

Exchange interactions in antiferromagnetic complex perovskites

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Abstract

Magnetic interactions between Ni^{2+} spins in ordered complex perovskites, cubic Ba_2NiWO_6 and tetragonal Sr_2NiWO_6 , have been investigated. Analysis of the spin-wave excitation spectrum has shown that the 90° -interaction is substantially small compared with 180° -interaction at low temperatures. The results have remarkable resemblance to NiO. This would imply that the interactions between spins in these oxides should be discussed more carefully by taking the hybridization of $\text{Ni}3d$ – $\text{O}2p$ – $\text{W}5d$ and the spin structure into consideration. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Magnetic materials; A. Oxides; C. Neutron scattering; D. Magnetic properties

1. Introduction

Mixed metal oxides $\text{A}_2\text{Me}_1\text{Me}_2\text{O}_6$ with perovskite-related structure exhibit wide variety of structural, magnetic and transport properties [1–4]. Cubic Ba_2NiWO_6 (BNW) is among the simplest antiferromagnet in these complex perovskites [5]. Because of the large charge difference between Ni^{2+} and W^{6+} , almost complete ionic ordering of smaller Ni^{2+} and W^{6+} ions is realized. One of the interesting features in the ordered perovskite is that the magnetic properties are dominated by the long range (8.066 Å apart) superexchange interaction mediated along the chain Ni^{2+} – O^{2-} – W^{6+} – O^{2-} – Ni^{2+} . Direct exchange can be neglected because the distance between the nearest Ni^{2+} ions is as large as 5 Å. As Ni and W are ordered, Ni^{2+} ions form a face-centered lattice like NiO. It has been argued that so-called 90° -interaction (J_1) is not so weak as that in NiO, when compared with the 180° -interaction (J_2), because the superexchange interactions are always intervened by the diamagnetic W^{6+} [2,6]. Antiferromagnetic (AF) structure of BNW was determined by neutron diffraction to be of the second-kind (type-II) [7], which is similar to that of NiO. Since, however, detectable lattice distortion accompanied by the spin ordering of the type-II structure [8,9] has not been observed, J_1 cannot be large compared with J_2 . In order to see this contradictory situation from a viewpoint of magnetic excitation spectrum, measurements of spin-waves in single crystal samples have been carried out.

Another antiferromagnetic ordered perovskite Sr_2NiWO_6 (SNW), which is tetragonal below 520 K and cubic above

this temperature [6,10], has also been investigated. The spin ordering in SNW is considered to be the same type-II AF structure.

2. Experimental

Single crystal samples of BNW and SNW have been prepared for this study because measurements on single crystals are essential. Powdered materials were synthesized from a mixture of BaCO_3 (SrCO_3 for SNW), NiO and WO_3 at 1400°C . Single crystals were grown by the floating-zone method in air atmosphere from the sintered rods. The size of the crystals are 20–30 mm \times 6 mm \varnothing . Magnetic susceptibilities were measured with a SQUID magnetometer on powdered specimens in the temperature range from 5 to 300 K. From the susceptibility measurements, the Néel temperature T_N has been determined to be 48 and 54 K for BNW and SNW, respectively.

Inelastic scattering experiments were carried out using 4G triple-axis spectrometer of ISSP at JRR-3 M reactor of JAERI. Incident neutron energies, in some cases scattered neutron energies, were fixed to 13.7 or 30.0 meV, and the collimation of the spectrometer was $40'-20'-20'-40'$. The inelastic scans were made along the [100], [110], [111] and $[-111]$ directions at 10 K. Well-defined inelastic peaks of spin-wave excitation have been observed for all the directions. Although there exist broadenings or some structure in the peak at some q -positions, we cannot find any clear indication of the domain structure in BNW. Therefore, in other

Table 1

Transition temperatures, exchange and anisotropy parameters (in K) for three antiferromagnetic oxides. J_1 and J_2 (J_1^* and J_2^*) are the exchange parameters obtained from the spin-waves (from the molecular field expressions of T_N and Θ_A). $S = 1$ is assumed. $D_{1,2}$ in SNW have been fixed to zero because of large errors. D_1 has some correlation with J_1

	T_N, Θ_A	J_1^*, J_2^*	J_1, J_2	D_1, D_2
Ba_2NiWO_6	48, 120	-4.5, -6.0	$-0.11 \pm 0.16, -9.2 \pm 0.1$	$0.75 \pm 1.6, 0.0$ (fixed)
Sr_2NiWO_6	54, -188	-8.4, -6.8	$-0.14 \pm 0.44, -10.5 \pm 0.5$	0.0 (fixed), 0.0 (fixed)
NiO [13,14]	523, -1310	-50, -85	8, -110	0.6, 0.03

words, all the domains are practically identical and the Brillouin zones can be simplified. J_1, J_2 , the in-plane and out-of-plane anisotropy (D_1 and D_2 , respectively) have been determined by fitting the spin-wave dispersion calculated for the type-II AF structure to the observation. The results are summarized in Table 1. When the lowering of the lattice symmetry is significant in the type-II AF structure, the twelve nearest neighbor sites should be split into two groups [11]. In our case, however, the lattice distortion is not detectable, we use the single J_1 . Fig. 1 shows examples of the measured and fitted dispersion relations.

In the type-II AF structure, contribution of J_1 should clearly be seen in the spin-wave energy along the [111] and $[-111]$ directions, even if the sample is a monodomain crystal. The excitation energy difference at $q_{A1} = (-1/4, 1/4, 1/4)$ and $q_{A2} = (1/4, 1/4, 1/4)$ can be calculated as $(\hbar\omega_{A1})^2 - (\hbar\omega_{A2})^2 \approx (2S)^2 48J_1(J_1 + J_2)$. (Terms of D_1 and D_2 have been dropped.) Almost the same energies at q_{A1} and q_{A2} clearly demonstrate the smallness of J_1 in BNW. Although further analysis is required for tetragonal SNW, features of the spin-waves [12] are essentially the same as in BNW.

It is of some interest to compare the exchange interactions

with those obtained from T_N and the asymptotic Curie temperature Θ_A . From the susceptibility data above T_N and with the use of the molecular field expressions for T_N and Θ_A , J_1 and J_2 are calculated as listed in Table 1.

It should be emphasized that the magnetic properties of BNW and SNW have striking resemblance to that in NiO. In NiO the lattice distortion is small and the splitting of the dispersion due to the domain structure is not so clear and, as is well known, J_1 is ferromagnetic and much smaller than J_2 at low temperatures [14]. On the contrary, the high temperature susceptibilities always give significant negative J_1 and smaller J_2 than that obtained from the spin-waves. Although the molecular field approximation would not be accurate enough to obtain reliable parameter at high temperatures, the remarkable similarity between these oxides strongly suggests the same underlying mechanism of the interaction.

3. Discussion

The measurements of the spin-wave excitation have confirmed that the 90° -interaction in BNW and SNW is much smaller than the 180° -interaction at low temperatures,

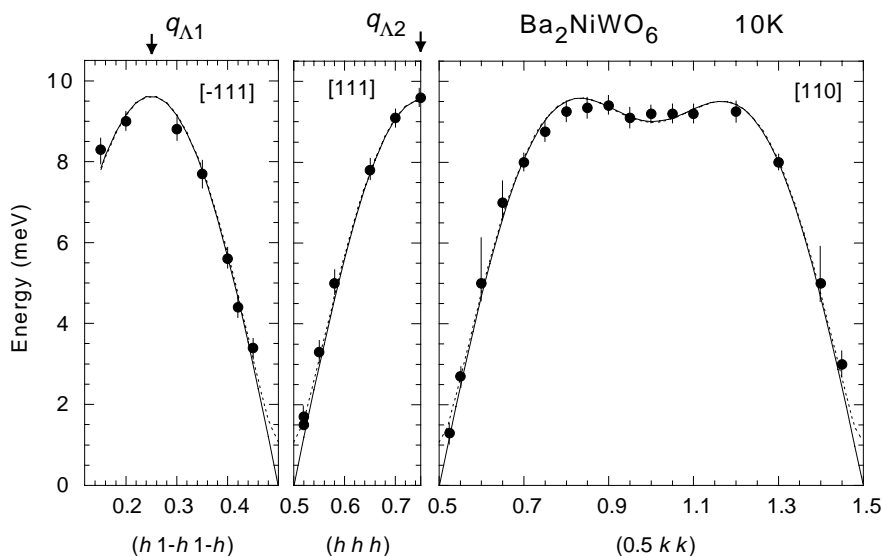


Fig. 1. Examples of measured and fitted dispersion relations. The lines show the calculated dispersion relations.

in spite of the intervention of the diamagnetic W^{6+} . The results substantiate the striking similarity between BNW and NiO. Here, considering this similarity, we put a conjecture on the smallness of J_1 in BNW.

Recently, the important role of O2p in the transition metal oxides has widely been recognized [15–18]. In the case of NiO, it has been suggested that the hybridization of Ni3d orbitals with O2p cannot be neglected. In addition, band calculations of ReO_3 [19] and cubic WO_3 [20] have suggested the covalent nature of the bonding of W5d and O2p; in the octahedral configuration of WO_6 unit in BNW, as in cubic WO_3 , the O2p orbitals seem to mix strongly with W5d. Apparently, this covalent nature corresponds to surprisingly high T_N in BNW and SNW in spite of the very long path of magnetic interaction. Recent studies of the superexchange in NiO [15] have shown that, contrary to the conventional interpretation, the smallness (and ferromagnetic nature) of J_1 can be attributed to the p–d mixing and that the covalent interaction should be dependent on the relative angle of spins. It should be noted that the situation is essentially the same in BNW. If the discussions for NiO are applied to BNW, it is probable that the mixing of W5d and O2p is affected by the spin ordering. Of course the paramagnetic state of BNW is not metallic, but some difference in the spin correlation and in the magnetic interaction would be possible as suggested by the difference in the exchange parameters obtained from the high temperature susceptibilities. Interestingly, at the tetragonal–cubic transition temperature (523 K) in SNW, apparent anomaly in the paramagnetic susceptibility is accompanied [6]. As this structural transition is not of the ferroelectric origin, a substantial magnetic contribution can be expected. Further detailed studies are desirable in order to understand the nature of the magnetic interaction. We also note that these complex perovskites are suited for this study because the energy scale of the spin excitation is much smaller than the monoxides.

Acknowledgements

The author would like to thank Prof H. Yoshizawa for support of the neutron scattering experiments on 4G-TAS, to Prof A. Itoh for help of single crystal preparation, and to Prof J. Akimitsu for help of magnetization measurements. This work was supported by a Grant-in-Aid from the Ministry of Education, Science, Culture and Sports of Japan.

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