Inorg. Chem. **1980**, *19*, 2179–2180

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Chemical Control of Superconductivity in the Hexaborides

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Received November 27, 1979

The metal hexaborides MB_6 are particularly interesting for study of the chemical control of superconductivity. The structure is a very rigid one, containing a simple cubic array of M atoms in a covalently bonded boron-atom network.[1] The unit cell, describable as a cube with octahedra of boron atoms at the corners and a metal atom M in the body center, corresponds to two electron hole states per B_6 unit with two electrons from each atom needed to fill the holes.[2] If M is divalent as with Ca, the $M^{II}B_6$ is nonmetallic; if M is trivalent as with some rare earth elements, the third valence electron goes into the conduction band and $M^{III}B_6$ is metallic. Because of the rigidity of the covalently bonded boron network, the MB_6 structure is not expected to deform much when divalent M^{II} is gradually replaced by trivalent M^{III} or vice versa. Hence, by varying the ratio M^{II}/M^{III}, the conduction electron density can be manipulated; by choosing M to be magnetic, the interaction of conduction electrons with magnetic dipoles can be investigated.

Of special interest is lanthanum hexaboride, LaB_6. Studies of its Fermi surface, band structure, generalized magnetic susceptibility, and electron–phonon coupling indicate large enhancement factors and hence superconducting transition temperatures between 27 and 61 K.[3] Surprisingly, the measured T_c, even on high purity single crystals, is only 0.12 K.[3]

Sobczak and Sienko,[4] by studying very pure LaB_6 and also the effect of magnetic impurities on the critical temperature of YB_6, the only reasonable superconductor of the hexaborides, found that the probable reason for the very low critical temperature of LaB_6 is a small magnetic moment coming from the lanthanum itself. The present investigation was undertaken to try to reduce this moment by partly replacing the boron by beryllium or the lanthanum by calcium. To get more complete information on the superconductivity of the hexaborides, we also explored the effect on T_c of $Y_{1-x}M_xB_6$, where M is a divalent or tetravalent nonmagnetic metal.

Experimental Section

Samples were prepared by heating appropriate oxide mixtures with boron at 1700 °C. Starting materials were 99.999% La_2O_3, 99.9999% Y_2O_3, and 99.99% Yb_2O_3 from United Mineral, 99.95% ThO_2, 99.999% B powder, and 99.5% Be powder from Alfa Inorganics, and CaO from General Chemical Co. Starting materials appropriate to the reaction $RE_2O_3 + 15B \rightarrow 2REB_6 + {}^3/_2B_2O_2$ were carefully mixed, pressed into pellets, and sintered in an rf induction furnace using ZrB_2 crucibles at a temperature of ~1700 °C. The pressure in the reaction tube was typically 10^{-5} torr. Usually the cooled samples were reground and reheated. Analysis of the samples was by atomic absorption spectroscopy by the Analytical Facility of the Materials Science Center. Lattice parameters were determined by X-ray powder diffraction with Cu Kα radiation.

The determination of the superconducting critical temperature was done by a flux expulsion method as described elsewhere.[5] The magnetic susceptibility measurements were performed on a Faraday balance with Spectrosil quartz buckets and Cahn Electrobalance recording.[6]

Table I

sample	lattice parameter, Å (±0.001 Å)	sample	lattice parameter, Å (±0.001 Å)
YB_6	4.0994	$Y_{0.70}Th_{0.30}B_6$	4.1023
$Y_{0.96}Yb_{0.04}B_6$	4.1012	$Y_{0.41}Th_{0.59}B_6$	4.1051
$Y_{0.91}Yb_{0.09}B_6$	4.1036	$Y_{0.35}Th_{0.65}B_6$	4.1057
$Y_{0.84}Yb_{0.16}B_6$	4.1063	$Y_{0.28}Th_{0.72}B_6$	4.1062
$Y_{0.72}Yb_{0.28}B_6$	4.1121	ThB_6	4.1099
YbB_6	4.1450	$Y_{0.85}Ca_{0.15}B_6$	4.1069
$Y_{0.88}Th_{0.12}B_6$	4.1009	CaB_6	4.1575

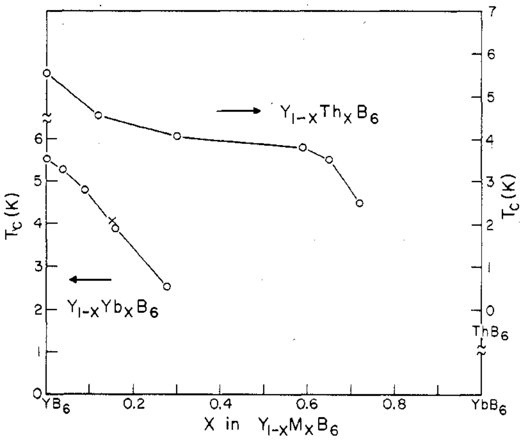

Figure 1. Superconducting critical temperature T_c vs. composition in series $Y_{1-x}Yb_xB_6$ and $Y_{1-x}Th_xB_6$. The × point on the lower curve corresponds to $Y_{0.85}Ca_{0.15}B_6$. Note shift of temperature scale to separate the plots.

Results and Discussion

The magnetic moment that arises at low temperatures in LaB_6 could not be accounted for by the analyzed trace iron impurities, so it was suggested that a small amount of La^{2+} or a certain fraction of f electrons belonging to the lanthanum as a whole was responsible. Chemical doping with divalent elements seemed to be a possible way to reduce the electron pressure in the structure and hence reduce this magnetic moment. Accordingly, samples were produced with compositions $La(B_{1-x}Be_x)_6$ ($x \leq 0.3$) and $La_{1-x}Ca_xB_6$ ($x \leq 0.5$). For the beryllium-doped samples, the lattice parameter increased with x, confirming that Be replaces B rather than La. (The latter possibility was taken into account, as there exists a BeB_6.[7] However, in such case there would have been a decreasing lattice parameter.) None of the samples was observed to be superconducting down to the lowest temperature (1.5 K) we could reach. Either the doping does not help to reduce the magnetic moment or there is an additional effect that quenches the superconductivity.

Given that YB_6 readily superconducts below about 6 K and given that the replacement of La for Y rapidly decreases the superconducting critical temperature,[8] we investigated the influence on the T_c of substituting for Y either Yb or Th, neither of which has a magnetic moment.

Ytterbium is known to be in the 2+ state in the hexaboride. YbB_6 behaves like a semiconductor, and Hall measurements confirm a low current-carrier density.[7] On the assumption of

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a closed f shell (Yb^{2+}, $4f^{14}$, $^1S_0$), no magnetic moment should be involved. Several samples of $Y_{1-x}Yb_xB_6$ ($x \leq 0.3$) were produced. Lattice parameters, which are listed in Table I, show that Vegard's law is closely obeyed. Figure 1 shows that the corresponding T_c drops almost linearly with concentration.

Since thorium is typically Th^{4+} ($5f^0$, $^1S_0$), it also should show no magnetic moment. Table I gives the observed lattice parameters for $Y_{1-x}Th_xB_6$ ($x \leq 0.7$). Again Vegard's law is followed but with somewhat slower lattice expansion. Figure 1 shows the dependence of T_c on concentration. At low Th doping in $Y_{1-x}Th_xB_6$, the T_c drops linearly with almost the same slope as if Yb had been added, but then the T_c levels out until about 60% replacement of Y, whereupon it again drops more rapidly.

Magnetic susceptibilities of several of the samples were measured over the range 1.5–300 K. In the case of $Y_{0.6}Th_{0.4}B_6$ the susceptibility is diamagnetic ($\chi_g = -0.12 \times 10^{-6}$) and remains at this value down to 6 K. This is almost exactly what we calculate for the diamagnetic cores plus the Pauli paramagnetism of the electron gas. Clearly the thorium has no localized moment. In the case of $Y_{0.84}Yb_{0.16}B_6$, the room-temperature susceptibility is again diamagnetic (observed $\chi_g = -0.16 \times 10^{-6}$ compared to calculated -0.23×10^{-6}) but there is a pronounced Curie tail below 100 K leading eventually to a paramagnetism of $\chi_g = +1.28 \times 10^{-6}$ at 4 K. Similar behavior is observed for $Y_{0.72}Yb_{0.28}B_6$. Chemical analysis of the samples showed that the temperature-dependent susceptibility could not be due to Fe impurities, as the amount of Fe could not account quantitatively for the observed susceptibility and in any case the samples with less impurity showed a higher paramagnetism. Hence, we concluded that the observed paramagnetic moment of $Y_{1-x}Yb_xB_6$ arises from partial occurrence of the ytterbium as Yb^{3+} ($4f^{13}$, $^2F_{7/2}$) rather than Yb^{2+} ($4f^{14}$, $^1S_0$). Yb^{3+} has a moment of 4.54 μ_B, so less than 1% of it would have been enough to account for our observations.

Comparison of the T_c vs. x data for $Y_{1-x}M_xB_6$ where M = Yb, Th, or La shows that in all three cases the decrease is linear with the same slope in the concentration range $0 \leq x \leq 0.2$. A sample of $Y_{0.85}Ca_{0.15}B_6$ was also made and measured; it also fits the same line.

The nonstoichiometry range of $Y_{1-x}B_6$[9] is coincident with the above concentration range, so it might be that the observed decrease of T_c in this region is a stoichiometry effect such as is observed in carbide and nitride systems.[10] However, the divergence of the curves at higher concentrations has to be blamed on the rising magnetic moment in the $Y_{1-x}Yb_xB_6$ system just as occurs in $Y_{1-x}Ce_xB_6$[4] and in $Y_{1-x}La_xB_6$.[8] Nevertheless, in the $Y_{1-x}Th_xB_6$ system no magnetic moments are involved. Therefore, the following conclusion is arrived at: Band filling in YB_6 is such that the Fermi energy coincides with a maximum in the density of states curve. Replacing trivalent Y by a divalent metal or a tetravalent metal leads to a lower density of states as the Fermi energy falls or rises, respectively. Hence, T_c generally falls. Additional magnetic effects lower the T_c even more rapidly.

Acknowledgment. This research was sponsored by the Air Force Office of Scientific Research under Grant No. 80-0009 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University. We are also grateful to the Council for International Exchange of Scholars for award of a Fulbright travel grant to Kurt Hiebl.

Registry No. YB_6, 12008-32-1; YbB_6, 12008-33-2; ThB_6, 12229-63-9; CaB_6, 12007-99-7.

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Redetermination of the Structure of $MoO_2(S_2CN(C_2H_5)_2)_2$: Confirmation of the Usual MoO_2^{2+} Geometry

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Received November 7, 1979

Recent EXAFS studies[1,2] indicate that the Mo atoms in the oxidized (Mo(VI)) forms of xanthine oxidase[1] and sulfite oxidase[2] are coordinated by oxygen atoms at approximately 1.7 Å. These results have led to an increased interest in the structural chemistry of oxomolybdenum(VI) species.[3,6] A large number of structures of this type have been published.[4,5] With the exception of the recently reported complex $MoO_2(SC(CH_3)_2CH_2NHCH_3)_2$,[6] the dioxomolybdenum compounds have distorted octahedral geometries with the oxo groups cis to each other. Generally, the Mo=O distances are between 1.68 and 1.72 Å with the O=Mo=O angles ranging from 102 to 108°.

The structure of $MoO_2(S_2CN(C_2H_5)_2)_2$, originally reported in 1972, appears to be substantially inconsistent with similar structures with regard to the reported Mo=O distances (1.634 (25) Å) and O=Mo=O angle (114.0 (20)°).[7] Despite the fact that the uncertainty about the accuracy of this structure had been noted,[5,8] it has continued to be cited in the literature for comparison with other dioxomolybdenum(VI) complexes.[9] We report here a redetermination of this structure which reveals that the structure of $MoO_2(S_2CN(C_2H_5)_2)_2$ is, in fact, completely consistent with similar structures and has Mo=O distances of 1.703 (2) Å and an O=Mo=O angle of 105.61 (12)°.

Experimental Section

The compound was prepared by the method of Moore and Larson.[10] Large, well-formed orange crystals were grown from hot toluene. A relatively small hexagonal rod (0.15 × 0.15 × 0.20 mm) was mounted on a glass fiber for X-ray diffraction studies. The diffraction experiments were performed on a Syntex $P2_1$ diffractometer using Mo Kα radiation. Fifteen reflections chosen from a rotation photograph were used to determine preliminary cell parameters which were found to be essentially identical with those originally reported.[7] Least-squares refinement of the setting angles for 15 reflections with $15° < 2\theta < 20°$ yielded the monoclinic cell dimensions $a = 17.350$ (6) Å, $b = 8.662$ (2) Å, $c = 13.575$ (3) Å, and $\beta = 124.61$ (2)°. There are four molecules in the unit cell. All reflections of the form $+h, +k, \pm l$ with $3° < 2\theta < 60°$ were collected by using the θ–2θ scan method. Three standard reflections were monitored every 60 reflections, and no significant variations in intensity were observed. The data were processed as described previously.[11] An analytical absorption cor-

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(6) The coordination geometry of this complex is best described as skew trapezoidal bipyramidal. There are no donor atoms trans to the oxo groups. The average Mo=O distance is 1.717 (6) Å and the O=Mo=O angle is 122.2 (3)°: Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.*, in press.

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