Magnetic Ordering in $CoTa_2O_6$ and $NiTa_2O_6$

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Magnetic measurements on $CoTa_2O_6$ and $NiTa_2O_6$ are reported. The samples were obtained by a chemical transport reaction using chlorine as the transporting agent. Susceptibility data show, in contrast to former investigations, long-range magnetic ordering at $T_c = 6.64$ K (Co) and 10.3 K (Ni). Broad maxima in the magnetic susceptibility above T_c are attributed to low-dimensional short-range magnetic ordering. The relevancy of these observations for the chemistry of the title compounds is discussed. © 1988 Academic Press, Inc.

Introduction

$MeTa_2O_6$ (Me = Co, Ni) crystallize in the well-known trirutile structure type (*1, 2*) (Fig. 1) which can be derived from the rutile type by a tripling of the c-axis, the latter occurring as a consequence of the chemical ordering of the divalent and pentavalent cations.

Apart from small orthorhombic distortions, the Me and Ta ions are octahedrally coordinated by oxygen. The cation–oxygen octahedra form edge-sharing chains which are occupied alternately by MeO_6 and TaO_6 octahedra in a ratio $1:2$ provided that chemical ordering is complete. Chemical order in these materials is confirmed by the presence of superlattice reflections of the type $h, k, l, l \neq 3n$ in the X-ray powder patterns.

Early magnetic measurements (*3*) revealed broad maxima at low temperatures for both compounds, $T = 14$–18 K (Co) and $T = 22$–30 K (Ni). Initially, these temperatures were interpreted as Néel temperatures for three-dimensional antiferromagnetic ordering.

On the other hand, considering the layered arrangement of the magnetic cations in the trirutile structure the broad feature in the susceptibility might be the expression of an interesting low-dimensional magnetic effect with short-range ordering of the magnetic moments (*4*), as has been shown recently for the isostructural $FeTa_2O_6$ (*5*). To enlighten these issues we have carried out a careful reinvestigation of the low-temperature magnetic properties of the title compounds.

Experiments

Magnetic measurements were done in a S.H.E. SQUID susceptometer on a coarse crystalline powder at magnetic fields typi-
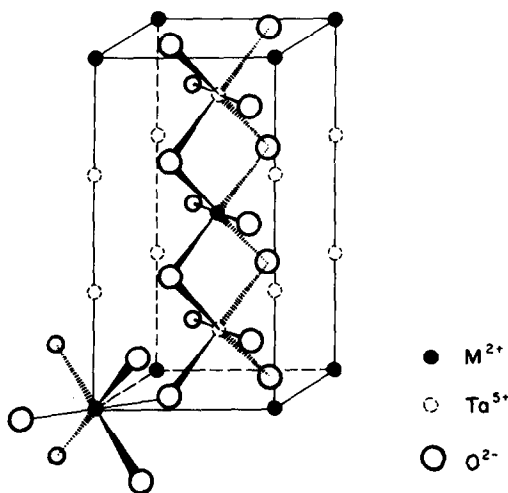
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● M²⁺

○ Ta⁵⁺

○ O²⁻

FIG. 1. Trirutile structure type. The c-axis is tripled with respect to that of a normal rutile unit cell.

cally below 1000 G. The samples for the magnetic measurements were obtained by a chemical transport reaction using Cl_2 as the transporting agent. Starting materials were prepared by sintering CoO/NiO and Ta_2O_5 at 1050°C in air. Red-violet (Co) and yellow (Ni) translucent crystals of $Me Ta_2O_6$ (Me = Co, Ni) (structure confirmed by powder X-ray investigations) were found at the cold end of the quartz ampoule after transporting several days in a temperature gradient

1000 → 930°C. The crystals obtained have typical sizes of $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ mm³ but usually are grown together irregularly. The transport reaction reported here for $Me Ta_2O_6$ (Me = Co, Ni) for the first time was carried out to further purify the samples from spurious magnetic oxides of Co and Ni.

Results and Conclusions

The low-temperature magnetic susceptibility of the title compounds is shown in Fig. 2, high-temperature data are in agreement with literature data (3) and are not given here.

In addition to the broad maxima at T_{max} = (15.6 ± 0.2) K, χ_{mole} (T_{max}) = 5.10×10^{-2} emu/mole for $CoTa_2O_6$ and T_{max} = (25.5×1.0) K, χ_{mole} (T_{max}) = 1.64×10^{-2} emu/mole we observe for both compounds additional well-marked features below T_{max} which we interpret as the actual onset of long-range antiferromagnetic ordering. Plotting the quantity d/dT $(T \chi_{mole})$ (Fig. 3) λ-shaped anomalies appear from which we obtain the transition temperatures T_c = (6.63 ± 0.05) K (Co Ta_2O_6) and T_c = (10.3 ± -0.2) K (Ni Ta_2O_6). Our values for T_c derived from the magnetic properties are in good accord with those found in preliminary specific heat
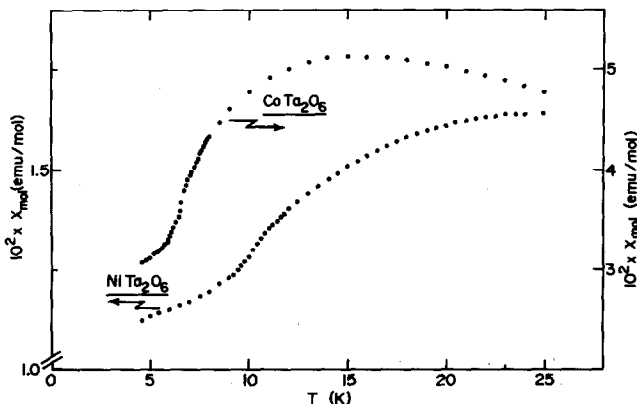

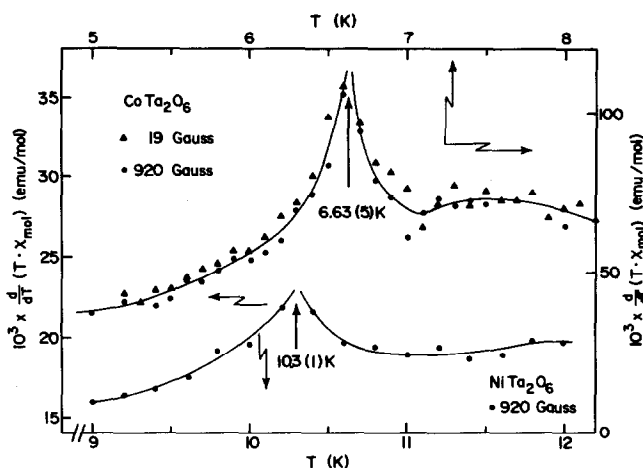FIG. 2. Low-temperature molar susceptibility χ_{mole} of $CoTa_2O_6$ and $NiTa_2O_6$ for B = 920 G.

FIG. 3. First temperature derivative d/dT $(T \chi_{mole})$ for $CoTa_2O_6$ and $NiTa_2O_6$. The solid lines are guides for the eye.

measurements showing sharp singularities at the quoted temperatures (5).

Following our results, the conclusion of previous workers (3) interpreting T_{max} as onset of long-range ordering cannot be maintained. On the contrary, we consider the broad maximum in χ_{mole} as an indication that in $MeTa_2O_6$ (Me = Co, Ni) short-range ordering is present well above T_c where the magnetic system finally undergoes long-range ordering. Similar conclusions were drawn for $FeTa_2O_6$ crystallizing in the trirutile type as well (5). This confirms the expectation stated earlier that low-dimensional magnetic lattice effects and associated short-range magnetic ordering are a feature of the trirutiles of the $MeTa_2O_6$ structure type. Apparently, this is due to the layered nature of their crystal structure which encourages stronger intralayer than interlayer exchange interactions.

Finally, we want to draw closer attention to Fig. 3. Fisher (6) pointed out that in the vicinity of T_c the quantity d/dT $(T \chi_{mole})$ is a close approximation to the magnetic contribution to the specific heat. Figure 3 therefore allows some general conclusions: The anomaly in the specific heat associated with

the transition to long-range order in both cases is very sharp and is therefore consistent with the X-ray results which show that chemical disordering of the magnetic ions is rather unlikely. From the height of the anomaly at T_c it appears that the entropy removal while undergoing long-range antiferromagnetic ordering is much lower for $NiTa_2O_6$ than it is for $CoTa_2O_6$. This might point to a marked difference in the spin-dimensionalities of both magnetic systems although the exact scaling factors between the susceptibility and the true specific heat are not known. This point is being investigated with quantitative specific heat measurements.

Summarizing, we found by investigating the low-temperature magnetic susceptibility of $CoTa_2O_6$ and $NiTa_2O_6$ that both compounds undergo long-range antiferromagnetic ordering at temperatures considerably lower than was concluded from previous works. The broad features in the susceptibility above T_c which were mistakenly associated with an antiferromagnetic transition originate from magnetic short-range ordering as a consequence of a reduced dimensionality of the magnetic lattice. A detailed

study of susceptibility and specific heat is near completion and will be published shortly (7). Chemical disorder of the divalent and pentavalent cations seems very unlikely. We have further shown that crystals of $CoTa_2O_6$ and $NiTa_2O_6$ can be grown by a chemical transport reaction using chlorine as transporting agent. We are presently varying the experimental conditions of the transport reaction to achieve a higher yield and better shaped crystal.

Acknowledgments

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