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Complex Magnetic Behaviour of $Ho_3Cu_4X_4$ Compounds ($X = Si$ and Sn)

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Dedicated to Professor Jerzy Janik on the occasion of his 80th birthday

Ternary $Ho_3Cu_4X_4$ compounds exhibit very complex magnetic phase diagrams. The rare earth ions occupy two non-equivalent crystal positions. Within both magnetic sublattices, magnetic moments exhibit different magnetic ordering temperatures. Moreover, in light of our results, it seems that both sublattices are weakly coupled between each other. This may be observed as independent changes of propagation vectors etc. The major difference of ordering temperatures between both compounds is likely related to substantial change of interatomic distances. Consequently, completely different crystalline electric field effects are observed.

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1. Introduction

$Ho_3Cu_4X_4$ compounds ($X = Si$ and Sn) crystallise in the orthorhombic crystal structure of *Immm* symmetry. 3:4:4 family seems to be particularly interesting due to unusual and complex magnetic properties [1, 2]. These properties originate from the crystal structure, where the magnetic ions are located at two different crystal positions. A number of compounds of 3:4:4 composition exhibiting different ordering temperatures of both sublattices has been reported so far. However, only $Ho_3Cu_4X_4$ compounds were investigated in a very detailed way using many complementary methods. In this paper we discuss differences in magnetic properties of these compounds.

The mechanism of magnetic interaction seems to be still doubtful. When taking the long-range Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction into account it is hard to explain a very weak coupling between magnetic sublattices.

On the other hand, local-like interactions can be hardly responsible for complicated incommensurate magnetic structures as there is no topological frustration within this crystal structure. In this paper we compare magnetic properties of two isostructural $Ho_3Cu_4X_4$ compounds with respect to their magnetic, electronic, and structural properties.

2. Experimental

The polycrystalline $Ho_3Cu_4Si_4$ and $Ho_3Cu_4Sn_4$ samples were prepared using high purity (Ho — 3N; Cu, Si, Sn — 4N) elements by arc melting in a purified argon atmosphere. To ensure homogeneity samples were remelted several times. Then, samples were annealed at 800°C for 10 days. Purity of our samples was examined using X-ray powder diffraction measurements (Cu K_α radiation) at room temperature. The measurements confirmed desired *Immm* crystal structure for both samples.

Magnetic measurements were carried out using the PPMS magnetometer in fields up to 5 T in the 1.7–300 K temperature range.

Powder neutron diffraction measurements were performed using the fine resolution E9 diffractometer at the BENSC Hahn–Meitner Institute (Berlin). The neutron diffraction patterns were collected in the 1.5–25 K temperature range with the incident neutron wavelength of 1.89 Å or 2.89 Å.

3. Results

3.1. Crystal structure

Investigated $Ho_3Cu_4Si_4$ and $Ho_3Cu_4Sn_4$ compounds exhibit *Immm* structure. For $Ho_3Cu_4Si_4$ the lattice constants are as follows: $a = 13.6384(1)$ Å, $b = 6.52149(6)$ Å and $c = 4.11141(5)$ Å. For $Ho_3Cu_4Sn_4$ they are $a = 14.5796(1)$ Å, $b = 6.90736(5)$ Å and $c = 4.41981(3)$ Å. The crystal structure of investigated compounds is presented in Fig. 1. The most interesting feature is an existence of two independent magnetic sublattices 2d and 4e of different point symmetries. The Ho2d–Ho4e distances of 3.71 Å (X = Si) and 3.94 Å (X = Sn) are only slightly higher than the shortest Ho4e–Ho4e distance of 3.56 Å (X = Si) and 3.78 Å (X = Sn). In both cases the shortest Ho2d–Ho2d distance is equal to the c lattice constant.

3.2. Magnetometric measurements

Magnetometric properties of both compounds were reported in detail elsewhere [1, 2]. The ordering temperature of $Ho_3Cu_4Si_4$ (19.4 K) is much higher than for $Ho_3Cu_4Sn_4$ (7.6 K). For $Ho_3Cu_4Si_4$ sample no metamagnetic transition was observed [2], the opposite holds for $Ho_3Cu_4Sn_4$ sample [1]. In order to study it in more detail new isothermal magnetisation measurements for $Ho_3Cu_4Sn_4$ sample were performed. In Fig. 2 the first derivative of isothermal magnetisation $\mathrm{d}\sigma(H)/\mathrm{d}H$ is presented. A clearly visible maximum of $\mathrm{d}\sigma(H)/\mathrm{d}H$ vanishes in between 3 K and 4.5 K. This is a clear coincidence of vanishing of the 4e sublattice magnetic ordering, that takes place at temperature of 3.3 K.

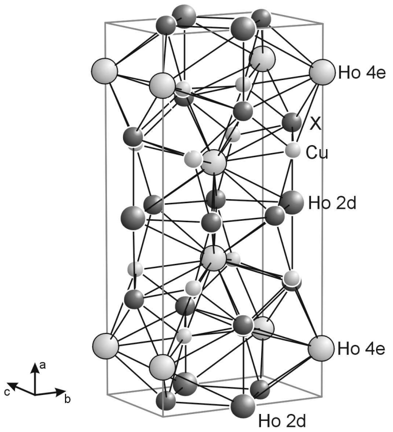

Fig. 1. Crystal structure of $Ho_3Cu_4X_4$ compounds.

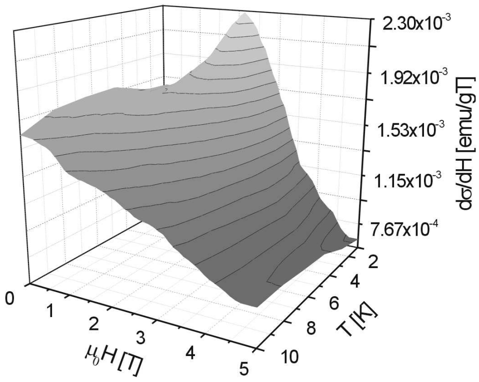

Fig. 2. The first derivative of isothermal magnetisation $\sigma(H)$ for $Ho_3Cu_4Sn_4$.

3.3. Neutron diffraction studies

Neutron diffraction studies were performed using the fine resolution diffractometer. Moreover, for studying a very complicated magnetic structure of $Ho_3Cu_4Si_4$ a long wavelength of 2.89 Å was used. In Fig. 3 low angle parts of neutron diffraction pattern are shown. For both compounds the two holmium 4e and 2d sublattices order magnetically at different temperatures of 5.4 K and 19.4 K ($Ho_3Cu_4Si_4$) or 3.3 K and 7.6 K ($Ho_3Cu_4Sn_4$). In both cases the 4e sublattice undergoes a change of magnetic structure below its ordering temperature at about 2 K (X = Si) and 2.3 K (X = Sn). Nevertheless, the nature of this transition is different in both compounds. In $Ho_3Cu_4Si_4$ the 4e sublattice reorientation is connected with disappearing of component aligned along the c axis, whereas the component aligned along the a axis remains unperturbed. It is worth noting that both c and a components exhibit different propagation vectors. On the other hand, for $Ho_3Cu_4Sn_4$ sample the 4e sublattice reorientation is connected

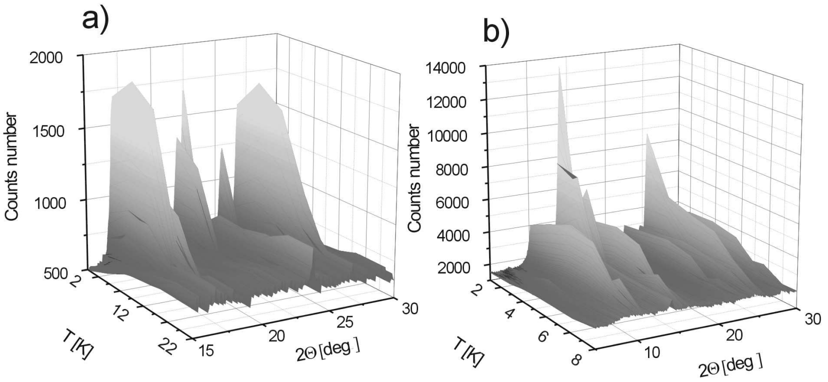

Fig. 3. Low angle parts of neutron diffraction patterns of $Ho_3Cu_4Si_4$ (a) and $Ho_3Cu_4Sn_4$ (b).

with a change of propagation vector only (this sublattice exhibits one component along the *a* axis). The lack of significant change of the second 2d magnetic sublattice as a response to the above mentioned 4e reorientation is an extremely interesting feature of 3:4:4 compounds. Similarly to the behaviour evidenced for 4e sublattices, both 2d sublattices exhibit additional transition just below its ordering temperatures. However, its origin seems to be different. For $Ho_3Cu_4Si_4$ only a change of magnetic moments sequence is evidenced. On the other hand, a change of magnetic propagation vector for $Ho_3Cu_4Sn_4$ was observed. The latter change from commensurate into incommensurate propagation vector just below the ordering temperature is quite common in rare earth-based intermetallics and predicted theoretically [3]. In general, magnetic moments of Ho ions are lower than expected. This may be due to crystalline electric field effects that are clearly visible in specific heat studies [1, 2].

4. Discussion and summary

The interatomic distances between rare-earth atoms within distinct sublattice as well as between different sublattices are comparable, thus the weak magnetic coupling between 2d and 4e sublattices is unlikely to be due to geometrical structure of the unit cell. Therefore, a question arises about origin of magnetic interactions. From one point of view, the independent changes of propagation vector in both sublattices seem to be hardly explainable within the long-range RKKY model. Any change of conduction band's polarisation originating from one sublattice should be reflected with change of magnetic ordering of the second sublattice as long as oscillatory character of the RKKY exchange does not minimise the 2d–4e coupling. On the other hand, such quasi-independent ordering could be easily understood within the local-like Campbell model. Although, the existence of incommensurate propagation vectors in case where there is no geometrical frustration is doubtful within the local interaction model. It is noticeable that lowering the Ho–Ho distance leads to an increase in the ordering temperatures. This observation is in agreement with both long-range and local-like magnetic interaction models.

A comparison of neutron diffraction with complementary specific heat data brings some evidence of possible origin of unusual magnetic properties of Ho$_3$Cu$_4$X$_4$ (X = Si, Sn) compounds. The phase diagrams of both compounds are given in Fig. 4 and Table. As one can see, the magnetic ordering of the 2d sublattice is very stable. Magnetic moments are aligned along the b axis with small exception in phases III and V for Ho$_3$Cu$_4$Sn$_4$. This may be an indication of strong crystal electric field in this position preferring such orientation of rare-earth magnetic moment. The same holds for the 4e sublattice, where the 4e magnetic moments lie along the a axis (the only exception is phase I, where they lie within the a–b plane). It is very interesting that except the phase V in Ho$_3$Cu$_4$Sn$_4$ the propagation vector of the 2d sublattice is commensurate (0;0.5;0). This might hint at local-like interaction within this sublattice, whereas the second one would be governed by long-range RKKY ones as no commensurate propagation vector was observed there. We found it very surprising that sample with X = Si exhibits much higher ordering temperature than sample with X = Sn despite the opposite behaviour of the modulus of the paramagnetic Curie temperature (–2.4 K and –6.6 K for X = Si and Sn, respectively). The latter suggests that magnetic in-

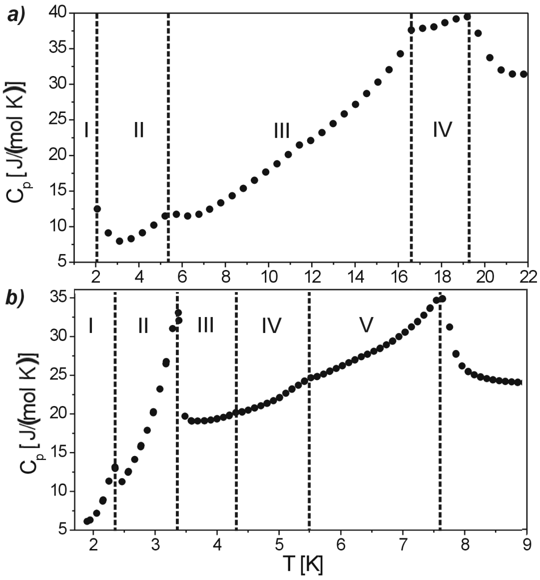

Fig. 4. Magnetic phase diagrams for Ho$_3$Cu$_4$Si$_4$ (a) and Ho$_3$Cu$_4$Sn$_4$ (b) as derived from specific heat and neutron diffraction data. The phases are denoted as Roman numerals. Relevant description is included in Table.

TABLE

Magnetic structures of $Ho_3Cu_4X_4$ (X = Si and Sn) compounds. Roman numerals denotes respective phases as given in Fig. 4. The θ and φ symbols denote angles between the c and a axes, respectively.

Phase	$Ho_3Cu_4Si_4$			$Ho_3Cu_4Sn_4$		
	μ_{2d} μ_{4e} $[\mu_B]$	2d: θ and φ 4e: θ and φ [°]	$\boldsymbol{k}_{2d}$ $\boldsymbol{k}_{4e}$	μ_{2d} μ_{4e} $[\mu_B]$	2d: θ and φ 4e: θ and φ [°]	$\boldsymbol{k}_{2d}$ $\boldsymbol{k}_{4e}$
I	8.4	90 and 90	0;0.5;0	8.3	90 and 90	0;0.5;0
	3.9	90 and 0	0.121;0.221;0.023	9.9	90 and 0	0.3712;0.5;0.5
	6.4	0 and 0	0.5;0.5;0.454			
II	8.2	90 and 90	0;0.5;0	8.6	90 and 90	0;0.5;0
	3.3	90 and 0	0.121;0.221;0.023	8.0	90 and 0	0.5;0.5;0.4694
III	8.1	90 and 90	0;0.5;0	8.6	80 and 90	0;0.5;0
IV	4.5	90 and 90	0;0.5;0	8.5	90 and 90	0;0.5;0
V	–	–	–	9.1	90 and 77	0.0695;0.4821;0

teractions are stronger for $Ho_3Cu_4Sn_4$. For this compound, the electronic specific heat coefficient γ is about 60% larger than in $Ho_3Cu_4Si_4$. This implies higher density of states at the Fermi level for the stannide. The conclusion is similar as in case of discussion of paramagnetic Curie temperature behaviour. A comparison of the magnetic specific heat data shows that the first excited crystal field level for $Ho_3Cu_4Si_4$ lies a bit lower than in the corresponding stannide. From this point of view, the observed difference of ordering temperature is justified.

The results presented above give a clear evidence of unusual and very interesting magnetic properties of 3:4:4 compounds, that must be investigated in the future.

Acknowledgments

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