. Paul, Heat capacity and magnetic properties of a EuVO$_3$ single crystal, Phys. Rev. B 76 (2007) 064424.