

⁵⁷Fe Mössbauer study of some $M_2(M')B_2$ borides

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METAL borides of the form $M_2(M')B_2$ where M represents a molybdenum or tungsten atom and M' is a 3d transition metal atom have been studied by Mössbauer transmission spectroscopy. Two crystal systems of these ternary borides occur[1]. Mo_2FeB_2 has a tetragonal unit cell; W_2FeB_2 is orthorhombic. In general, the $M_2(M')B_2$ borides have the cementite lattice structure with M atoms forming tetrahedral layers, the edges of the tetrahedra forming interstitial spaces of triangular prisms between coincident M layers, forming isolated pairs. M' atoms are thought to enter preferentially the closely-cubic (5 per cent tetragonal distortion) interstices [2]. The environment of the M' atoms should therefore be similar to that of the ordered CsCl structure.

The borides $Mo_2(Fe_{1-x}Co_x)B_2$ with $x = 0.0, 0.2, 0.3, 0.8$, and W_2FeB_2 were prepared by direct melting and homogenized by vacuum annealing. These intermetallics have the typical hard, brittle character of borides. The X-ray lattice parameters for Mo_2FeB_2 were determined as $a = 6.115\text{\AA}$ and $c = 3.433\text{\AA}$, somewhat larger than previous results [3]. A trace of the monoboride phase MoB was detected in the powder pattern. The X-ray of the orthorhombic W_2FeB_2 revealed very weak lines from WB and W_2B impurity phases. Mössbauer absorbers were prepared from 325 mesh powders. Data was accumulated in a 1024 channel analyzer with typically 200 K total counts stored per channel.

The 300 K Mössbauer spectrum of Mo_2FeB_2 is a single Lorentzian line. Its narrow width (0.32 mm/sec) indicates that all the iron atoms are at equivalent sites. Hence the preferential ordering of the iron in the cubic interstices

is apparent. The low temperature Mössbauer data displays magnetic hyperfine structure with a 173 K ordering temperature and a small internal saturation (4.2 K) field H_{sat} of 86 kOe. In spite of the small internal field, the six resonance lines are well defined below 100 K. The existence of this hyperfine splitting in Mo_2FeB_2 is a sensitive demonstration of spontaneous atomic magnetic order. If one assumes the hyperfine field is proportional to the magnetic moment on the Fe atom, then $\mu(Fe) = 0.59\mu_B$. The reduced internal field H_{int} vs T data is shown in Fig. 2 together with Brillouin curves. Weak absorption lines from ordered iron ($H_{int} = 330$ kOe) are noticeable in the background, with intensity 0.03 that of the Mo_2FeB_2 spectrum. The pure Fe is not detected in the X-ray analysis; Fe diffraction lines may be diffuse due to the crushing process.

Additional mixed $Mo_2(Fe_{1-x}Co_x)B_2$ boride absorbers were prepared to test the extent of magnetic order. Replacing 20 at.% of the Fe by Co lowers the ordering temperature significantly to 110 K with no change in H_{sat} . The ordering point for 30 at.% Co falls linearly to 79 K with $H_{sat} = 75$ kOe. This insensitivity of H_{sat} to iron concentration implies that the Fe atoms are well screened by the Mo matrix.

The sample $Mo_2(Fe_{0.2}Co_{0.8})B_2$ has the orthorhombic structure. Absorbers of both this phase and W_2FeB_2 give single asymmetric lines at 300 K. The two compounds do not show resolved hyperfine structure, but between 300 and 4.2 K the respective resonance lines broaden: $Mo_2(Fe_{0.2}Co_{0.8})B_2$ (0.37 \rightarrow 0.5 mm/sec) and W_2FeB_2 (0.6 \rightarrow 1.2 mm/sec). This broadening may arise from several sources:

(a) Occurrence of spontaneous magnetic order with a small saturation field (18–25 kOe in the case of W_2FeB_2).

(b) Superimposed spectra from the impurity phases if they contain iron.

(c) The Fe atoms may be positioned on both M and M' sites. Then the observed

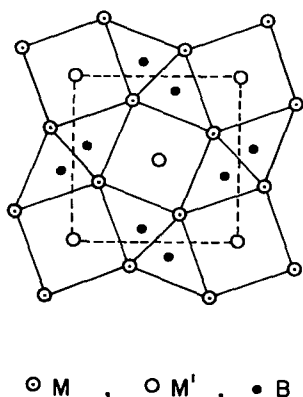


Fig. 1. $M_2(M')B_2$ structure viewed along the c axis. The M' and B atoms lie on planes midway between layers of M atoms. The dotted square outlines the unit cell.

broadening could arise from isomer shifts and quadrupole coupling at the two inequivalent sites.

The chemically ordered Fe atoms in $M_2(M')B_2$ borides have eight M near neighbors, just as Fe impurities have when substituted into the pure b.c.c. Mo and W metals. Mössbauer studies of such dilute alloys with 300 ppm Fe give saturation fields of 115 kOe for FeMo and 76 kOe for FeW[4, 5]. Ordering in the borides is presumably ferromagnetic as in the alloys. The alloy-boride correspondence indicates that the W_2FeB_2 broadening is probably due to spontaneous magnetic order, though one would expect to find a larger hyperfine field.

The isomer shifts with respect to sodium nitroprusside of these five borides are all positive (0.24 mm/sec), similar to many other borides. Hence in general the electron density at the Fe nucleus decreases in the presence of boron.

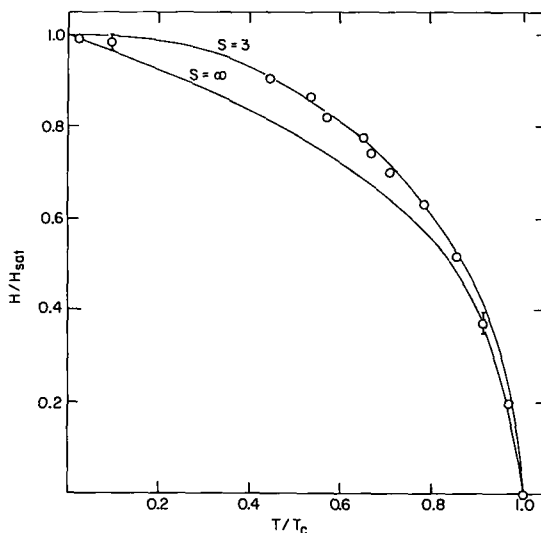


Fig. 2. Reduced hyperfine field H/H_{sat} , vs reduced temperature, T/T_c , for ^{57}Fe in Mo_2FeB_2 , with $T_c = 173$ K and $H_{sat} = 86$ kOe. The solid curves are Brillouin functions for $S = 3$ and $S = \infty$.

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Ames Laboratory-USAEC
and Department of Physics,
Iowa State University,
Ames,
Iowa 50010,
U. S. A.

D. B. DE YOUNG
R. G. BARNES

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