

Low Temperature Heat Capacities of Transition Metal Borides

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Low temperature heat capacities from 1.5 to 15 K have been measured for a number of transition metal borides with the compositions Me_2B , MeB and MeB_2 , and their solid solutions. The measurements show that the borides are characterized by a narrow d-band with a relatively large density of electron states. The variation of γ with position of the transition metal in the Periodic Table for the borides is considerably different from that of the transition metals and solid solutions. This result suggests considerable differences in the shapes of the respective band structures. There is evidence for an electron transfer from the boron atoms to the d-bands of the transition metal.

Introduction

Transition metal borides form an interesting class of compounds which are characterized by relatively high melting points and metallic-like properties. Several of the borides are ferromagnetic and in many ways the magnetic behavior of the borides resemble those of the transition series. Transition metals and boron form a large number of intermetallic compounds with chemical formulas ranging from Me_4B to MeB_{12} . The crystal structures of these phases are unusual in that the apparent interactions between boron atoms change systematically with the progression from the Me_4B to MeB_{12} phases. In the metal-rich compounds the boron atoms are essentially isolated from one another, in the monoborides the boron atoms are arranged along one dimensional zig-zag chains, in the diborides the boron atoms form two dimensional layers and in the hexa and dodecaborides three dimensional boron structures exist with isolated metal atoms. The diborides studied here all crystallize in the hexagonal AlB_2 structure (C32). The monoborides occur with three structures: the orthorhombic CrB (B_f) and FeB (B27) and the tetragonal MoB type. The half-borides all have the tetragonal CuAl_2 structure (C16).

Information about the bonding or band structure in borides is scarce. The complexity of the crystal chemistry makes theoretical calculations of the band

structure difficult and no attempts at such calculations have been reported to date. Most of the information about borides is based upon correlations of their physical properties with those of the pure transition series. On the basis of these correlations a number of authors¹⁻⁴ have suggested that boron acts as an electron donor. UBBELOHDE⁵ was the first to propose this theory which is commonly referred to as the electron transfer theory. It assumes that the band structure of the transition metal remains approximately the same as boron enters the lattice to form the compound. The boron atoms donate electrons to the d bands of the transition metal and thus the position of the Fermi level rises over its position in the metal. There is little net ionic component to the transfer since the spatial distribution of the d-like wave functions overlaps the position of the boron atom. There is, however, little general agreement on the number of boron atoms transferred per boron atom with the number necessary to correlate various properties varying from one to three^{2, 4}.

Comparison of the Hall coefficients⁴, melting points and electrical resistivities² of the borides with those of the transition metals lends experimental support to the theory. The most convincing support, however, is the comparison of the magnetic behavior. The monoborides from $(\text{Cr}, \text{Mn})\text{B}$ to CoB and the half-borides from $(\text{Mn}, \text{Fe})_2\text{B}$ to $(\text{Co}, \text{Ni})_2\text{B}$ are ferromagnetic. The comprehensive studies of

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CADÉVILLE and DANIEL⁶ show that borides have a magnetization versus composition curve analogous to the Slater-Pauling magnetization curve for the transition metals. Many of the fine details of the Slater-Pauling curve are reproduced in the analogous system. The curve for the borides is shifted in composition, however, so that the peak in the curve occurs at MnB instead of at $\text{Fe}_{10}\text{Co}_3$ and ferromagnetism disappears at CoB instead of at Ni_6Cu_4 . The two curves can be made to nearly coincide if one assumes that each boron atom contributes between 1.7 and 1.8 electrons to the d bands formed by the metal atoms.

Cadéville and Daniel suggest that low temperature heat capacity studies could be used to test certain assumptions of the electron transfer theory. The electronic specific heat coefficient, γ , is proportional to the density of states at the Fermi level, N_γ , and if the rigid band hypothesis is assumed, then a graph of γ versus composition for the borides should qualitatively map out the band structure. While γ is proportional to N_γ , it is not a true measure of the band structure density of states $N(0)$ because of electron-phonon and electron-electron interactions. These interactions will differ in the pure transition series and in the borides. Nevertheless, a plot of γ versus compositions should delineate the position of the d bands, and thus a comparison of the boride band structure with that for selected transition metals is possible.

Here we report on low temperature heat capacities of several borides from groups V to VIII. Previously we reported on measurements on groups IV to VI⁷. These studies, together with the results of other research groups, allow a qualitative mapping of the band structure for the borides.

Experimental

The boride samples were prepared by powder metallurgy techniques. The size of the samples was typically 3/4 in. dia. by 1 in. high. High purity metal and boron powders, 200–400 mesh, were thoroughly mixed and cold pressed into cylindrical pellets. See Table 1 for a list of purities of the starting materials. These

Starting Material	Nominal Purity
V	99.7
Nb	99.9
Ta	99.9
Cr	99.9, 99.999
Mn	99.99
Fe	99.9
Co	99.9
B	99.5

Table 1.
Nominal Purities
of Starting Materials.

pellets were then inserted into close fitting graphite crucibles and capped with a graphite piston. The graphite assembly was then inserted into an induction heated hot-press and surrounded by an inert atmosphere of argon. The samples were reacted and homogenized at temperatures slightly less than their melting points, typically at 1300–1600 °C. At these temperatures the samples were kept under pressure for approximately 1.5 hours. The outer surface of the sample which was in contact with the graphite was removed by grinding. X-ray diffraction patterns were taken from several parts of the sample to check the structure, determine the lattice parameters and to insure that the samples were homogeneous.

The calorimeter used in these studies was the same as described previously⁸. The measurements were typically from 1.2 to 15 K. Because of the porosity of the powder metallurgy samples, a mechanical heat switch was used to cool and adiabatically isolate the sample.

Experimental Results

Table 2 lists the chemical compositions, crystal structures and lattice parameters of the samples used in the present studies. All of the lattice parameters are in close agreement with the generally accepted values⁹.

Figures 1–5 show the low temperature heat capacities for the borides measured in this work plotted in the form C_p/T versus T^2 . The data are given in the form of one gram atom of metal atom; this convention has become the customary way of reporting the heat capacities of the interstitial compounds although a number of investigators prefer to use the convention one gram atom of solution¹⁰. The use of the former convention is preferable here, we believe, because it allows a direct comparison with the γ values for the pure transition series.

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Table 2. Lattice parameters and crystal structures of phases studied. Literature values were taken from PEARSON⁹.

Compound	Structure	Lattice Parameter	
		Present Work	Literature Value
V ₃ B ₂	D 5a	<i>a</i> = 5.724 <i>c</i> = 3.030	<i>a</i> = 5.728 <i>c</i> = 3.026
VB	B _f	<i>a</i> = 3.059 <i>b</i> = 8.046 <i>c</i> = 2.971	<i>a</i> = 3.058 <i>b</i> = 8.043 <i>c</i> = 2.971
V _{.8} Cr _{.2} B	B _f	<i>a</i> = 3.042 <i>b</i> = 8.005 <i>c</i> = 2.961	—
V _{.6} Cr _{.4} B	B _f	<i>a</i> = 3.023 <i>b</i> = 7.967 <i>c</i> = 2.950	—
V _{.4} Cr _{.6} B	B _f	<i>a</i> = 3.006 <i>b</i> = 7.929 <i>c</i> = 2.942	—
V _{.2} Cr _{.8} B	B _f	<i>a</i> = 2.984 <i>b</i> = 7.884 <i>c</i> = 2.932	—
CrB	B _f	<i>a</i> = 2.967 <i>b</i> = 7.853 <i>c</i> = 2.927	<i>a</i> = 2.969 <i>b</i> = 7.858 <i>c</i> = 2.927
Mn _{.75} Fe _{.25} B	B 27	<i>a</i> = 4.125 <i>b</i> = 5.553 <i>c</i> = 2.968	—
Mn _{.5} Fe _{.5} B	B 27	<i>a</i> = 4.104 <i>b</i> = 5.532 <i>c</i> = 2.961	—
Mn _{.2} Fe _{.8} B	B 27	<i>a</i> = 4.043 <i>b</i> = 5.521 <i>c</i> = 2.951	—
FeB	B 27	<i>a</i> = 4.038 <i>b</i> = 5.493 <i>c</i> = 2.952	<i>a</i> = 4.053 <i>b</i> = 5.495 <i>c</i> = 2.946
Fe _{.75} Co _{.25} B	B 27	<i>a</i> = 4.038 <i>b</i> = 5.422 <i>c</i> = 2.963	—
TaB	B _f	<i>a</i> = 3.279 <i>b</i> = 8.670 <i>c</i> = 3.155	<i>a</i> = 3.276 <i>b</i> = 8.669 <i>c</i> = 3.157
VB ₂	C 32	<i>a</i> = 2.990 <i>c</i> = 3.054	<i>a</i> = 2.991 <i>c</i> = 3.050
CrB ₂	C 32	<i>a</i> = 2.972 <i>c</i> = 3.069	<i>a</i> = 2.969 <i>c</i> = 3.066
NbB ₂	C 32	<i>a</i> = 3.112 <i>c</i> = 3.255	<i>a</i> = 3.112 <i>c</i> = 3.264
TaB ₂	C 32	<i>a</i> = 3.096 <i>c</i> = 3.224	<i>a</i> = 3.097 <i>c</i> = 3.225

Most of the C_p data can be fitted to a two parameter equation:

$$C_p = \gamma T + A T^3. \quad (1)$$

The addition of higher order terms in the expansion of the phonon contribution does not seem to be necessary, probably because these compounds have high Debye temperatures. The borides VB₂ and CrB₂ exhibited an anomalous heat capacity in which the functional form is

$$C_p = \alpha + \gamma T + A T^3 \quad (2)$$

where α is a constant. The appearance of the constant term in the heat capacity is not new; it has been observed in a large number of alloy systems¹¹⁻¹⁴, even boride systems^{15,16}, and has been treated theoretically several times¹⁷⁻¹⁹. Figure 3 shows anomalous heat capacities in CrB₂ and in Cr_{.4}V_{.6}B₂. The constant term is sensitive to metallurgical variables; several samples of CrB₂ were prepared with less pure starting materials and the magnitude of the constant term changed by about 15%. The γ and A terms also changed slightly. The presence of a magnetic field of 11.5 kG did not significantly alter the heat capacities of these samples. Since, as we will discuss later, the anomaly is probably due to magnetic impurities, we point out that the same starting materials were used in the preparation of the V₃B₂, VB and Cr_xV_{1-x}B solid solutions and that no anomalies were present in any of these alloys.

Tables 3-6 list the γ and Θ_D values for the borides studied here as well as those reported previously. All γ values are based on one gram atom of transition metal. The Debye temperatures are also reported using the same convention: Θ_D is obtained with the formula

$$\Theta_D = \left(\frac{234 N_A k_B}{A} \right)^{1/3} \quad (3)$$

where N_A is Avogadro's number and A is the slope ($(d(C_p/T)/d(T^2))$) of the straight lines in Figures 1-5.

Whenever interstitial compounds are involved one has to be careful about the interpretation of Θ_D . There are several experimental means of obtaining Θ_D including heat capacities and elastic constant measurements. When comparing literature

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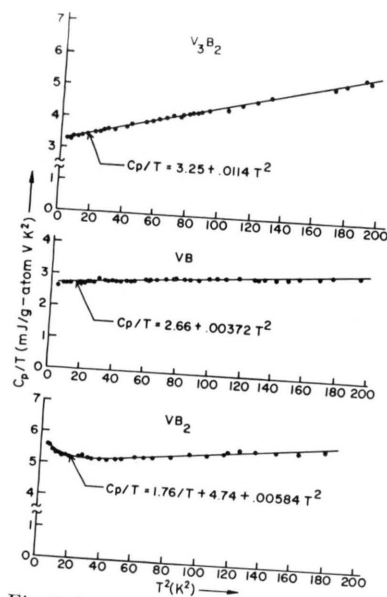


Fig. 1. Low temperature specific heats of V_3B_2 , VB and VB_2 .

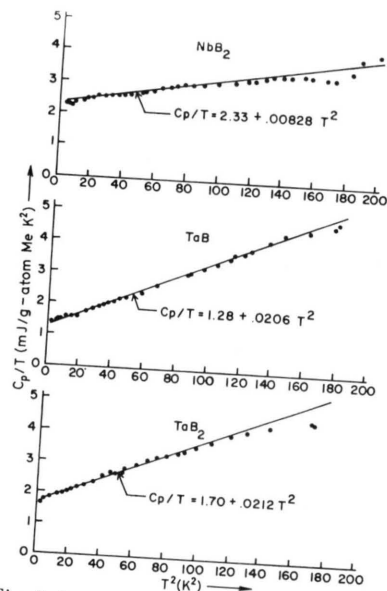


Fig. 2. Low temperature specific heats of NbB_2 , TaB and TaB_2 .

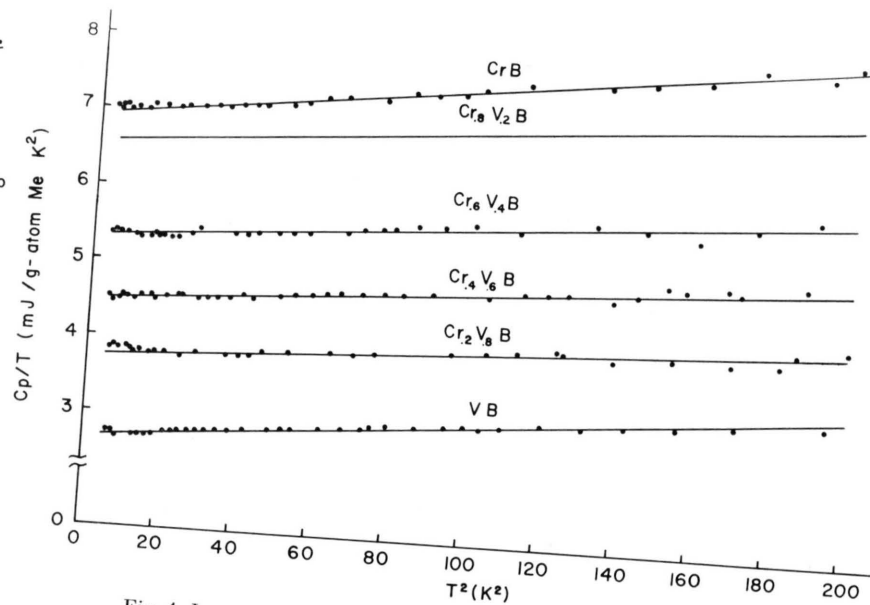


Fig. 4. Low temperature specific heats of the $Cr_xV_{1-x}B$ system.

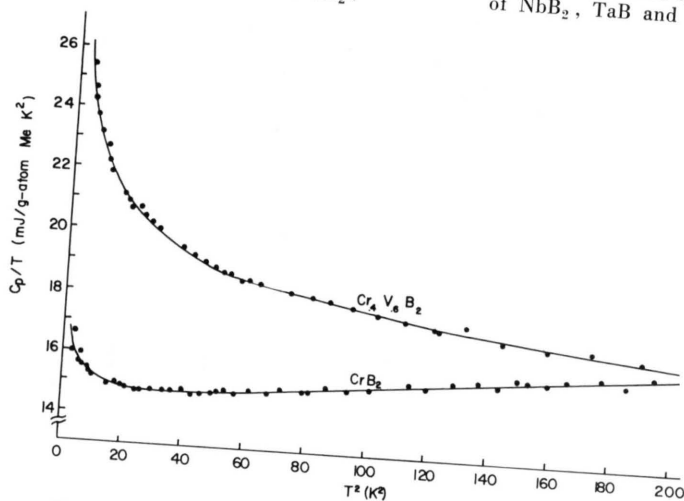


Fig. 3. Low temperature specific heats of CrB_2 and $Cr_4V_6B_2$.

Fig. 5. Low temperature specific heats of FeB , $Fe_{.75}Co_{.25}B$ and the $Mn_xFe_{1-x}B$ system.

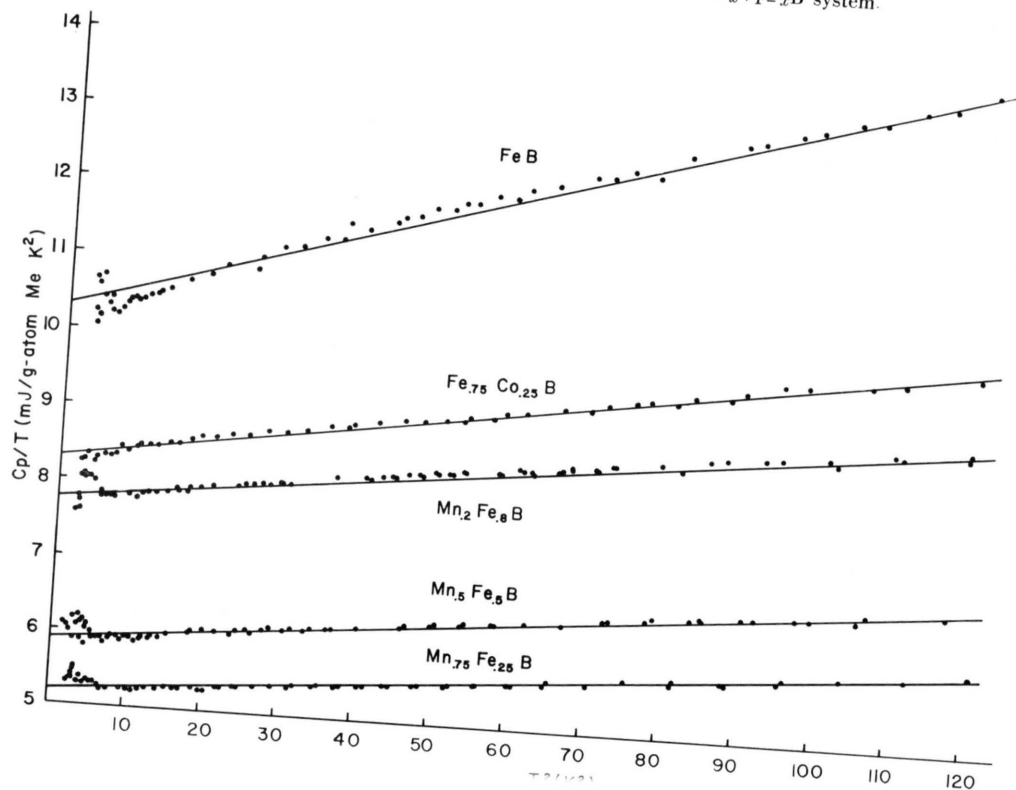


Table 3. γ and Θ_D values for half borides.

Composition	Structure	γ (mJ/g-atom Me K ²)	θ_D [K]	Reference
Cr ₂ B	CuAl ₂	5.75	515	16
Mn ₂ B	CuAl ₂	6.88	320	16
(Mn _{0.0} Fe _{1.0}) ₂ B	CuAl ₂	10.50	327	16
(Mn _{0.4} Fe _{0.6}) ₂ B	CuAl ₂	19.60	362	16
(Mn _{0.2} Fe _{0.8}) ₂ B	CuAl ₂	9.94	340	16
(Mn _{0.1} Fe _{0.9}) ₂ B	CuAl ₂	8.21	362	16
Fe ₂ B	CuAl ₂	5.32	300	16
(Fe _{0.7} Co _{0.3}) ₂ B	CuAl ₂	6.20	394	16
(Fe _{0.5} Co _{0.5}) ₂ B	CuAl ₂	6.67	386	16
(Fe _{0.3} Co _{0.7}) ₂ B	CuAl ₂	7.98	432	16
(Fe _{0.15} Co _{0.85}) ₂ B	CuAl ₂	9.66	414	16
Co ₂ B	CuAl ₂	6.70	270	16
(Co _{0.0} Ni _{1.0}) ₂ B	CuAl ₂	11.40	346	16
(Co _{0.8} Ni _{0.2}) ₂ B	CuAl ₂	14.10	348	16
(Co _{0.55} Ni _{0.45}) ₂ B	CuAl ₂	19.00	222	16
(Co _{0.5} Ni _{0.5}) ₂ B	CuAl ₂	19.60	262	16
(Co _{0.45} Ni _{0.55}) ₂ B	CuAl ₂	17.70	288	16
(Co _{0.3} Ni _{0.7}) ₂ B	CuAl ₂	1.99	383	16
Ni ₂ B	CuAl ₂	1.95	700	16
Mo ₂ B	CuAl ₂	4.26	478	7
Ta ₂ B	CuAl ₂	2.88	328	7
W ₂ B	CuAl ₂	2.60	373	7

Table 4. γ and Θ_D values for monoborides.

Composition	Structure	γ (mJ/g-atom Me K ²)	θ_D (K)	Reference
TiB	FeB	2.96	662	7
VB	CrB	2.66	805	23
V _{0.8} Cr _{0.2} B	CrB	3.75	890	27
V _{0.6} Cr _{0.4} B	CrB	4.49	858	27
V _{0.4} Cr _{0.6} B	CrB	5.34	839	27
V _{0.2} Cr _{0.8} B	CrB	6.55	805	27
CrB	CrB	6.91	697	23
MnB	FeB	5.48	356	24
Mn _{0.75} Fe _{0.25} B	FeB	5.18	645	27
Mn _{0.5} Fe _{0.5} B	FeB	5.86	602	27
Mn _{0.2} Fe _{0.8} B	FeB	7.75	562	27
FeB	FeB	10.30	403	27
FeB	FeB	10.33	332	25
FeB	FeB	10.30	—	15
Fe _{0.75} Co _{0.25} B	FeB	8.3	510	27
Fe _{0.7} Co _{0.3} B	FeB	8.08	—	15
Fe _{0.55} Co _{0.45} B	FeB	7.57	—	15
Fe _{0.3} Co _{0.7} B	FeB	7.16	—	15
Fe _{0.15} Co _{0.85} B	FeB	15.2	—	15
Fe _{0.1} Co _{0.9} B	FeB	21.2	—	15
CoB	FeB	0.66	696	26
NbB	CrB	1.39	566	7
MoB	MoB	2.32	553	7
TaB	CrB	1.28	467	23
WB	MoB	2.12	351	7

Table 5. γ and Θ_D values for diborides.

Composition	Structure	γ (mJ/g-atom Me K ²)	θ_D (K)	Reference
ScB ₂	AlB ₂	2.2	550	21
Sc _{0.5} Ti _{0.5} B ₂	AlB ₂	1.78	735	21
TiB ₂	AlB ₂	1.40	807	7
TiB ₂	AlB ₂	1.08	820	21
Ti _{0.5} V _{0.5} B ₂	AlB ₂	2.97	850	21
VB ₂	AlB ₂	4.84	850	21
VB ₂	AlB ₂	4.74	693	23
CrB ₂	AlB ₂	13.7	570	23
CrB ₂	AlB ₂	13.6	545	20
Cr _{0.5} Mn _{0.5} B ₂	AlB ₂	14.9	530	20
MnB ₂	AlB ₂	4.45	540	20
MnB ₂	AlB ₂	2.8	632	24
ZrB ₂	AlB ₂	0.93	585	7
Zr _{0.75} Nb _{0.25} B ₂	AlB ₂	1.32	614	22
NbB ₂	AlB ₂	2.33	617	23
MoB ₂	AlB ₂	3.38	534	7
HfB ₂	AlB ₂	1.0	499	7
TaB ₂	AlB ₂	1.70	452	23

Table 6. γ and Θ_D values for other borides.

Composition	Structure	γ (mJ/g-atom Me K ²)	θ_D (K)	Reference
Co ₃ B	Fe ₃ C	7.05	345	26
Co _{0.28} B _{0.02}	hcp	4.48	345	26
Pd B _{0.0325}	fcc	7.25	268	28
Pd B _{0.057}	fcc	5.80	264	28
Pd B _{0.108}	fcc	4.56	258	28
V ₃ B ₂	tetragonal	3.27	545	23

values for Θ_D 's obtained from different techniques, one finds large discrepancies that cannot be explained by the experimental error. The reason for the discrepancy is that different conventions have been adopted for calculating Θ_D from the experimental data. The convention associated with elastic constant measurements assumes that Θ_D is computed as if the interstitial compound were a solid-solution alloy. The convention associated with heat capacities is to compute Θ_D on the basis of one gm-atom of transition metal atom. To obtain agreement between the two conventions Θ_D in Eq. (3) should be calculated with a $((dC_p/T)/d(T^2))$ value for a gm-atom of solution. We have discussed this problem previously and suggested that Θ_D be calculated on the basis of one gm-atom of solution¹⁰. We do *not* follow this suggestion here, however, be-

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²² Y. S. TYAN, unpublished.

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²⁷ Present work.

²⁸ M. MAHNIG and L. E. TOTH, Phys. Letters A 32, 319 [1970].

cause all previous Θ_D values for borides are reported in the old convention and the change might result in more confusion.

Discussion

A) Transfer Theory

In Figs. 6–8 we have plotted the results given in Tables 3–5 of the γ values versus composition for each boride class. The data for the curve in Fig. 6 for the half-borides was originally presented by KUENTZLER¹⁶. Smooth curves have been drawn through the individual γ values. The gaps in the monoboride curve (Fig. 7) between TiB and VB, and also between CrB and MnB correspond to crystal structure changes and little mutual solubility. Therefore, the existence of a major peak in γ between groups 6 and 7 could not be confirmed.

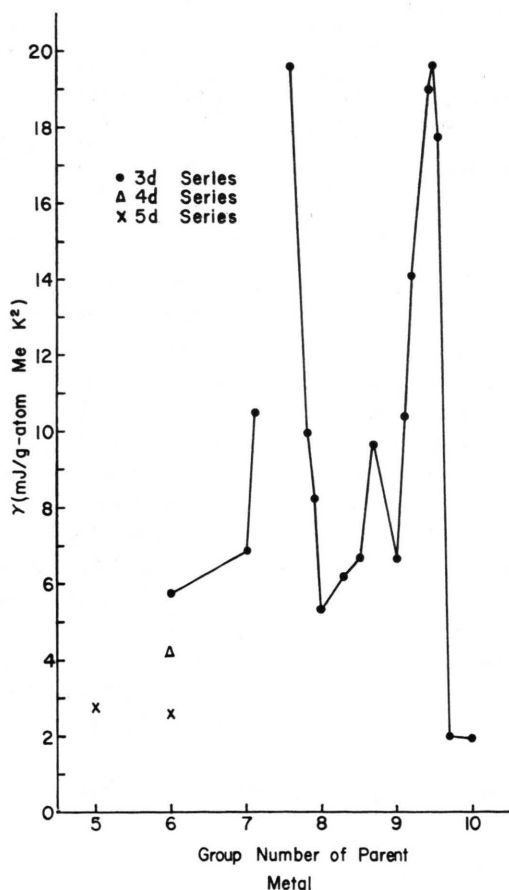


Fig. 6. γ versus group number of the parent metal for the half-borides.

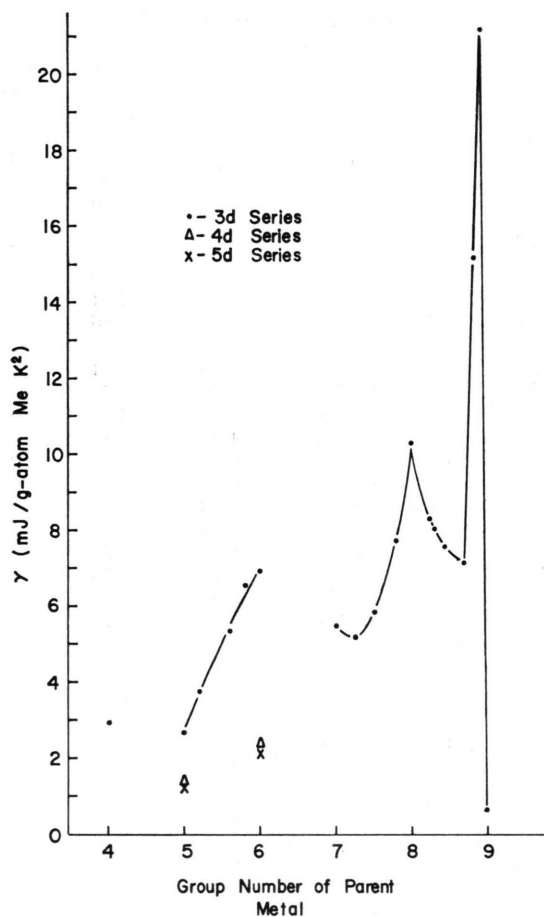


Fig. 7. γ versus group number of the parent metal for the monoborides.

Since γ is roughly proportional to the density of states at the Fermi level, the curves give a qualitative indication of the band structure of the borides. The γ values are, of course, enhanced by electron-phonon interactions and possibly by spin fluctuations. These enhancements can vary with position in the Periodic Table. The observed γ values are typical of metals with their Fermi levels within a d band.

As can be seen by comparing Figs. 6 and 7, the band structures of the half-borides and monoborides are similar, although the peaks are shifted with respect to the group number of the transition metal. The similarity of the band structure is paralleled by the similarity found in the magnetization versus composition curves for these two classes of borides. Both the half-borides and the monoborides have a Slater-Pauling type magnetization curve⁶. The compositions which correspond to the maxima in the

curves are shifted with respect to each other by the same amount as in the γ curves.

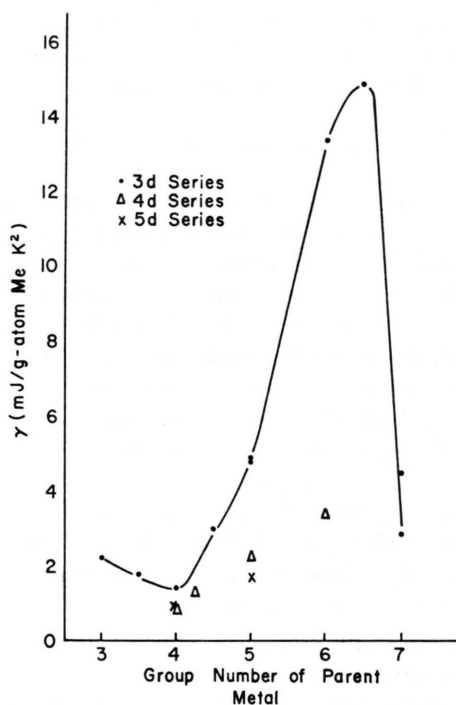


Fig. 8. γ versus group number of the parent metal for the diborides.

The γ versus composition curve for the 3-d diborides (Fig. 8) is considerably different from those of the half-borides and monoborides, showing only one broad maximum. There are, however, fewer experimental points.

In Fig. 9 we have superimposed the γ versus composition curves for the 3-d borides on a similar curve for the 3-d elements and solid solutions²⁰. The curves for the borides have been shifted in composition by an amount corresponding to a transfer of 1.75 electrons from each boron atom to the d-bands. To simplify the discussion of Fig. 9, we will use electrons/atom ratio, e/a , in place of composition. Therefore, e/a for the borides will be the group number of the transition metal plus 1.75 electrons per boron atom in the formula (i.e. e/a for $\text{CrB} = 7.75$, for $\text{Fe}_2\text{B} = 8.875$).

The comparison of the γ versus e/a curves for the various boride classes shown in Fig. 9 shows one common feature of all four curves. Each curve falls abruptly to a low value of γ at approximately the same electron concentration: $(\text{Co}_3\text{Ni}_{1.7})_2\text{B}$ for the half-borides, CoB for the monoborides and MnB_2 for the diborides. The abrupt fall of the γ values may be interpreted as signifying the end of the d band. In general, however, the half-boride, monoboride and diboride curves show little similarity

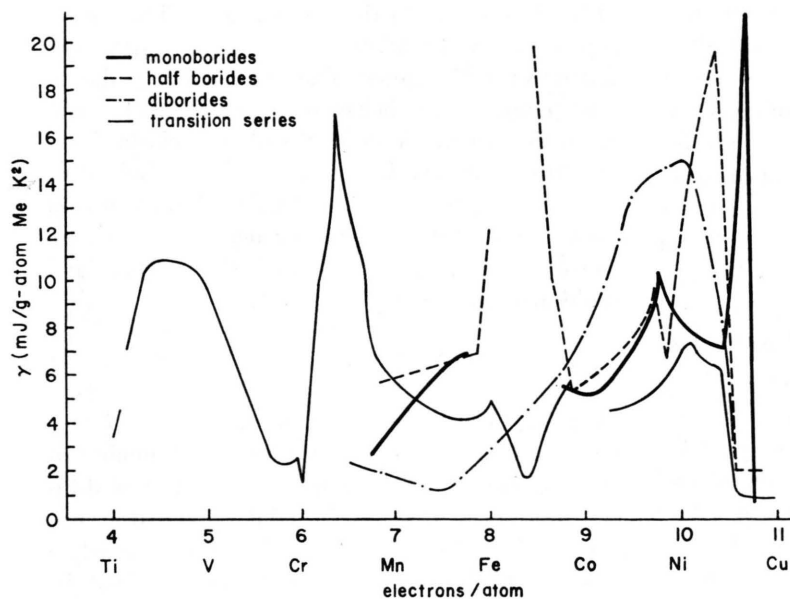


Fig. 9. Comparison of γ versus " e/a " for the half-borides, monoborides, diborides and transition metals and solid solutions. The γ curves for the borides are shifted by an amount corresponding to a transfer from the boron to the d bands of 1.75 electrons per boron atom.

²⁰ F. HEINIGER, E. BUCHER, and J. MÜLLER, Phys. Kondens. Materie 5, 243 [1966].

to the curve for the transition metals and solid solutions. This result refutes one basic hypothesis of the electron transfer theory, the assumption that the band structures of the 3-d borides are similar to that of the 3-d transition metals. There is little similarity between the band structures of the 3-d borides and that of the 3-d transition metals.

If one basic assumption of the electron transfer theory is incorrect, how then can it so simply and successfully account for the existence of the Slater-Pauling curves for the half-borides and monoborides which are analogous to those of the transition metal series? The Slater-Pauling curves, at least the portion where the magnetization decreases linearly with increasing composition and where the similarity between boride curves and transition metal curve is best, reflect only the filling of the upper half-band. No information is given about the shape of the band. Thus, the Slater-Pauling curve supports only the second assumption of the electron transfer theory, that the electrons are transferred from the boron atoms to the d bands. Although there is good agreement in the decreasing portion of the Slater-Pauling curves of the half-borides, monoborides and transition metals, the maxima of the half-boride and monoboride curves are displaced from the maximum of the transition metal curve. This displacement would seem to indicate that the relative position of the half bands changes as one goes from a transition metal or solid solution to a half-boride or monoboride. The maximum in the Slater-Pauling curve occurs at a composition of $\text{Fe}_{0.7}\text{Co}_{0.3}$ for the transition metals, at Fe_2B for the half-borides and at MnB for the monoborides. These maxima correspond to an e/a ratio of 8.3 for the transition metals, 8.88 for the half-borides and 8.75 for the monoborides. While the maxima of the half-borides and the monoborides are in fairly good agreement with each other, they are displaced by approximately .5 electrons from the maximum of the transition metals. This change in relative position of the half bands in the borides lends further support to our proposal that there is little similarity between the band structure of the borides and that of the transition metals.

Thus we can draw two conclusions about the electron transfer theory: (1) there is little similarity between the band structure of the various classes of

borides and that of the transition elements and solid solutions, and (2) the boron atoms contribute electrons to the d bands. While a transfer of 1.75 electrons results in the correct electron concentration for the end of the band, the degree of transfer may differ according to the transition element.

B) Anomalous Heat Capacities

There are a number of interesting and different features about the anomalous heat capacities in VB_2 , CrB_2 and $(\text{V}_{0.6}\text{Cr}_{0.4})\text{B}_2$. Similar heat capacities have been found in binary solutions of transition elements, which contain 5–80 at % of a ferromagnetic element. The anomaly appears to occur near critical concentrations for ferromagnetism and it is sensitive to metallurgical treatments. The anomalies in the borides are different because they occur in pure binary compounds. While VB_2 and CrB_2 may be near in composition to the onset of ferromagnetism, because of the type of electron transfer discussed above, CrB_2 is known to be antiferromagnetic with a Neel temperature of about 80 K²¹.

Two types of theories have been offered to explain the anomaly. One theory is a many-body calculation which treats interactions between d-electrons and persistent spin fluctuations whose lifetimes increase as the critical concentration for ferromagnetism is approached¹⁷. This calculation leads to a term $(T/T_S)^3 \ln(T/T_S)$ in the heat capacity. The second approach, by SCHRÖDER¹⁸ and by HAHN and WOHLFARTH¹⁹, suggests that the anomaly is due to superparamagnetic behavior of very small ferromagnetic clusters. Associated with each cluster is an anisotropy energy, $E_A = kT_A$. As heat is added to the specimen, the direction of magnetization in each cluster is altered in a manner dependent upon an anisotropy energy. In the limit $T \ll T_A$, Hahn and Wohlfarth show that

$$\frac{\alpha(T)}{Nk} = 1 + \beta(T/T_A) + 0(T/T_A)^2 \quad (4)$$

where $\alpha(T)$ corresponds to α in Eq. (2), β is a numerical constant of order 1, N is the number of clusters and k is Boltzmann's constant. It is difficult to estimate T_A , but it is of the order of tens of degrees. Thus in the limit $T \ll T_A$, $\alpha(T)$ is nearly a constant. In the analysis of the data we find that the constant term gives a much better least squares fit than the $(T/T_S)^3 \ln(T/T_S)$ term.

The constant term α is a direct measure of the number of clusters N or $\alpha = Nk$. For CrB_2 , $N = 3.6 \cdot 10^{20}$ clusters/mole- CrB_2 . Further the moment on each cluster can be determined by measuring the magnetization as a function of field. TYAN²² found for these samples $dM/dH = 1.1 \cdot 10^{-3}$ cm/mole at 4.2 K which corresponds to about 240 Bohr magnetons per cluster. If we assume that the clusters are due entirely to iron impurity atoms, each with 2.2 aligned spins, then we calculate that 110 Fe atoms are in each cluster and that the needed impurity concentration is 50,000 ppm. This is an unreasonable result since it is far greater than the results of chemical and neutron activation analysis. Furthermore, no anomalies were observed in the other Cr and V borides prepared in the same manner from the same material.

Thus, if we are to retain the notion of the cluster model, it is necessary to propose a new type of cluster other than those caused by impurities. These

would result primarily from a random fluctuation of localized boron concentration in the diboride. The diborides are known to exist over a range of compositions, in contrast to the more metallic borides, which have narrower composition ranges. Thus it is possible that boron-poor and boron-rich regions coexist in the diborides. These regions coupled with small impurity concentrations of ferromagnetic elements could result in a spontaneous magnetization and account for the anomaly. Presently we are preparing samples with different impurity concentrations to determine the effect on the anomaly and the magnetization and we will report on these results at a later date.

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Vibration Spectra and Debye Temperatures of Some Transition Metals

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The lattice vibration spectra and the associated constant volume specific heats of the transition metals niobium, tantalum, chromium, and palladium have been determined by using Sharma and Joshi's three-force constant model which includes the effect of electrons on lattice vibrations in metals. The calculated values of the specific heats and the equivalent Debye temperatures are compared with available calorimetric data. The frequency versus wave vector dispersion relations along the three major symmetry directions of chromium and palladium are determined and compared with curves deduced from recent neutron scattering experiments. Reasonably satisfactory agreement between theory and experiment is obtained.

I. Introduction

With the development of inelastic neutron scattering technique, in recent years a considerable amount of work has been devoted to the study of lattice vibrations in transition metals by measuring the frequency versus wave vector dispersion relations along the symmetry directions¹. This has

stimulated much interest in their thermodynamic properties, in particular the lattice specific heat. During the last few years, a number of models² have been worked out for calculating the phonon frequencies of metals by taking cognizance of electrons as a compressible gas. One of the authors (P. K. S.) and JOSHI^{3, 4} have propounded a successful theory of this type by considering the volume

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¹ B. N. BROCKHOUSE, in: Phonons in Perfect Lattices and in Lattices with Point Imperfections, edit. by R. W. H. STEVENSON, Oliver & Boyd, Edinburgh 1966, p. 110.

² J. DE LAUNAY, in: Solid State Physics, edited by F. SEITZ and D. TURNBULL, Academic Press, Inc., New York 1956, Vol. 2, p. 220.

³ P. K. SHARMA and S. K. JOSHI, J. Chem. Phys. 39, 2633 [1963].

⁴ P. K. SHARMA and S. K. JOSHI, J. Chem. Phys. 40, 662 [1964].