Solid State Communications Vol. 3, pp. 327-330, 1965. Pergamon Press Ltd. Printed in Great Britain.

MAGNETIC SUSCEPTIBILITIES OF SOME 3d TRANSITION METAL BORACITES

Hans Schmid, Harry Rieder and Edgar Ascher

Institut Battelle, Centre de recherche, 7, route de Drize, Genève, Switzerland.

(Received 31 July 1965 by B.G. Busch)

Effective magneton numbers and Curie-Weiss temperatures of eleven 3d-metal boracites have been determined from susceptibility versus temperature measurements. All investigated boracites display negative Curie-Weiss temperatures. Cr-I- and Ni-I-boracites become anti-ferromagnetic at about 90° and 120°K, respectively. Ni-I-boracite shows an anomalous peak of susceptibility at about 60°K which coincides with the temperature of the simultaneous onset of ferro-electricity and weak ferromagnetism.

Introduction

RECENTLY we have reported that nickel-chlorine-boracite, $Ni_3B_7O_{13}Cl$, is a paramagnetic ferro-electric[1]. Other 3d-metal boracites with the general formula $Me_3B_7O_{13}X$ (Me = a bivalent metal and X = Cl, Br or I) were expected to display also ferro-electricity and furthermore, at low temperatures, a magnetic order. We therefore measured the magnetic susceptibility of several 3d-transition metal boracites with a view to finding out the range of coexisting magnetic order and ferro-electricity wherein magneto-electric interactions might occur.

Nearly all known boracites have a high and a low temperature modification. So far the structures have been determined only for the high and the low temperature phases of the natural Mg-Cl-boracite, the result being the space groups T_d^5 and C_{2V}^5, respectively[2]. Sonine and Zheludev[3] have shown that this transition is not of the ferro-electric type. It will be shown[7] that the two groups T_d^5 and C_{2V}^5 cannot correspond to the type of transformation described in reference (2). Contrary to what is stated there, C_{2V}^5 is not a subgroup of T_d^5. Although the essential features of the structure determined in reference (2) are certainly correct, this is probably not the case for the low temperature symmetry C_{2V}^5.

We have measured the magnetic susceptibility of the boracites Cr-I, Mn-I, Fe-Cl, Fe-I, Co-Cl, Co-Br, Co-I, Ni-Cl, Ni-Br, Ni-I and Cu-Br with the Faraday method at H=2 700 Oe from 80°K upwards, Ni-I and Cr-I also down to about 10°K. The samples were prepared from powdered single crystals, and pseudo single crystals, which were obtained stoichiometrically by gas phase transport reactions[4]. Mohr's salt was used as a calibrating substance.

Results

At more or less high temperatures, all of the boracites obey a Curie-Weiss law, $\chi = C/(T-\theta)$, with negative asymptotic Curie-Weiss temperatures (see Figs. 1a, 1b and Table 1). Thus anti-ferromagnetic coupling at sufficiently low temperatures is to be expected.

The magnetic moments, as determined from the straight parts of the curve in the Curie-Weiss region, are all higher than the spin-only values, but of the same order of magnitude as the highest experimental values known for the Me^{2+} ions in question (see e.g. (6)).

Some of the compounds (Ni-Cl-, Ni-Br-, Co-Cl- and Co-Br- boracite) show kinks in their $1/\chi - T$ - curves which may be related to their phase transitions. The transition temperatures are marked with an arrow in the figures.

Cr-I and Ni-I showed the highes asymptotic Curie-temperatures of those investigated; relatively high magnetic transition temperatures were therefore to be expected for these compounds.

TABLE 1

Effective magnetic moments and the Curie-Weiss temperatures θ (°K) of some boracites.

Boracite	n_{eff} (B.M.) experimental $= \sqrt{8\,C_M}$	spin-only $\sqrt{4S(S+1)}$ (B.M.)	Highest experim. n_{eff} values of Me^{++} ions (7)	Curie-Weiss temperature (°K)	Extrapolation temperatures (°K) T_1	T_2
$Fe_3B_7O_{13}Cl$	5.77	4.9	5.88	- 37	80	710
$Co_3B_7O_{13}Cl$	5.61	3.87	5.6	- 85	400	660
$Ni_3B_7O_{13}Cl$	4.13	2.83	4.7	- 108	500	720
$Co_3B_7O_{13}Br$	5.32	3.87	5.6	- 10	360	800
$Ni_3B_7O_{13}Br$	4.14	2.83	4.7	- 133	460	910
$Cu_3B_7O_{13}Br$	2.05	1.73	2.0	- 35	80	490
$Cr_3B_7O_{13}I$	(5.55)*	4.9	5.1	(- 302)*	190	300
$Mn_3B_7O_{13}I$	(6.13)*	5.92	5.94	(- 88)*	80	300
$Fe_3B_7O_{13}I$	(6.16)*	3.87	5.88	(- 130)*	80	300
$Co_3B_7O_{13}I$	5.15	3.87	5.6	- 25	300	925
$Ni_3B_7O_{13}I$	4.15	2.83	4.7	- 325	300	900

*The Bohr magneton numbers in parentheses must be considered as too high because of the too narrow temperature range used for extrapolation.

Furthermore, on nickel-iodine-boracite a phase transition was detected optically at about 60°K which was supposed to be a para-electric/ferro-electric one. Consequently this compound appeared of particular interest, since the same order of magnitude of a ferro-electric and magnetic transition temperature would mean the existence of both magnetic and ferro-electric mobile domains. We have measured the susceptibility of Ni-I- and Cr-I- boracite also below 80°K (see Fig. 1a): Cr-I- boracite has a smeared maximum of χ at about 90°K, but no discontinuity below this temperature (at least down to 10°K). The same sort of maximum can be observed with Ni-I- boracite at about 120°K, but for this compound an additional anomalous peak is observed at about 60°K.

Discussion

We believe that the smooth maxima of the two compounds are related to the onset of antiferromagnetic coupling. As reported elsewhere[5], the acute maximum of χ of Ni-I- boracite coincides with the simultaneous onset of a weak ferromagnetism and of ferro-electricity. Since there appears a ferromagnetic moment, the sudden rise of susceptibility at 60°K can be understood.

Cr-I-boracite does not become ferro-electric in the antiferromagnetic range, at least not above ~ 10°K, and the susceptibility characteristic and optical studies in polarized light do not indicate the appearance of weak ferromagnetism in this region. It is therefore

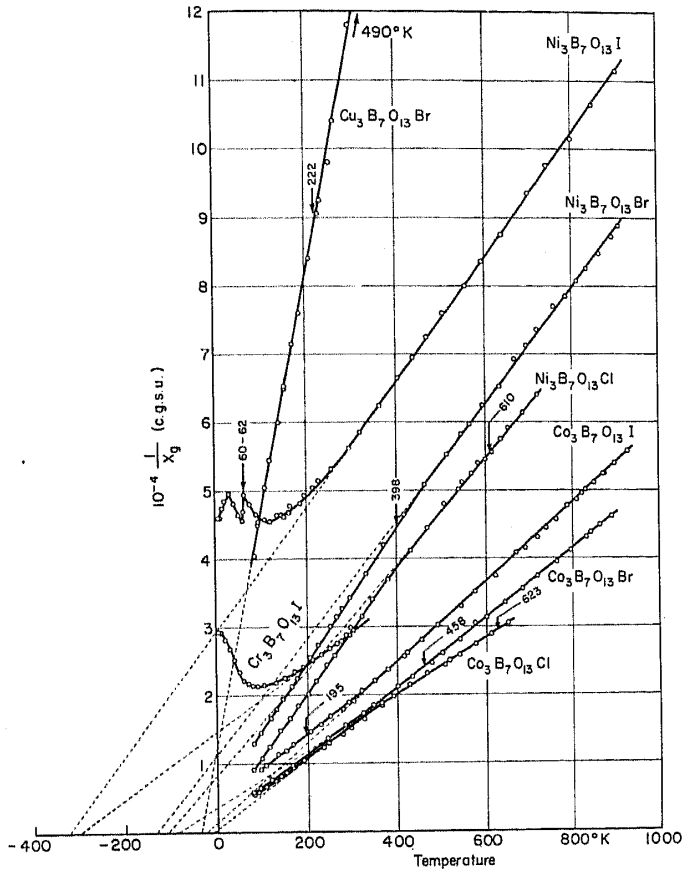

Fig. 1 a

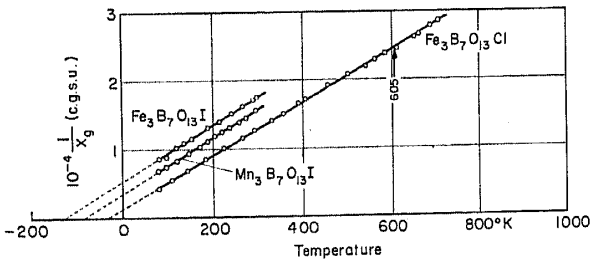

Fig. 1 b

Reciprocal gram susceptibility versus temperature of some transition metal boracites.

highly probable that the appearance of the weak ferromagnetism in Ni-I-boracite is caused by an interaction of the emerging electric polarization with the antiferromagnetic matrix.

Below about 30°K, the susceptibility of Ni-I rises again. This behavious is not yet understood but may indicate a change in magnetic order.

Conclusions

From the results gained on Ni-I- boracite it can be expected that also in boracites with ferro-electric transition temperatures higher than the Néel temperatures, and with equal crystallographic and magnetic symmetries, weak ferromagnetism will appear at the Néel temperature.

Acknowledgement - We acknowledge the support of the Centre National d'Etudes des Télécommunications, Paris, Issy-les-Moulineaux, for the initial stages of this investigation.

References

1. ASCHER E., SCHMID H., and TAR D., Solid State Comm. 2, 45 (1964).
2. ITO T., MORIMOTO N., and SADANAGA R., Acta Cryst. 4, 340 (1951).
3. SONINE A.S., and ZHELUDEV I.S., Kristallografiya 8, 183 (1963).
4. SCHMID H., J. Phys. Chem. Solids 26, 973 (1965).
5. To appear.
6. GOODENOUGH G.B., Magnetism and the Chemical Bond, Interscience Publishers, p. 98, (1963).
7. ASCHER E., to appear.

Au moyen de mesures de susceptibilité magnétique, les magnétons de Bohr effectifs et les températures de Curie-Weiss ont été déterminés pour onze boracites de métaux 3d. Toutes les boracites considérées montrent des températures Curie-Weiss négatives. Les boracites de Cr-I et de Ni-I deviennent antiferromagnétiques respectivement à 90° et à 120°K. La boracite de Ni-I déploie un pic anomal de la susceptibilité à environ 60°K et qui coincide avec la température de l'apparition simultanée de ferro-électricité et de ferromagnétisme faible.