Journal of Solid State Chemistry **154**, 114–129 (2000)
doi:10.1006/jssc.2000.8821, available online at http://www.idealibrary.com on IDEAL®

Chemical and Superconducting Properties of the Quaternary Borocarbides *Ln*–*M*–B–C (*Ln* = rare earths, Y; *M* = Ni, Pd)

E. Tominez,* E. Alleno,* P. Berger,† M. Bohn,‡ Chandan Mazumdar,* and C. Godart*

LCMTR, UPR209, CNRS, 2–8 rue Henri Dunant, 94320 Thiais, France; †LPS, CEA, CNRS, CEN, Saclay, 91191 Gif/Yvette Cedex, France; and ‡IFREMER de Brest, BP70, 29280 Plouzanec, France

Received September 9, 1999; in revised form January 18, 2000; accepted January 30, 2000

We present a status report on the quaternary rare-earth transition metal borocarbides. We discuss in particular the superconducting and magnetic properties of $LnNi_2B_2C$ (Ln = rare earths, Y) in connection with sample preparation and composition. We also report new results on the analysis of the chemical composition of the superconducting phase at 23 K in the Y–Pd–B–C system, using electron microprobe and, for the first time in these materials, nuclear microprobe. We will briefly comment on new borocarbides and other related systems.

INTRODUCTION

Superconducting Materials

Superconductivity was first observed experimentally by K. Onnes when he was studying the resistance of Hg at low temperature ($T_c \sim 4.15$ K) way back in 1911 (1). Since then, the field of superconductivity has witnessed a considerable progress. Among the elements, Nb was found to have the highest T_c (~ 9.25 K) under normal pressure (2). However, under application of pressure of 200 kbar, La metal exhibits superconductivity at as high as 12.9 K (2). Many binary and ternary intermetallic compounds were also found to exhibit superconductivity; some with even higher T_c values. Among the binary intermetallics, Nb_3Ge, in thin film form, exhibits a record transition temperature of 23.2 K, whereas the record for bulk intermetallic material is only 20.3 K for Nb_3Ga (2). Since as a general trend binary materials were found to have T_c higher than values those of elements, it was hoped that the ternary compounds may exhibit even higher T_c. Moreover as the possible number of ternary compounds outnumbers the binaries in a great way, the probability of finding ternary compounds with higher T_c enhances greatly. However, the highest T_c known so far in any true ternary compound is ~ 16 K in $SnMo_6S_8$. Some of the ternary compounds exhibit a few novel phenomena, e.g., (i) coexistence of superconductivity and magnetism in a few members of Chevrel's phases RMo_6S_8 and RMo_6Se_8 (R = rare earths, Sn, Pb, Hg) (3) and tetraborides $LnRh_4B_4$ (4); (ii) heavy fermion superconductors as in $CeCu_2Si_2$ (5a, 5b) and URu_2Si_2 (6) (also found in a few binaries, e.g., UPt_3 and UBe_{13}); (iii) coexistence of superconductivity and intermediate valence in $CeRu_3Si_2$ (7); and (iv) very high upper critical field in $PbMo_{5.1}S_6$ ($H_{c2} \sim 510$ kG at 4.2 K). Then, in the late 1980s, the discovery of cuprate superconductors (8) largely displaced the research interest from intermetallic superconductors. These ceramic superconductors exhibit T_c at very high temperature (~ 135 K under normal pressure and up to 164 K under 30 GPa pressure in Hg-based superconductors) (9, 10). Since many of the ceramic superconductors have T_c above liquid nitrogen temperature and hence are easier to work with, the study on intermetallics had come to a temporary standstill during the beginning of the 1990s. However, the recent discovery of the quaternary Ln–M–B–C system (M = Ni, Pd) restored interest in the intermetallics (11–16). It is not only that progress in the field of ceramic superconductors has become slow over the course of time (and sometimes monotonous), and that the researchers were looking for some other new topics to divert their attention, but also that the Ln–M–B–C system has been found to be really exciting to study for its own merit: e.g., (i) it exhibits record T_c among bulk intermetallic superconductors: $\sim$23 K in multiphase Y–Pd–B–C systems; (ii) a few members of the $LnNi_2B_2C$ series exhibit coexistence of magnetism and superconductivity (17) with a high value of both T_c and T_N and with a ratio of T_c/T_N that varies from less than 1 to more than 1, thus helping to study the interplay of superconductivity and magnetism; and (iii) $CeNi_2B_2C$ exhibits intermediate valence (IV) behavior (18) and $YbNi_2B_2C$ shows heavy fermion (HF) behavior (19). Moreover, a variety of magnetic structures have been observed in the magnetic members of the $LnNi_2B_2C$ series (20, 21). In this review, following others (22a–22f) in a comprehensive way, we present the current status of research on borocarbide superconductor, starting from its discovery.

0022-4596/00 $35.00

Quaternary Borocarbides

In 1993, Mazumdar *et al.* reported their observation of trace superconductivity in YNi_4B around 12 K (11), which was quite high for intermetallic superconductors, especially in an Ni-based one. In a few months time, *Phys. Rev. Lett.* reported work from TIFR, India and CNRS, France showing that the superconductivity in YNi_4B was actually caused by the presence of carbon impurity present in their compound, thus consequently discovering the first quaternary intermetallic superconducting alloy (12), with an Y/Ni ratio of 1/2. However, from their EPMA (electron probe microanalysis) measurements, they could not determine the atomic fractions of the light elements boron and carbon of the superconducting phase. In the same month, *Nature* published three separate articles from Bell Laboratories, USA and Center for Microscopy at Delph, Netherlands (13–15). The first article reported another multiphase compound Y–Pd–B–C having the record T_c of ~23 K for bulk intermetallic compounds. One of the other two publications reported the crystal structure of superconducting *Ln*–Ni–B–C phase, which turned out to be a filled variant of the $ThCr_2Si_2$-type structure. The third paper described the successful synthesis of most $LnNi_2B_2C$ materials in single phase and reported observation of coexistence of superconductivity and magnetism in $TmNi_2B_2C$, $ErNi_2B_2C$, and $HoNi_2B_2C$. This is a remarkable result as not many intermetallic superconductors are known to exhibit such coexistence. The flurry of subsequent work (more than 500 papers in 6 years) testifies the importance of the field thus born.

$LnNi_2B_2C$

Crystal Structure and Preparation

The $LnNi_2B_2C$ compounds form in a filled variant of the well-known tetragonal $ThCr_2Si_2$-type structure (space group *I*4/*mmm*), where a carbon atom occupies the vacant 2b position (1/2, 1/2, 0) in the rare earth plane (15). The structure is highly anisotropic ($c/a \sim 3$), having alternating sheets of Ni_2B_2 tetrahedra and *Ln*–C layers. This structure can be considered as one of the members of the series $(LnC)_m(NiB)_n$ (see Fig. 1) (16). The structure is rather similar to the layered crystal structure of oxide superconductors, and is very much different from those of other intermetallic magnetic superconductors (MS), viz., RRh_4B_4, RMo_6S_8, and $LnRu_3Si_2$ systems (23) where transition metal atoms form clusters (24). The Ni–Ni distances (~2.45 Å in $LuNi_2B_2C$), than those in the Ni-metal (2.5 Å) compounds, indicate a strong metallic character in these materials. The *a*-axis parameter of LnM_2B_2C compounds becomes smaller than that of equivalent analogues in LnM_2B_2 compounds while the corresponding *c*-axis parameter increases, indicating stronger *Ln*–C bonding and expansion of B–B bond

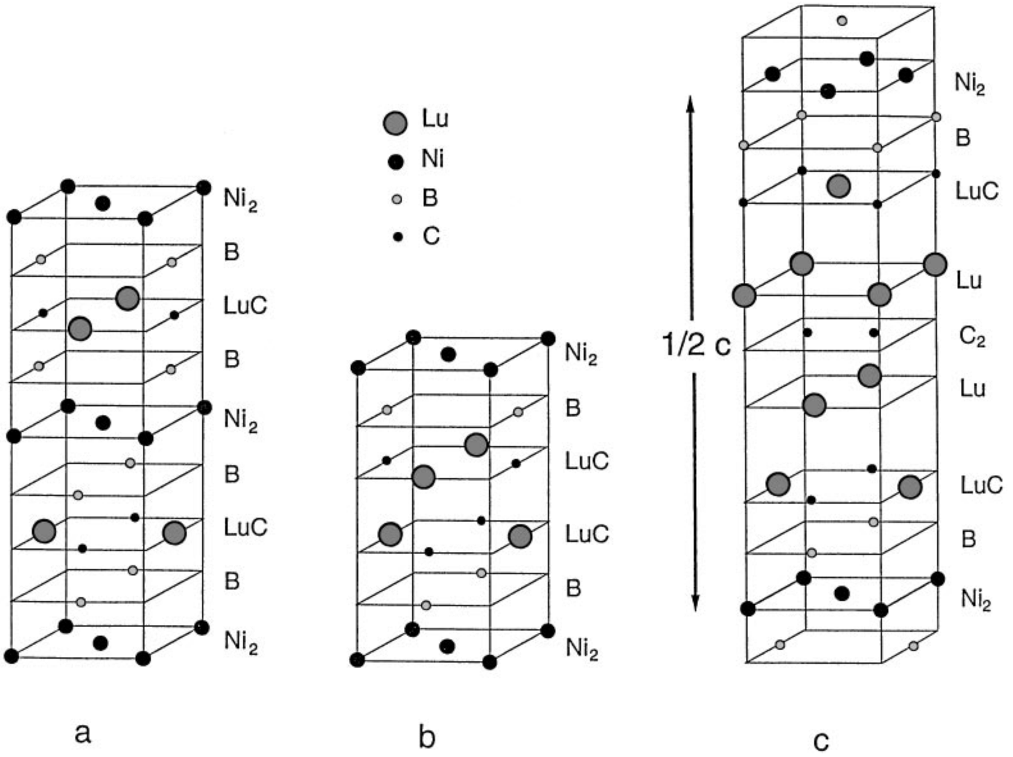

FIG. 1. Schematic representation of the structures of different members of the $(LnC)_m(NiB)_n$ series: (a) $LuNi_2B_2C$, (b) LuNiBC, and (c) Lu_2NiBC_2, according to Zandbergen *et al.* (158).

lengths, respectively (25). Across the rare earth (RE) series, as atomic number increases, and with the exception of $\mathrm{CeNi_2B_2C}$, the *a*-axis parameter decreases and the *c*-axis parameter increases (26); i.e., (i) the *c* parameter does not follow the lanthanide contraction law and (ii) the anisotropy of the structure increases. Neutron diffraction results show that all the crystallographic sites are fully occupied (within the accuracy of such calculations involving two light elements, viz., B and C), and there is no or insignificant site mixing (27), although neutron and positron annihilation experiments suggest possible carbon vacancies (27, 28). High-resolution electron microscopy (HREM) results show that these compounds show no existence of superstructure, although sometimes a very small fraction of intergrowths of $Ln\mathrm{NiBC}$ and $Ln\mathrm{Ni_2B_2C}$ could be seen (16). No crystallographic change was initially observed down to 25 K (25, 29) (see later, magneto-elastic distortion below magnetic transition temperature). From high-temperature X-ray diffraction (XRD) measurements on $\mathrm{YNi_2B_2C}$, it was found that this compound starts to oxidize and decompose above 850°C with the formation of secondary phases like $\mathrm{Ni_2B}$, $\mathrm{YB_2C_2}$, $\mathrm{Y_2O_3}$, and $\mathrm{YBO_3}$ (30). It was also shown that chemical bonds among the atoms in the unit cell are highly anisotropic in nature (30). The electrical resistivity measurement at room temperature up to 8 GPa pressure does not indicate any possible structural phase transition (31a, 31b). We should also point out that when polycrystalline $Ln\mathrm{Ni_2B_2C}$ compounds are prepared in an arc furnace, quite often one may encounter, along with a few different minor impurity phases, notably $Ln\mathrm{B_2C_2}$ along with very small amounts of $\mathrm{Ni_3B}$, $\mathrm{Ni_3C}$, and $Ln\mathrm{Ni_4B}$ among others (including various oxides) (25). These impurity phases can be suppressed to a large extent when annealed at a suitable temperature. In $\mathrm{TmNi_2B_2C}$, $\mathrm{HoNi_2B_2C}$, and $\mathrm{GdNi_2B_2C}$, respective $Ln\mathrm{B_2C_2}$ phase can only be suppressed best when annealed at 700 to 900°C (32), but at 1050°C for $\mathrm{CeNi_2B_2C}$. However, it was found that annealing at 1050°C produces the best magnetic and superconducting properties of $\mathrm{GdNi_2B_2C}$ and $\mathrm{HoNi_2B_2C}$, respectively (33, 34). Since magnetic members of $Ln\mathrm{B_2C_2}$ phases order magnetically (ferro or antiferro, depending on *Ln*) (35a, 35b). one must really be careful when interpreting magnetic data in the quaternaries. It was also shown that nonstoichiometry due to weight losses or impurity phase formation can very strongly affect the superconducting properties of these compounds (see the text below for details). Because of the noncongruent nature of the melting of these compounds (36), single crystals cannot be prepared by Bridgmann or Czochralsky techniques but by floating zone (36a, 36b) or $\mathrm{Ni_2B}$ flux methods (37). Superconducting $\mathrm{YNi_2B_2C}$ and $\mathrm{ErNi_2B_2C}$ can also be formed in thin film form (38a–38d). By using rapid-quenching techniques, Ström *et al.* could also prepare ribbons out of $\mathrm{YNi_2B_2C}$ (39). A few compounds like $\mathrm{ScNi_2B_2C}$ (40) and $\mathrm{ThNi_2B_2C}$ (41a–41c) which also superconduct at 15 and 6 K respectively, were found to be metastable.

Superconductivity and Magnetism

Table 1 summarizes the superconducting and magnetic transition temperatures of several borocarbide compounds.

TABLE 1
Superconducting and Magnetic Transition Temperatures of Different Ln–M–B–C and related compounds (IV = Intermediate Valence, HF = Heavy Fermion)

Ln	Compound	T_c	T_M	Ref.
Y	Ln–Pd–B–C	23 10	—	13,105
Th	Ln–Pd–B–C	21.5 14.5	—	124, 41a
Y	$Ln\mathrm{{-}Pd_2B_2C}$ phase	23	—	130
Ce	$Ln\mathrm{Co_2B_2C}$	—	IV	145
Gd	$Ln\mathrm{Co_2B_2C}$	—	21	144
Ho	$Ln\mathrm{Co_2B_2C}$	—	5.4	151
Lu	$Ln\mathrm{Co_2B_2C}$	—	—	48c
Y	$Ln\mathrm{Co_2B_2C}$	—	—	149
La	$Ln\mathrm{Ir_2B_2C}$	—	—	141
La	$Ln\mathrm{Ni_2B_2C}$	—	—	14
Ce	$Ln\mathrm{Ni_2B_2C}$	—	IV	14
Pr	$Ln\mathrm{Ni_2B_2C}$	—	4.0	113b
Nd	$Ln\mathrm{Ni_2B_2C}$	—	4.8	168, 169
Sm	$Ln\mathrm{Ni_2B_2C}$	—	9.8	170, 171
Gd	$Ln\mathrm{Ni_2B_2C}$	—	13.6, 19.4	172, 76b
Tb	$Ln\mathrm{Ni_2B_2C}$	—	15	170
Dy	$Ln\mathrm{Ni_2B_2C}$	6	11	170, 173–175
Ho	$Ln\mathrm{Ni_2B_2C}$	8	8.5 and 6	14, 17, 81a, 82a
Er	$Ln\mathrm{Ni_2B_2C}$	10.5	6	17, 47, 70b, 120b, 176, 177
Tm	$Ln\mathrm{Ni_2B_2C}$	11	1.5	17, 120b, 70b, 14
Yb	$Ln\mathrm{Ni_2B_2C}$	0	0-HF	57a, 57b
Lu	$Ln\mathrm{Ni_2B_2C}$	16.5	—	15, 70a, 176, 178, 179
Y	$Ln\mathrm{Ni_2B_2C}$	15.4	—	27, 56, 88, 180
Sc	$Ln\mathrm{Ni_2B_2C}$	15	—	40
Th	$Ln\mathrm{Ni_2B_2C}$	8	—	59
U	$Ln\mathrm{Ni_2B_2C}$	—	IV,218	41c, 59
La	$Ln\mathrm{Pt_2B_2C}$	11	—	138, 139a
Ce	$Ln\mathrm{Pt_2B_2C}$	—		138, 139a
Pr	$Ln\mathrm{Pt_2B_2C}$	6.5	—	138
Nd	$Ln\mathrm{Pt_2B_2C}$	—	9.6	139b
Dy	$Ln\mathrm{Pt_2B_2C}$	—	5.9	139b
Y	$Ln\mathrm{Pt_2B_2C}$	10	—	138
Th	$Ln\mathrm{Pt_2B_2C}$	7	—	41b
La	$Ln\mathrm{Rh_2B_2C}$	—	—	141, 412
Ce	$Ln\mathrm{Rh_2B_2C}$	—	IV	145
Pr	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Nd	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Sm	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Gd	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Tb	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Dy	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Ho	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Er	$Ln\mathrm{Rh_2B_2C}$	—		142, 143
Th	$Ln\mathrm{Rh_2B_2C}$	—	—	142, 143
U	$Ln\mathrm{Rh_2B_2C}$	—	185	41c

TABLE 1—*Continued*

Ln	Compound	T_c	T_M	Ref.
La	$Ln_3Ni_2B_2N_3$	12.3	—	135, 181
La	*Ln*NiBN	—	—	135, 181
Tb	*Ln*–Re–B–C	4?	—	167
Gd	*Ln*–Re–B–C	4?	—	167
Lu	*Ln*–Re–B–C	6?	—	167
Lu	Ln_2NiBC_2	—	—	158
Y	Ln_2NiBC_2	—	—	159
Ho	$Ln_2Re_2Si_2C$	—	8.8	166
Er	$Ln_2Re_2Si_2C$	—	7.6	166
Y	$Ln_3Ni_4B_4C_3$ multiphase	3/ 10	—	160
Lu	$LnNi_{1-x}Cu_xBC$	6.6	—	154
Y	$LnNi_{1-x}Cu_xBC$	8.9	—	154
Dy	*Ln*NiBC	—	15.7	156d
Er	*Ln*NiBC	—	4	57c, 183
Gd	*Ln*NiBC	—	8-10/14/ 33	76a, 156d, 182
Ho	*Ln*NiBC	—	10	156d
Lu	*Ln*NiBC	2.9?	—	152
Tb	*Ln*NiBC	—	16.5	156d
Y	*Ln*NiBC	—	—	160
Yb	*Ln*NiBC	—	4	57c, 182
Y	$LnNiCuB_2C$	—	—	163
Y	$LnNi_2Si_2C$	—	—	163
Y	$LnCu_2Si_2C$	—	—	163

In the $LnNi_2B_2C$ series of materials, it was found that Dy, Ho, Er, Tm, Lu, Y, Sc, and Th compounds exhibit superconductivity, out of which the magnetic rare earth analogues also exhibit magnetic transition. ^{13}C NMR (nuclear magnetic resonance) (42), Y and B NMR (43), pressure (44), ESR (electron spin resonance) (45), and some heat capacity measurements (22c) suggest these materials to be simple BCS (Bardeen–Cooper–Schrieffer)-type superconductors, although a few measurements, viz., microwave (46) and preliminary specific heat analysis (47) did not fully agree with this conclusion. According to the BCS theory of superconductivity,

$$T_c = 1.14\frac{h\omega_D}{k_B}\exp\left(-\frac{1}{N(E_F)V}\right),$$

these rather high T_c values might have originated due to large Debye temperature (and frequency ω_D) favored by the presence of two light elements boron and carbon and/or due to high density of states (DOS) at Fermi level, $N(E_F)$, originating mostly from the 3*d* band of Ni (48a–48d). The observation of rf-SQUID effect in YNi_2B_2C suggests that the superconducting grains are coupled at grain boundaries through Josephson effect (49). Inelastic neutron scattering and tunneling measurements on these compounds suggest a superconducting energy gap (Δ) in Lu(Y)Ni_2B_2C in the range 2.5–4.5 meV (50a–50d) in agreement with $2\Delta/kT_c \approx 3.5$ obtained from the BCS theory. A sizeable boron isotope effect ($\alpha_B \approx 0.25$) (but not 0.5 as predicted by BCS theory) was also observed in this system suggesting these materials are electron–phonon-mediated superconductors (51a, 51b). However, the carbon isotope effect did not induce any change in T_c (51a, 51b).

From the upper critical field behavior, it was claimed by Wang and Maki (52) for possible superconductivity of *d*-wave type, although the positive curvature of the H_{c2} curve near T_c was not taken into account by these authors. Shulga *et al.* proposed a two-band model to explain this curvature (53). Unconventional pairing from field effects on specific heat measurements (54) was also suggested, although detailed magnetic experiments (55) and μSR (muon spin resonance) experiments on single crystals (56) concluded to conventional s-wave pairing.

Among these compounds, magnetic transition temperatures increases with the de Gennes scaling factor, $G = (g_J - 1)^2J(J + 1)$, whereas superconductivity temperatures decrease (17). $YbNi_2B_2C$ turned out to be a moderately heavy fermion compound (see Fig. 2) and does not superconduct down to 20 mK (57a–57c). $TbNi_2B_2C$ also does not show any superconducting transition temperature down to 300 mK (58), although extrapolating the de Gennes scaling, $YbNi_2B_2C$ and $TbNi_2B_2C$ are expected to show T_c at about 12 and 4 K, respectively.

The other nonmagnetic member of the series, $LaNi_2B_2C$, does not show superconductivity, which would agree with the theoretical calculations showing that the DOS at E_F for

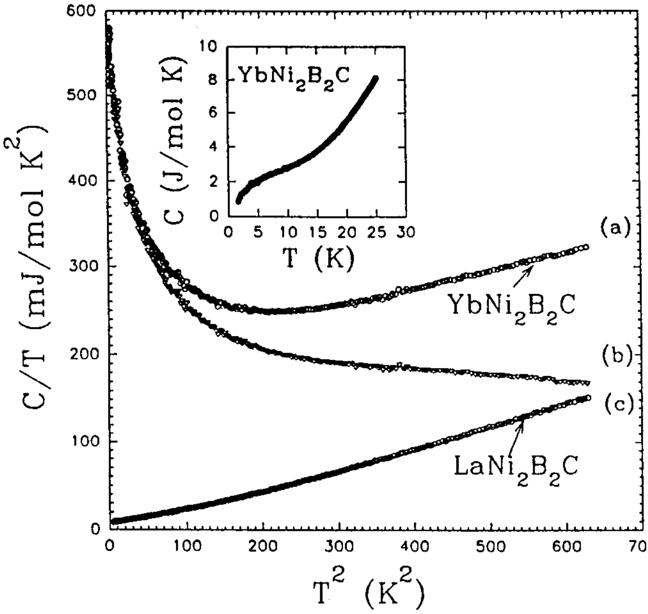

FIG. 2. Heat capacity *C*, in a $C/T(T^2)$ plot, of (a) $YbNi_2B_2C$, (c). $LaNi_2B_2C$, and the difference spectra (b) = (a)–(c), indicating heavy fermion behavior of $YbNi_2B_2C$, according to Dhar *et al.* (57).

$LaNi_2B_2C$ is nearly half that for $LuNi_2B_2C$ (48). When plotted as a function of Ln^{3+} ionic radius, T_c shows a maximum for ionic radius of 0.86 Å, the value for Lu^{3+} (59). The same is also true when one plots T_c as a function of Ni–Ni distances and the maximum of T_c comes at about 2.47 Å (59). The absence of correlation between T_c and either the *Ln* ionic radii or the Ni–Ni distance also suggests that either the density of states at E_F or the electron–phonon coupling, or both play an important role in determining the superconducting properties of these materials. Moreover, from band structure calculation, Mattheis *et al.* have suggested that compounds with idealized Ni_4B tetrahedra should have maximum T_c in the series of compounds, and that $LuNi_2B_2C$ is the closest one (60). However, it seems difficult to understand from this model why $ScNi_2B_2C$ has a T_c value (15 K) nearly equal to that of the Y-based material (15.6 K) but has such different crystallographic characteristics (in the plots of *a* and *c* parameters of $LnNi_2B_2C$ versus the trivalent ionic radius of *Ln*, a_{Sc} follows the lanthanide contraction curve but c_{Sc} is totally anomalous). On the other hand, photoemission studies of polycrystalline superconducting YNi_2B_2C, nonsuperconducting $LaNi_2B_2C$ (61a–61c), and $Y_{1-x}Lu_xNi_2B_2C$ superconducting series (62) and single-crystalline YNi_2B_2C and $YbNi_2B_2C$ (63a–63b) did not show any differences in the Fermi level position, suggesting that electron–phonon interaction is probably the key parameter which controls T_c (in agreement with boron isotope effect). The X-ray absorption spectra measured at the Ni-L_{III} edge and B-K edge of different $LnNi_2B_2C$ members also could not categorically clear this point (64).

From the magnetic measurements, all these compounds are found to be type-II superconductors. As a typical candidate, polycrystalline YNi_2B_2C was studied in detail and the following parameters were obtained (55),

$$\lambda(0) \approx (3.5 \pm 0.5) \times 10^{-5}\text{cm}, \qquad \xi(0) \approx (10 \pm 2) \times 10^{-7}\text{cm},$$

$$H_{c1} \approx 80\text{ G}, \ \mathrm{H_{c2}} \approx 47.6\text{kG},$$

though these parameters vary from measurement to measurement (22d). For example, μSR measurements on single-crystalline YNi_2B_2C yield the parameters (56)

$$\lambda(0) \approx 1.03 \times 10^{-5}\text{cm}, \quad \xi(0) \approx 8.1 \times 10^{-7}\text{cm}, \quad \mathrm{H_{c1}} \approx 37\text{ G},$$

$$H_{c2} \approx 60\text{ kG}.$$

The critical fields are anisotropic in nature (with an effective mass anisotropy $m_c^*/m_{ab}^* \sim 1.7$) for YNi_2B_2C (22e) and $LuNi_2B_2C$ (65), although the isotropic nature of magnetic parameters (66) and resistivity (67) is also found in the literature (see Fig. 3). From torque magnetometric measurements it was found that YNi_2B_2C is an isotropic superconductor but $HoNi_2B_2C$ is not, possibly because of the Ho spins ordering (68). Amplitude of the de Haas–van Alphen (dHvA) oscillations in YNi_2B_2C are found to be unaffected by the phase transition at H_{c2}, indicating the very weak nature of field-dependent quasi-particle damping (69a, 69b).

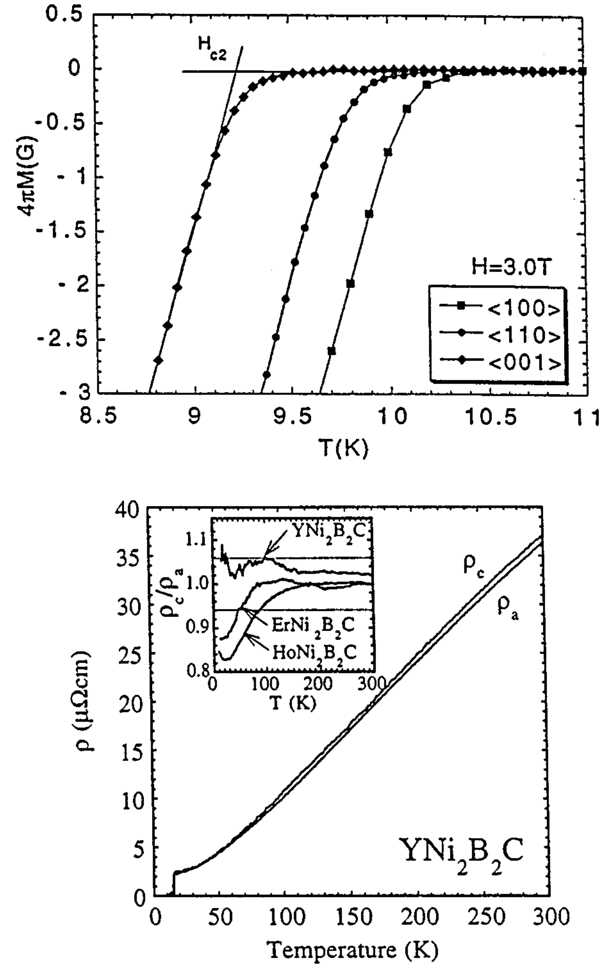

FIG. 3. (Top) Anisotropic behavior of $H_{c2}(T)$ of $LuNi_2B_2C$, according to Metlushko *et al.* (65). (Bottom) Isotropic behavior of the resistivity versus temperature of YNi_2B_2C according to Fisher *et al.* (67).

Application of hydrostatic pressure decreases T_c for most of the members of the series, except in $LuNi_2B_2C$, where T_c increases marginally (44, 70a–70e). However, the application of chemical pressure by substituting Sc in place of Lu does not increase T_c and the interpretation of this result still remains unclear (70b, 22d). It was also seen that a very low amount (0.2) of hydrogen can be absorbed by these materials without affecting the lattice parameters or T_c (71).

Another very important feature of these type of compounds is the nature of vortex lattice in the mixed state. From small-angle neutron scattering (SANS) in $ErNi_2B_2C$ (72a–72e) and scanning tunneling microscope (STM) measurements in $LuNi_2B_2C$ under field (73), one can clearly observe: (i) a transformation from hexagonal to squared vortex lattice and (ii) that the flux line turns away from the direction of applied field at T_N of $ErNi_2B_2C$, implying microscopic coexistence of superconductivity and magnetism. This is the first time that such observations have been made in a magnetic superconductor.

Unlike the magnetic members of oxide superconductors $Ln\mathrm{Ba_2Cu_3O}_{7-\delta}$, the magnetic transition temperatures of these borocarbide materials affect T_c. All these materials primarily order antiferromagnetically with a wide variety of magnetic structures (see Fig. 4 and Table 2) (20, 21, 74a–74c). The relatively large values of T_N imply that the prevalent magnetic exchange interaction is of Ruderman–Kittel–Kasuya–Yosida (RKKY) type. The superconducting transition temperatures decrease nearly linearly with the de Gennes factor. The ratio of T_c/T_N is > 1 for $\mathrm{TmNi_2B_2C}$ and $\mathrm{ErNi_2B_2C}$, ~ 1 for $\mathrm{HoNi_2B_2C}$, and < 1 for $\mathrm{DyNi_2B_2C}$, implying the appearance of superconductivity in the already magnetically ordered lattice of $\mathrm{DyNi_2B_2C}$. Not so many such cases are known ($\mathrm{Tb_2Mo_3Si_4}$ orders below 19 K and becomes superconductor around 1 K (75) but none have such high T_c. $\mathrm{GdNi_2B_2C}$ exhibits two magnetic transitions (76a, 76b), as confirmed by X-ray resonant exchange scattering (XRES) (77) and ^{155}Gd Mössbauer (78) experiments. The magnetic structure of $\mathrm{NdNi_2B_2C}$ and $\mathrm{SmNi_2B_2C}$ have also been determined by XRES (79). The magnetic phase diagram of $\mathrm{HoNi_2B_2C}$ is the most complex (80) among this series of materials. Below 5 K, it has a simple commensurate antiferromagnetic structure with spins along the (*a*, *b*) plane, whereas in the range of 5–8 K it has a spiral magnetic structure (along the *c* axis) (81a, 81b). Moreover, in the range of 5–6.5 K, it has an *a*-axis modulated incommensurate additional component, introducing a ferromagnetic component in these temperature range (20, 21, 82a, 82b). This particular property gives rise to the double reentrant behavior seen in the transport and magnetic properties of $\mathrm{HoNi_2B_2C}$ (83). One puzzling characteristic is that these double reentrant behaviors may not be always observed in all the experiments. Schmidt *et al.* (83) have shown that in the same sample, ac magnetic susceptibility can show the phenomenon but the resistivity may not (see Fig. 5). This behaviour is also very sensitive to the individual stoichiometry of each element in the sample. This also emphasizes the importance of sample preparation techniques, as discussed earlier. Moreover, it is normally found that $\mathrm{HoNi_2B_2C}$ forms in equilibrium with many other possible phases, such as $\mathrm{HoB_2C_2}$ ($T_{\mathrm{Curie}} \sim 7$ K) (35), $\mathrm{Ho_2Ni_3B_6}$ ($T_{\mathrm{Curie}} \sim 12$ K) (34, 84), and $\mathrm{HoNi_4B}$ ($T_{\mathrm{Curie}} \sim 6$ K) (85), which order magnetically around the region of interest (4–8 K) (84) and coexist with $\mathrm{HoNi_2B_2C}$ microscopically.

TABLE 2
Magnetic Structures of Different Members of $Ln\mathrm{Ni_2B_2C}$ Series

Ln	Non magn.	T_N	Type	T_{mag2}	Type
La, Ce	Non				
Pr		4.0	AFM (Comm.)		
Nd		4.8	AFM (Comm.)		
Sm		9.8	AFM (Comm.)		
Eu					
Gd		19.4	SDW incomm.	13.6	+ moment along *c*
Tb		15.0	Longi. SDW incomm.		
Dy		11.0	AFM (Comm.)		
Ho		8.5	AFM + others	8.5	*c*-axis spiral
		5.0	AFM (Comm.)	6.5	*a*-axis mod. incomm.
Er		6.8	Trans. SDW incomm.		
Tm		1.5	Trans. SDW incomm.		
Yb, Lu	Non				

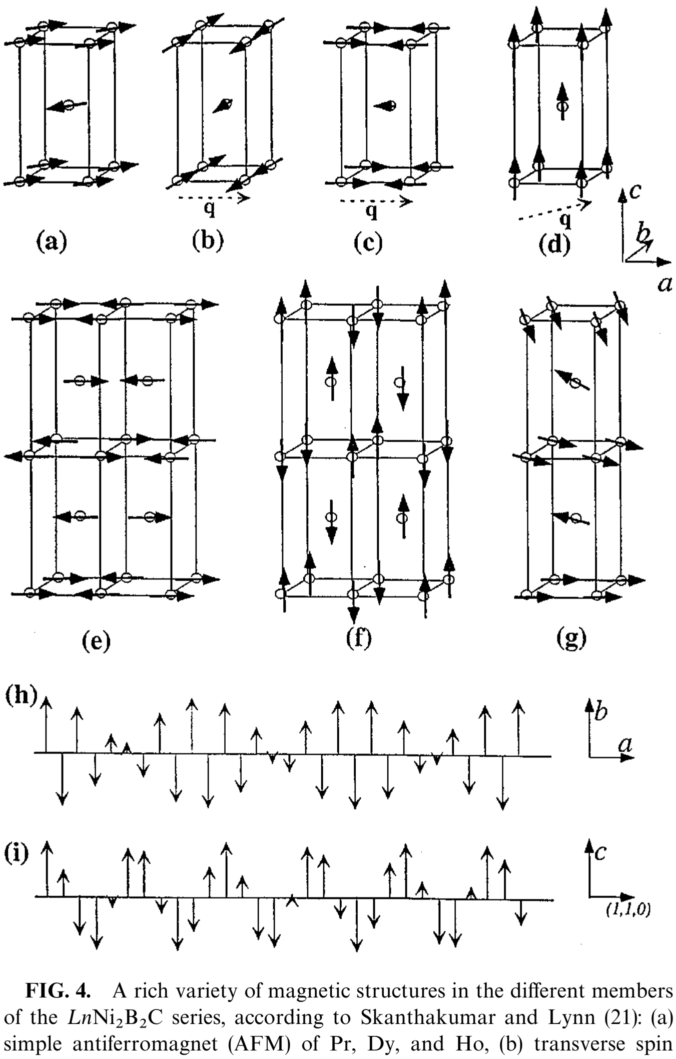

FIG. 4. A rich variety of magnetic structures in the different members of the $Ln\mathrm{Ni_2B_2C}$ series, according to Skanthakumar and Lynn (21): (a) simple antiferromagnet (AFM) of Pr, Dy, and Ho, (b) transverse spin density wave (SDW) of Er and Gd, (c) longitudinal SDW of Tb, (d) transverse SDW of Tm, (e, f) commensurate structures of Nd and Sm, and (g) spiral structure of Ho in the temperature range of reentrance. (h, i) Modulation of the transversely polarized SDW of Er and Tm.

Some controversy also exists about the moment on Ni ion in these materials. Although on the basis of heat capacity measurements Hong *et al.* (86) claimed that the Ni *d* band is filled, the X-ray absorption measurement at the Ni–$\mathrm{L_{III}}$ edge clearly demonstrates that Ni has nearly $3d^9$ character in

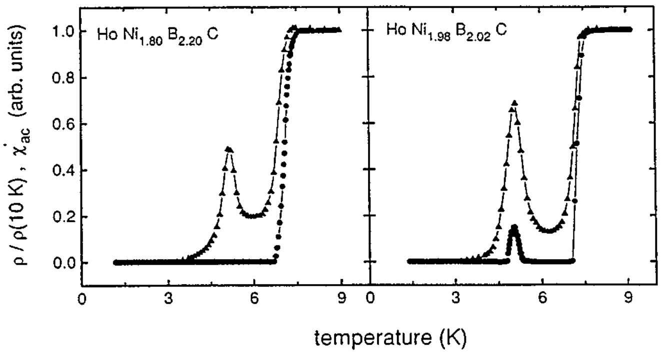

FIG. 5. Reentrance as seen from electrical resistance (circle) and ac susceptibility (triangle) for two samples of the series HoNi$_{2-x}$B$_{2+x}$C, indicating a measurement-dependent behavior, according to Schmidt *et al.* (83).

these materials, implying that Ni may carry a magnetic moment (64). Temperature dependence of magnetic susceptibility of YNi$_2$B$_2$C shows a weak Curie–Weiss behavior with 0.24μB/Ni ion and a Curie–Weiss temperature θ — 3 K (86), but due to the presence of minor quantities of magnetic impurity phases, this result is not conclusive on the existence of an intrinsic Ni moment. On the basis of an ^{11}B NMR experiment on polycrystalline YNi$_2$B$_2$C and LaPt$_2$B$_2$C, Kohara *et al.* (87), Borsa *et al.* (88), Elankumaran *et al.* (89), and Oda *et al.* (90), as well as Cooke *et al.* from μSR experiments (91), conclude that Ni has a moment, though from a similar experiment performed later on single-crystalline YNi$_2$B$_2$C, Suh *et al.* (92a, 92b) completely disagree with this idea and instead attributed the temperature dependence to boron *s* electrons. From the Mössbauer experiments on different *Ln*Ni$_2$B$_2$C (1% Fe) compounds in the temperature range 4.5–5.5 K, Sanchez *et al.* observed the presence of transferred hyperfine field in nonsuperconducting Tb and Ho (in the reentrant temperature range) compounds, but not for superconducting Er and Dy compounds (93). This result was contested by Tominez *et al.*, who did not find any significant difference in the Fe Mössbauer spectra of HoNi$_{1.99}$Fe$_{0.01}$B$_2$C, a sample in which reentrance was strongly reinforced by Fe, measured at 6, 5.2, and 4.2 K (34).

^{166}Er Mössbauer measurements on ErNi$_2$B$_2$C show that the magnetic transition is of first order in nature (94a, 94b). From their observation of a Er^{3+} relaxation rate ($1/T_1$) anomaly at T_c, Bonville *et al.* have also suggested that the same conduction electrons, which are exchange coupled to the 4*f* spin, take part in the formation of the superconducting state. This is against the conventional wisdom as gathered from the knowledge of, for instance, the *Ln*Rh$_4$B$_4$ series, where the superconducting electrons and those electrons which take part in magnetic interaction are totally different (95). However, a recent ^{166}Er Mössbauer study on non-superconducting ErNi$_{1-x}$Co$_x$B$_2$C (96a) samples also exhibits a similar anomaly around the same temperature, indicating a slowing down of Er^{3+} spin relaxation rate around 10 K instead (96b). Bonville *et al.* have also observed a temperature-independent (up to 20 K) magnetic hyperfine field with a relative weight of ~10%, which they have explained in terms of "slow relaxation" (94). Below the magnetic ordering temperature, the material undergoes a tetragonal to orthorhombic distortion (see Fig. 6) (97).

From the magnitude of isomer shift of ^{161}Dy Mössbauer studies on DyNi$_2$B$_2$C it was also suggested that the Dy–C layer is nonmetallic (98) and that superconductivity occurs in the "Ni–B" sublayer, in agreement with the observation of an isotopic effect with B and not with C. However, the resistivity of these compounds are found to be almost isotropic (67, 99). The temperature dependence of the in-plane resistivity (ρ_{ab}) of this material shows an anomalously large hysteresis (with *H*//), again indicating strong interplay of

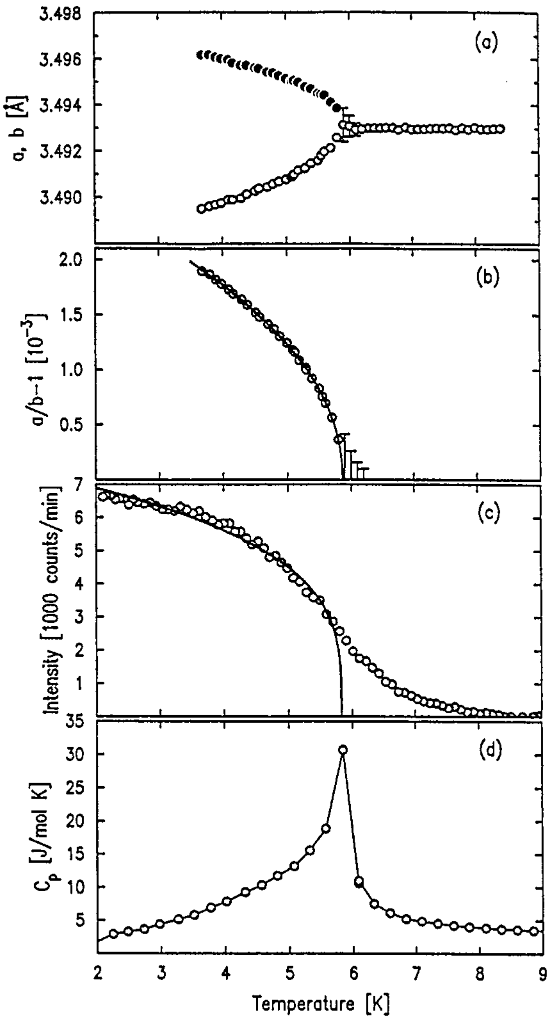

FIG. 6. Crystallographic distortion in ErNi$_2$B$_2$C as evidenced by (a) *a* and *b* parameters, (b) distortion parameter a/b — 1 at T_N defined by the intensity of *a*, (c) magnetic Bragg peak, and (d) specific heat peak, according to Detlefs *et al.* (97).

superconductivity and magnetism (under magnetic field) (99).

The effect of off-stoichiometry has recently been seen in the case of $TmNi_2B_2C$ also. μSR measurements show a spontaneous internal field, existing up to 30 K, which at low temperature saturates below 2.5 K, but with a very small moment of 0.1 μ_B (91, 100a, 100b). ^{169}Tm Mössbauer also indicates a similarly small Tm moment (101). This discrepancy was solved by inelastic neutron scattering measurements on two different samples of $Tm_{1.1}Ni_2B_2C$ and $TmNi_2B_2C_{1.1}$, which yielded values of Tm moments of 0.1 and 4.3 μ_B, respectively (102a–102c), indicating that Tm ions near carbon vacancies have a very small moment; otherwise they have their normal value. Depending on the crystalline electric field (CEF), as modified by vacancies, a quadrupolar doublet (0.1 μ_B) or sextuplet (4.3 μ_B) spectra is observed by Mössbauer spectroscopy (see Fig. 7). The effect of vacancies or of slight excess of constituting elements in $HoNi_2B_2C$ affect the superconducting properties to a great extent, along with some minor modification of its magnetic properties (34, 84, 103), as also indicated by ^{57}Fe Mössbauer experiments (34, 104).

The impurity effects in YNi_2B_2C have also been studied in detail. These effects can include, to name a few, size effects (chemical pressure), magnetic pair breaking, change of DOS at E_F, intermediate valence (IV) effects, and Kondo phenomenon. It was observed that when Y is replaced by other ions such as Ce, Gd, Dy, Ho, Er, Yb, or U, T_c always decreases (− 6 K/0.1 Ce, − 5 K/0.1 Gd, −1.4 K/0.1 Dy, −0.8 K/0.1 Ho, −0.4 K/0.1 Er, −13 K/0.1 Yb, nonsuperconductivity/0.1U) (18, 41, 47, 105–108). It is normally (except for Ce, Yb, or U doping, where 4*f* conduction electron hybridization probably plays a crucial role) found that T_c decreases while T_N increases nearly linearly as the effective de Gennes factor increases (with T_N less sensitive than T_c) due to magnetic pair breaking (within the assumption of "noninteracting," i.e., diluted, magnetic ions), but it becomes completely violated when $T_c < T_N$, as observed in the pseudobinary system $Dy_{1-x}R_xNi_2B_2C$ (R = Ho, Lu) and, hence, no extrapolation of physical properties is possible when one approaches from the other side of the phase diagram (109). As noted by Hossain *et al.* (110) and Gupta (111), nonmagnetic impurities on the atomic scale can have profound effect and play completely different roles above and below T_N. Above T_N, nonmagnetic impurities simply dilute the concentration of magnetic ions and thus reduce the magnetic pair breaking effect. Below T_N, nonmagnetic ions play the role of defects in antiferromagnetic lattice and thus give rise to pair breaking. Moreover, as superconductivity in $DyNi_2B_2C$ is, by itself, very sensitive to Dy nonstoichiometry (112), and as the Y or Lu substitution may also change the stoichiometry, this factor may be as well the main parameter for controlling the decrease of T_c.

T_c also decreases when Ni atoms in YNi_2B_2C are replaced by other transition metal elements, such as Fe, Co, Cu, Ru, and Pd (see Fig. 8) (113a–c). It was observed that Ru

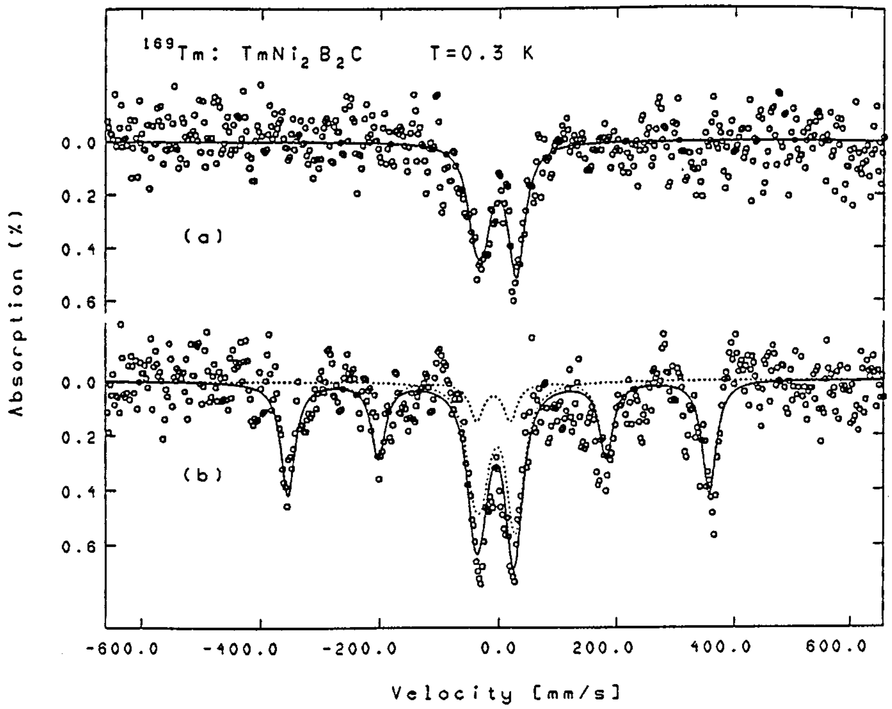

FIG. 7. ^{169}Tm Mössbauer spectra of (a) $Tm_{1.1}Ni_2B_2C$ and (b) $TmNi_2B_2C_{1.1}$, showing effect of stoichiometry, according to Gasser *et al.* (102a).

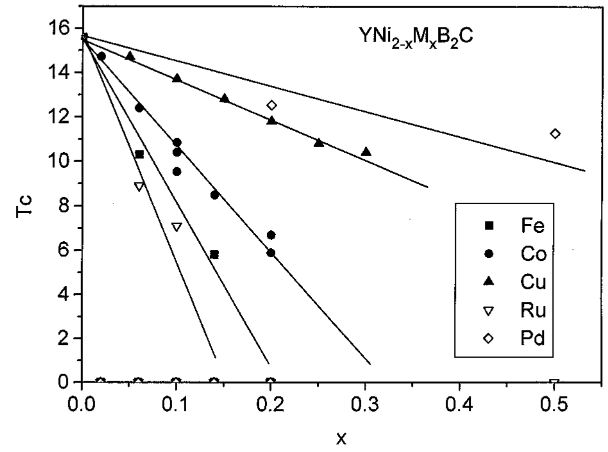

FIG. 8. Decrease of T_c as induced by M substitution in $YNi_{2-x}M_xB_2C$ with M = Fe, Co, Cu, Ru, and Pd.

has the largest rate of suppression among these elements. Although Pd and Ru have similar sizes, Pd substitution has one of the smallest effects on T_c of YNi_2B_2C, while Ru substitution causes a large T_c depression. No convincing explanation has been given yet. It was proposed that when the difference of the number of valence electrons of transition metal elements is negative, the shift of the Fermi level with respect to the peak in DOS is responsible for the lowering of T_c (114). But according to this argument, Cu substitution should have increased T_c, as Cu has more valence electrons than Ni, which is not the case. Hence, it was proposed that modification of the possible mixed valence character of Cu would be partially responsible for this decrease in T_c (115).

The other two notable compounds in this series are $CeNi_2B_2C$ and $YbNi_2B_2C$. From the lattice parameter anomaly, Ce ions in this compound are considered to be in a nontrivalent state (26). X-ray absorption measurements at the Ce–L_{III} edge show that Ce ions are indeed in an intermediate valence state, with valence changes from 3.15 at 300 K to 3.21 at 10 K (18). However, from the variation of T_c as a function of rare earth ionic radii or Ni–Ni distances, one would tend to believe that the suppression of T_c in $CeNi_2B_2C$ may not be caused by the intermediate valence behavior of Ce in this compound. Instead the size effect and subtle variation of band structure may play a very significant role. Very recently, from zero-field-cooled magnetic susceptibility and heat capacity measurements, El Massalami *et al.* (116) claimed that they have observed bulk superconductivity in $CeNi_2B_2C$ at ~0.1 K, which has yet to be verified by other researches.

$YbNi_2B_2C$ is found to be a moderately heavy Fermion system (Kondo temperature, $T_K \sim 10$ K), which is not very common for Yb-based materials (57, 117). From the de Gennes scaling of T_c across the series, one would have expected the material to be superconducting at about 12 K, whereas the material did not show a superconducting transition down to 1.5 K. The off-stoichiometric samples like $Yb_{1.1}Ni_2B_2C$, $YbNi_{1.8}B_2C$, and $YbNi_2B_{2.2}C$ also did not show any T_c down to 2 K (19). ^{170}Yb Mössbauer experiments measured down to 23 mK did not show any magnetic order (57c). A small hyperfine field was observed indicating a upper limit of 0.05–0.1 μB for Yb moment, if any. ^{11}B NMR measurements on $YbNi_2B_2C$ show a crossover from a local moment system above 50 K to itinerant correlated electron behavior below 5 K (118).

Samples with nominal composition of UNi_2B_2C could be prepared, with a significant percentage of $Ln$$Ni_2B_2C$ phase, as observed by XRD patterns (41a, 41c, 59, 119). These materials do not show superconductivity down to 2 K. Since U ions are known to show IV behavior, it will be of interest to study the valence properties of U ions in the single-phase compound, as the multiphase sample suggests an average valence of 5.2 for the U ions (59).

Ln–Pd–B–C SYSTEM

Superconductivity with the highest T_c (at about 23 K, 10% higher than that observed in the best bulk binary compound, Nb_3Ga) in bulk intermetallic material was reported in the multiphase $YPd_5B_3C_{0.35}$ system (13). Following this, a few more Pd-based multiphase materials, e.g., YPd_4BC_x $(0.2 \leq x \leq 1)$ (119, 120a, 120b), $YPd_4B_4C_y$ $(y < 0.1)$ and $YPd_3B_2C_z$ $(z < 0.1)$ (121), and $YPd_2B_2C_w$ ($w \sim 1$ (122) and ~ 1.5 (123a, 123b)), were reported to show superconductivity in the temperature range 22–23 K, though Hossain *et al.* have observed a difference in zero-field-cooled and field-cooled susceptibility in YNi_4BC_x even at ~26 K (120). All these materials have at least two common properties: (i) they are multiphase, and (ii) annealing them above 900°C destroys superconductivity, even though they remain multiphase. Another superconducting phase has also been found in various cases: at 10 K in $LnPd_4BC_x$ $(0.2 \leq x \leq 1$; Ln = Y, Lu (120), Th (41a–c, 120) and at 14.5 K in the Th–Pd–B–C system (124a, 124b). A large number of propositions were made for the possible structure of the "23-K superconducting phase." From HREM studies, a few have proposed a body-centered tetragonal structure with $a \approx 3.7$–3.8 Å and $c \approx 10.6$–10.8Å (123, 125a, 125b). Zandbergen *et al.* have found, besides free graphite, six other different phases in the Th–Pd–B–C system, viz., (i) $ThPd_2B_2C$, I-type tetragonal and, in their opinion, possibly related to the 14.5-K superconducting phase; (ii) $ThPd_{0.65}B_{4.7}$, P-type cubic and, in their opinion, possibly related to the 21-K superconducting phase; (iii) $ThPd_3$, P-type hexagonal; (iv) $ThPd_8B_3$, I-centered orthorhombic; (v) $ThPd_3B_2C$, unknown structure; and (vi) ThB_4, tetragonal (125a). In the case of the Y–Pd–B–C system, beside two noncrystalline phases, they found (i) YPd_2BC, I-centered tetragonal, and considered it to be the superconducting phase; (ii) $YPd_{1.2}B_{3.3}$, cubic; (iii) YPd_8B_3, I-centered orthorhombic; and (iv) $YB_{4-x}C_x$, tetragonal (125a). By analyzing their rapidly quenched sample of nominal composition, YPd_2B_2C, Ström *et al.* has attributed the superconducting phase to a cubic structure ($a = 4.15$ Å) (126), although a few of their superconducting samples do not contain this phase (127).

In view of all the above contradicting and often confusing information, it is really difficult to single out the phase responsible for superconductivity in the Y–Pd–B–C. Godart *et al.* (32) and Tominez *et al.* (128) have tried to make a systematic effort to find out the phase actually responsible for superconductivity in the Y–Pd–B–C phase diagram. The main problems to doing so are manifold; the samples, whether YPd_2B_2C or of any other nominal composition, are multiphase; slow cooled as cast YPd_2B_2C is not superconducting (32); and one must rapidly quench the sample to achieve superconductivity (126, 127). Annealing the sample always destroys the superconducting phase. The composition of the superconducting phase having two light elements must be determined. Due to the presence of two light elements, (boron and carbon), the various classical characterization techniques are almost inefficient in determining composition. Chemical analysis in a multiphase material (and even in a single phase with the two light elements) is totally inappropriate. Intensity analysis of XRD or neutron diffraction also does not yield satisfactory results. TEM/EPMA are rather insensitive to light elements. Even for those spectrometers (multilayer-based monochromator) specially designed to probe light elements, one also must consider the influence of neighboring atoms, which is significant for light atoms such as boron and carbon. In HREM studies, the image contrast between B and C is also very small and because of the close values of their atomic numbers, Y and Pd are also not well distinguishable. The only alternative, which is found to overcome these problem to a great extent, is the nuclear probe microanalysis (NPMA) (129). Particle-induced X-ray emission (PIXE) and Rutherford back scattering (RBS) techniques can be used to measure heavy element concentration and NRA (nuclear reaction analysis) to determine light element concentration. As NRA is a nuclear probe, the analysis is insensitive to the neighboring atoms of the light elements. The main difficulty in NPMA is to find the right type of particle beam (depending on the element to be studied) and to avoid time evolution of the sample under beam. Among the several superconducting nominal compositions, $YPd_5B_3C_{0.35}$ was choosen for NPMA analysis as it exhibits the largest magnetic-shielding fraction (~50%) and a large magnetic flux exclusion fraction (~15%). Therefore, as-cast and annealed samples of this composition were studied by NPMA (130). New experimental conditions and detailed results are described by Berger *et al.* in this *Proceedings* (131). The results are summarized in Table 3. Since only the needles (phase C) and dendrites (phase D) disappeared by annealing as also superconductivity, it was assumed that one of these two phases should be the true superconducting phase. However, (i) as the fraction content of phase C is higher and closest to the Meissner fraction and (ii) as the phase C has a needle-like structure, their connection can give rise to a path for zero resistance; it was then argued that phase C is responsible for the 23 K superconducting phase. This composition seems to be metastable, as the synthesis of single-phase material is still elusive, and hence no true measurements of its superconducting properties could be performed. Although a few attempts were made to determine the critical fields (132, 133), pressure dependence of compressibility (134), etc., because of the multiphase nature of the samples, not much importance can be attached to them.

TABLE 3
Compositions and Structures of the Phases in Heterogeneous Alloy of Nominal Composition '$YPd_5B_3C_{0.35}$'

φ	Morphology	Composition	Vol. % as cast	Cell (Å)
A	Matrix	$YPd_{7.1}B_{4.2}$	70	Centered ortho- I, $a = 8.441(4)$ $b = 8.984(5)$, $c = 16.543(8)$
B	Globules	$YPd_{3.0}B_{0.8}$		Cubic- P, $a = 4.122(1)$
C	Needles	$YPd_{2.0}B_{2.05}C_{1.05}$	20	Centered tetra- I, $a = 3.751(1)$, $c = 10.725(3)$
D	Dendrites	$YPd_{1.0}B_{4.7}$	7.5	Cubic- P, $a = 4.053(1)$
E	Squared inclusions	$YB_{4.6}$	1.5	Tetra - P, $a = 7.079(4)$ $b = 4.014(4)$
E	Spheric inclusions	$YPd_{0.3}B_{2.6-2.9}C_{5.2-5.5}$	1	Not detected

OTHER *Ln*–*M*–B–C AND RELATED SYSTEMS

Besides the $LnNi_2B_2C$ systems, a few more quaternary systems were discovered and studied. A few of them also show great promise for study. Beside borocarbides, $La_3Ni_2B_2N_3$ is another system which also shows superconducting transition with T_c ~12.3 K (135). This material also has a crystal structure nearly similar to the B–Ni_2–B–LaN–LaN–LaN type of stacking. This structure is found to be more 2-D in nature than that of borocarbides. However, the neutron diffraction study shows that the nitrogen site is only 90% occupied, yielding $La_3Ni_2B_2N_{2.9}$ as the actual composition (136). The material was found to be a hard type-II, phonon-mediated weak to medium coupling BCS superconductor (137a, 137b). LaNiBN, which also could be synthesized with 90% phase purity, though metallic, does not superconduct down to 4.2 K (135).

Although initially superconductivity was observed in $Ln\mathrm{Pt_2B_2C}$ for Ln = La, Pr, and Y (at 11, 6.5, and 11 K, respectively) only (138), $Ln\mathrm{Pt_{1.5}Au_{0.6}B_2C}$ (Ln = La, Ce, Pr, Nd, Dy, Y) was reported to form in single-phase (substituting Pt by a little excess of Au produces single phase material) (139a, 139b). Nd and Dy analogues order magnetically at 9.6 and 5.9 K respectively (139b). $\mathrm{ThPt_2B_2C}$ could be prepared having $Ln\mathrm{Ni_2B_2C}$ structure, with low impurity content, and was found to exhibit superconductivity at ~7 K (41a–c, 140). Phase formation conditions and existence of superconductivity, in the three series of *d* metal from the same column of the periodic table, do not seem to show any regular behavior as summarized in Table 4.

$\mathrm{LaIr_2B_2C}$ and $\mathrm{LaRh_2B_2C}$ are also reported to form in the same structure, but these compounds do not show any superconducting transition down to 1.4 K (141). Other members of $Ln\mathrm{Rh_2B_2C}$ (La–Er, not Pm, Eu) could also be synthesized in nearly single-phase form (26,142–144). $\mathrm{ThRh_2B_2C}$ does not show any superconductivity down to 1.5 K, while $\mathrm{URh_2B_2C}$ was found to order ferromagnetically below 185 K (41c). Both $\mathrm{CeRh_2B_2C}$ and $\mathrm{CeCo_2B_2C}$ were found to exhibit intermediate valence character (145).

The $Ln\mathrm{Co_2B_2C}$ series is difficult to prepare as single phase, although the majority phase has the $Ln\mathrm{Ni_2B_2C}$-type structure (144, 146, 147). Recent results (144) in $\mathrm{GdCo_2B_2C}_x$ seem to indicate that initial excess of carbon may lead to the purest phase. The $\mathrm{YCo_2B_2C}$ sample does not show any trace of superconductivity down to 2 K (146, 148–150), like $\mathrm{HoCo_2B_2C}$ (down to 30 m K), which exhibits antiferromagnetism (T_N ~ 5.4 K) (151).

Among the borocarbide compounds, the $Ln\mathrm{Ni_2B_2C}$-type of structure is not the only possibility for quaternaries. Siegrist *et al.* (15) have suggested homologous series of general formula $(Ln\mathrm{C})_m(\mathrm{NiB})_n$ by inserting more LnC and/or $\mathrm{Ni_2B_2}$ layers in the structure (see Fig. 1). LnNiBC is one such series (tetragonal, space group *P*4/*nmm*) and LuNiBC was found to possibly superconduct below 2.9 K (152). Unlike $Ln\mathrm{Ni_2B_2C}$, T_c is found to increase by doping with Cu in place of Ni, but decreases with V doping (153). T_c can be increased up to 6.6 K for the Lu- compound and up to 8.9 K for Y-based compounds (154), due to the Cu *d* band contribution to the DOS at E_F (155). LnNiBC (Ln = Gd, Tb, Dy, Ho, Yb) were found to order magnetically and no superconductivity was observed down to 2 K (156a–156f). A giant exchange interaction was found in YbNiBC from ^{170}Yb Mössbauer experiments (57b).

TABLE 4
Phase Formation and Superconductivity in $LnM_2\mathrm{B_2C}$ (M = Ni, Pd, Pt)

d Metal	Phase formation	Superconductivity
Ni	All *Ln*	Small *Ln* ion (Dy...,)
Pd	Large La ion	Small Ln ion (Y)
	Multiphase with small *Ln* ion	
Pt	Large *Ln* ion (La, … , Nd)	Large *Ln* ion (La, Pr)
	Small *Ln* Ion (Y, Dy)	Small *Ln* ion (Y)

Nearly single-phase tetragonal $Ln\mathrm{Ni_4B_4C_{1+\delta}}$ compounds (space group unknown) could also be synthesized for Ln = Y, Ho, Er, and Tm (157). Surprisingly, all these compounds have been reported to have T_c values very close to that of the corresponding $Ln\mathrm{Ni_2B_2C}$ phase, and one wonders whether this could be due to $Ln\mathrm{Ni_2B_2C}$ being an impurity phase in $Ln\mathrm{Ni_4B_4C}$.

$\mathrm{Lu_2NiBC_2}$ was also reported to form in a monoclinically distorted structure (158), while $\mathrm{Y_2NiBC_2}$ forms in a primitive tetragonal structure (159). $\mathrm{Y_3Ni_4B_4C_3}$ has also been reported to form with the possible space group *I*4 (160). This material contains both $\mathrm{YNi_2B_2C}$ and YNiBC as impurity phases. Two superconducting transitions were observed at 10 and 3 K, one of which might come from the pure $\mathrm{Y_3Ni_4B_4C_3}$ phase (160). An attempt was made to study superconductivity in rapidly quenched $\mathrm{YC(NiB)}_x$ (x = 2, 3, 4) borocarbides, and superconductivity was observed in all these materials around 14 K (161) and peaked at 16 K for x = 3, but the final compositions of these samples are unknown. From microwave measurement studies, the possibility of another superconducting Y–Ni–B–C phase with T_c about 23 K was also speculated (132) as a possible surface effect. Recently, from magnetic measurements some signal was also observed in this system around 24 K (162), also of unknown nature.

Single-phase $\mathrm{YNi_2Si_2C}$ ($\mathrm{YNi_2B_2C}$-type structure) and multiphase (but with significant components of $\mathrm{YNi_2B_2C}$-type structure) $\mathrm{YCu_2Si_2C}$ could also be synthezised, but no superconductivity was observed (163). Long ago, the structure of $\mathrm{Dy_2Fe_2Si_2C}$ was reported as monoclinic (*C*2/*m* space group) (164) and other materials ($Ln_2M_2\mathrm{Si_2C}$ with M = Fe and Re) having the same structure were recently reported (165) with possible IV Ce-based materials in both series. Antiferromagnetism was found in Ho- and Er-based $Ln_2\mathrm{Re_2Si_2C}$ (166). In the Ln–Re–B–C system, Lu material exhibit superconductivity at about 6 K; surprisingly both Tb and Gd analogue exhibit superconductivity at 4 K (167). Although it was claimed that superconductivity originates from a quaternary phase, the authors did not present any XRD analysis in their work.

FINAL REMARKS

Microscopic NMR investigations have shown that the superconducting properties of $\mathrm{YNi_2B_2C}$ are influenced by the "local" fluctuations of stoichiometry. Significant effects of off-stoichiometry on superconductivity of $\mathrm{DyNi_2B_2C}$ was known very early in the quaternary borocarbides era, as also on the double reentrance behavior of $\mathrm{HoNi_2B_2C}$ and more recently on measured values of magnetic moments in

$TmNi_2B_2C$. Consequently, to both chemists and physicists, the main interest of quaternary borocarbides, up to now, has been the novel way of coexistence between superconductivity and magnetism within the same energy scale ($T_c \sim T_N$), and its dependence on material preparation. This is also particularly true when identification of quaternary superconducting phase among various phases containing two light elements is involved. Recent development in microanalysis i.e., electron microprobe, and more recently, use of nuclear microprobe on these materials, has proved to be of significant interest. Many questions of fundamental interest are still pending; Are nonstoichiometry effects on superconducting properties of $HoNi_2B_2C$ intrinsic or due to changes in magnetic impurity phases? What is the origin of the anomaly of $1/T_1$ at 10 K in $ErNi_2B_2C$? Does an intrinsic or transferred moment on Ni exist? What is the valence state of U ion in nonsuperconducting UNi_2B_2C? What is the origin of the giant exchange in YbNiBC? and many more. These will require efforts right from "better" preparation and characterization of these materials up to improved understanding of the physics.

ACKNOWLEDGMENTS

During the course of our studies on borocarbide, we are grateful to have many collaborators from different laboratories. Although we specifically mention the names of Professor L.C. Gupta, Professor R. Nagarajan, Professor S. K. Dhar, and Dr. Z. Hossain of Tata Institute of Fundamental Research, Mumbai, India; Dr. E. Leroy and Mr. L. Touron of L.C.M.T.R., C.N.R.S., Thiais, France, Dr. P. Bonville and Dr. J. Hodges of CEA, Saclay, France; Professor I. Felner of University Jerusalem, Israel; Dr. J. P. Sanchez of CEA, Grenoble, France and Dr. J. Lynn of NIST, Gaithersberg, USA, there are many more who worked silently behind the curtain. One of us (C.M.) thanks IFCPAR, New Delhi for financial assistance. Part of this work was done under the IFCPAR (India–France) Project 1808-1.

REFERENCES

1. K. Onnes, *Leiden Comm.* 122b–124c (1911).
2. S. V. Vonsovsky, Yu. A. Izyumov, and E. Z. Kurmaev, "Superconductivity of Transition Metals, Their Alloys and Compounds," Springer Series in Solid State Science, Vol. 27, Chap. 1. Springer-Verlag, Berlin, 1982, and references therein.
3. R. A. Fisher, Treyvaud, Chevrel, and M. Sergent, *Solid State Commun.* **17,** 21 (1975).
4. B. T. Matthias, E. Corenzwit, J. M. Vandenberd, and H. E. Barz, *Proc. Natl. Acad. Sci. USA* **74,** 1334 (1977).
5. (a) F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, *Phys. Rev. Lett.* **43,** 1892 (1979); (b) F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, *J. Magn. Magn. Mater.* **15,** 889 (1980).
6. T. T. M. Palstra, A. A. Menovsky, J. Van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, *Phys. Rev. Lett.* **55,** 2727 (1985).
7. (a) U. Rauchschwalbe, W. Lieke, F. Steglich, C. Godart, L. C. Gupta, and R. D. Parks, *Phys. Rev. B* **30,** 444 (1984); (b) U. Rauchschwalbe, U. Alheim, U. Gottwick, W. Rieke, F. Steglich, C. Godart, L. C. Gupta, and R. D. Parks, *Physica B + C* **126,** 231 (1984).
8. Bednorz and Muller, *Z. Phys. B* **64,** 189 (1986).
9. Schilling, Cattoni, Guo, and Ott, *Nature* **363,** 56 (1993).
10. Chu, Gao, Chen, Huang, and Xue, *Nature* **365,** 323 (1993).
11. C. Mazumdar, R. Nagarajan, C. Godart, L. C. Gupta, M. Latroche, S. K. Dhar, C. Levy-Clement, B. D. Padalia, and R. Vijayaraghavan, *Solid State Commun.* **87,** 413 (1993).
12. R. Nagarajan, C. Mazumdar, Z. Hossain, S. K. Dhar, K. V. Gopalakrishnan, L. C. Gupta, C. Godart, B. D. Padalia, R. Vijayaraghavan, *Phys. Rev. Lett.* **72,** 274 (1994).
13. R. J. Cava, H. Takagi, B. Batlogg, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, R. B. Van Dover, R. J. Felder, T. Siegrist, K. Mizuhashi, J. O. Lee, E. Eisaki, S. A. Carter, and S. Uchida, *Nature* **367,** 146 (1994).
14. R. J. Cava, H. Takagi, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, F, T. Siegrist, B. Batlogg, R. B. Van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Elsaki, and S. Uchida, *Nature* **367,** 252 (1994).
15. T. Siegrist, H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Nature* **367,** 254 (1994).
16. H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Physica C* **224,** 6 (1994).
17. H. Eisaki, H. Takagi, R. J. Cava, B. Batlogg, J. J. Krajewski, W. F. Peck, K. Mizuhashi, J. O. Lee, and S. Uchida, *Phys. Rev. B* **50,** 647 (1994).
18. E. Alleno, Z. Hossain, C. Godart, R. Nagarajan, and L. C. Gupta, *Phys. Rev. B* **52,** 7428 (1995).
19. Z. Hossain, R. Nagarajan, S. M. Pattalwar, S. K. Dhar, L. C. Gupta, and C. Godart, *Physica B* **230&232,** 865 (1997).
20. J. W. Lynn, S. Shanthakumar, Q. Huang, S. K. Sinha, Z. Zossain, L. C. Gupta, R. Nagarajan, and C. Godart, *Phys. Rev. B* **55,** 6584 (1997), & references therein.
21. S. Skanthakumar and J. W. Lynn, *Physica B* **259&261,** 576 (1999).
22. (a) P. C. Canfield, P. L. Gammel, and D. J. Bishop, *Physics Today* 40 (1998); (b) L. C. Gupta, *Physica B* **223&224,** 56 (1995); (c) P. C. Canfield, P. L. Bud'ko, B. K. Cho, W. P. Beyermann, and A. Yatskar, *J. Alloys Compd.* **250,** 596 (1997); (d) G. Hilscher, H. Michor, N. M. Hong, T. Holubar, W. Perthold, M. Vybornov, and P. Rogl, *Physica B* **206&207,** 542 (1995); (e) H. Takagi, M. Nohara, and R. J. Cava, *Physica B* **237&238,** 292 (1997); (f) C. Godart, R. Nagarajan, and L. C. Gupta, *Condens. Matter News* **4,** 9 (1995).
23. J. M. Vandenberg and H. Barz, *Mater. Res. Bull.* **15,** 1493 (1980).
24. (a) M. B. Maple and O. Fisher, "Superconductivity in Ternary Compounds. II. Magnetism and Superconductivity." Springer-Verlag, Berlin, 1982; (b) M. B. Maple, "Ternary Superconductors, Proceedings, Lake Geneva," p. 409. North Holland, Amsterdam, 1981.
25. C. Godart, L. C. Gupta, R. Nagarajan, S. K. Dhar, H. Noel, M. Potel, C. Mazumdar, Z. Hossain, C. Levy-Clement, G. Schiffmacher, B. D. Padalia, and R. Vijayaraghavan, *Phys. Rev. B* **51,** 489 (1995).
26. T. Siegrist, R. J. Cava, J. J. Krajewski, and W. F. Peck, *J. Alloys Compd.* **216,** 135 (1994).
27. B. C. Chakoumakos and M. Paranthaman, *Physica C* **227,** 143 (1994).
28. C. S. Sundar, A. Bharathi, Y. Hariharan, T. S. Radhakrishnan, Z. Hossain, R. Nagarajan, L. C. Gupta, and R. Vijayaraghavan, *Phys. Rev. B* **53,** 2971 (1996).
29. A. Belger, U. Jaenicke-Rossler, D. Lipp, B. Wehner, P. Paufler, and G. Behr, *Physica C* **306,** 277 (1998).
30. M. Buchgeister and W. Pitschke, *Physica C* **264,** 250 (1996).
31. (a) S. Meenakshi, V. Vijayakumar, R. S. Rao, B. K. Godwai, S. K. Sikka, P. Ravindran, Z. Hossain, R. Nagarajan, L. C. Gupta, and R. Vijayaraghavan, *Physica B* **223&224,** 93 (1996); (b) S. Meenakshi, V. Vijayakumar, R. S. Rao, B. K. Godwai, S. K. Sikka, P. Ravindran, Z. Hossain, R. Nagarajan, L. C. Gupta, and R. Vijayaraghavan, *Phys. Rev. B* **58,** 3377 (1998).
32. C. Godart, E . Alleno, E. Tominez, L. C. Gupta, R. Nagarajan, Z. Hossain, J. W. Lynn, P. Bonville, J. A. Hodges, J. P. Sanchez, and I. Felner, *J. Solid State Chem.* **133,** 169 (1997).

33. C. Godart, I. Felner, H. Michor, Hilscher, E. Tominez, and Alleno, *J. Alloys Compd.* **275&277,** 642 (1998).
34. E. Tominez, E. Alleno, C. Godart, P. Bonville, and J. A. Hodges, *J. Alloys Compd.* **262&263,** 462 (1997).
35. (a) T. Sakai, G. Adachi, and J. Shiokawa, *J. Solid State Commun.* **40,** 445 (1981); (b) T. Sakai, G. Adachi, and J. Shiokawa, *J. Less-Common. Met.* **84,** 107 (1982).
36. (a) H. Takeya, T. Hirano, and K. Kadowaki, *Physica C* **256,** 220 (1996); (b) H. Takeya, K. Kadowaki, K. Hirata, and T. Hirano *J. Alloys Compd.* **245,** 94 (1996).
37. M. Xu, P. C. Canfield, J. E. Ostenson, D. K. Finnemore, B. K. Cho, Z. R. Wang, and D. C. Johnston, *Physica C* **227,** 321 (1994).
38. (a) S. Arisawa, T. Hatano, K. Hirata, T. Mochiku, H. Kitaguchi, H. Fujii, H. Kumakura, K. Kadowaki, K. Nakamura, and K. Togano, *Appl. Phys. Lett.* **65,** 1299 (1994); (b) A. Andreone, C. Aruta, F. Fontana, M. Iavarone, M. L. Russo, R. Vaglio, G. W. Crabtree, Y. De Wilde, and M. Polichetti, *Physica C* **312,** 1 (1999); (c) R. Vaglio, A. Andreone, C. Aruta, A. Cassinese, F. Fontana, G. W. Crabtree, M. Iavarone, Y. DeWilde, L. Maritato, C. Attanasio, C. Coccorese, M. Salluzzo, and M. Salvato, *Phys. Rev. B* **56,** 934 (1997); (d) A. Canesi, M. R. Cimberle, C. Ferdeghini, A. Diaspro, P. Guasconi, S. Gariglio, D. Marre, M. Putti, A. S. Siri, F. Canepa, P. Manfrinetti, and A. Palenzona, *Physica C* **299,** 15 (1998).
39. V. Ström, K. S. Kim, A. Mouroux, T. Turkii, A. M. Grishin, and K. V. Rao, *Physica C* **235&240,** 2537 (1995).
40. H. C. Ku, C. C. Lai, Y. B. You, J. H. Shieh, and W. Y. Guan, *Phys. Rev. B* **50,** 351 (1994).
41. (a) Z. Hossain, L. C. Gupta, R. Nagarajan, P. Raj, S. K. Dhar, C. Godart, P. Suryanarayana, S. N. Bagchi, V. G. Date, D. S. C. Purushotham, and R. Vijayaraghavan, *Europhys. Lett.* **28,** 55 (1994); (b) J. L. Sarrao, M. C. De Andrade, J. Herrmann, S. H. Han Z. Fisk, M. B. Maple, and R. J. Cava, *Physica C* **229,** 65 (1994); (c) T. Takabatake, Y. Maeda, T. Konishi, and H. Fujii, *J. Phys. Soc. Jpn.* **63,** 2853 (1994).
42. T. Saito, N. Oka, K. Koyama, K. Mizuno, K. Endo, and H. Deguchi, *J. Magn. Magn. Mater.* **177&181,** 557 (1998).
43. Y. Iwamoto, T. Oda, K. Ueda, and T. Kohara, *Physica B* **230&232,** 886 (1997).
44. C. Looney, A. K. Gangopadhyay, A. K. Klehe, and J. S. Schilling, *Physica C* **252,** 199 (1995).
45. P. G. Pagliuso, C. Rettori, S. B. Oseroff, P. C. Canfield, E. M. Baggio-Saitovitch, and D. Sanchez, *Phys. Rev. B* **58,** 3668 (1998).
46. T. Jacobs, B. A. Willemsen, S. Sridhar, R. Nagarajan, L. C. Gupta, Z. Hossain, C. Mazumdar, P. C. Canfield, and B. K. Cho, *Phys. Rev. B* **52,** 7022 (1995).
47. H. Michor, W. Perthold, T. Holubar, N. M. Hong, and G. Hilscher, *Physica C* **235&240,** 2553 (1994).
48. (a) W. E. Pickett and D. J. Singh, *Phys. Rev. Lett.* **72,** 3702 (1994); (b) L. F. Mattheis, *Phys. Rev. B* **49,** 13279 (1994); (c) R. Coehoorn, *Physica C* **228,** 331 (1994); (d) J. I. Lee, T. S. Zhao, I. G. Kim, B. I. Min, and S. J. Youn, *Phys. Rev. B* **50,** 4030 (1994).
49. N. Khare, A. K. Gupta, S. Khare, L. C. Gupta, R. Nagarajan, Z. Hossain, and R. Vijayaraghavan, *Appl. Phys. Lett.* **69,** 1483 (1996).
50. (a) T. Ekino, H. Fujii, M. Kosugi, Y. Zenitani, and J. Akimitsu, *Physica C* **235&240,** 2529 (1994); (b) E. Bar-Sadeh, I. Felner, U. Asaf, O. Millo, *Phys. Rev. B* **52,** 6734 (1995); (c) C. Stassis, M. Bullock, J. Zarestky, P. C. Canfield, A. I. Goldman, G. Shirane, and S. M. Shapiro, *Phys. Rev. B* **55,** 8678 (1997); (d) M. Bullock, J. Zaretsky, C. Stassis, A. Goldman, P. C. Canfield, Z. Honda, G. Shirane, and S. M. Shapiro, *Phys. Rev. B* **57,** 7916 (1998).
51. (a) D. D. Lawrie and J. P. Franck, *Physica C* **235&240,** 2401 (1994); (b) D. D. Lawrie and J. P. Franck, *Physica C* **245,** 159 (1995).
52. G. Wang and K. Maki, *Phys. Rev. B* **58,** 6493 (1998).
53. S. V. Shulga, S. L. Dreschler, G. Fuchs, K. H. Mueller, K. Winzer, M. Heinecke, and K. Krug, *Phys. Rev. Lett.* **80,** 1730 (1998).
54. M. Nohara, M. Isshiki, H. Takagi, and R. J. Cava, *J. Phys. Soc. Jpn.* **66,** 1888 (1997).
55. R. Prozorov, E. R. Yacoby, I. Felner, and Y. Yeshurun, *Physica C* **233,** 367 (1994).
56. R. Cywinski, Z. P. Han, R. Bewley, R. Cubitt, M. T. Wylie, E. M. Forgan, S. L. Lee, M. Warden, and S. K. Kilcoyne, *Physica C* **233,** 273 (1994).
57. (a) S. K. Dhar, R. Nagarajan, Z. Hossain, E. Tominez, C. Godart, L. C. Gupta, and R. Vijayaraghavan, *Solid State Commun.* **98,** 985 (1996); (b) A. Yatskar, N. K. Budraa, W. P. Beyermann, P. C. Canfield, and S. L. Bud'ko, *Phys. Rev. B* **54,** 3772 (1996); (c) P. Bonville, J. A. Hodges, Z. Hossain, R. Nagarajan, S. K. Dhar, L. C. Gupta E. Alleno, and C. Godar, *Euro. Phys. J. B* **11,** 377 (1999).
58. C. V. Tomy, L. A. Afalfiz, M. R. Lees, J. M. Martin, D. M. Paul, and D. T. Adroja, *Phys. Rev. B* **53,** 307 (1996).
59. C. C. Lai, M. S. Lin, B. You, and H. C. Ku, *Phys. Rev. B* **51,** 420 (1995).
60. L. F. Mattheis, T. T. Siegrist, and R. J. Cava, *Solid State Commun.* **91,** 587 (1994).
61. (a) A. Fujimori, K. Kobayashi, T. Mizokawa, K. Mamiya, A. Sekiyama, H. Eisaki, H. Takagi, S. Uchida, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Phys. Rev. B* **50,** 9660 (1994); (b) M. S. Golden, M. Knupfer, M. Kielwein, M. Buchgeister, J. Fink, D. Teehan, W. E. Pickett, and D. J. Singh, *Europhys. Lett.* **28,** 369 (1994); (c) S. Shin, A. Agui, M. Watanabe, M. Fujisawa, Y. Tezuka, T. Ishii, K. Kobayashi, A. Fujimori, M. Hinomura, and H. Takagi, *Phys. Rev. B* **52,** 15,082 (1995).
62. E. Alleno, C. Teodorescu, N. Franco, E. Tominez, and C. Godart, *in* "International Conference on Solid Compounds of Transition Elements, Rennes, France, 22–25 April, 1997," unpublished.
63. (a) D. M. Poirier, C. G. Olson, D. W. Lynch, M. Schmidt, P. C. Canfield, *J. Phys. Chem. Solids* **56,** 1881 (1995); (b) D. M. Poirier, C. G. Olson, D. W. Lynch, M. Schmidt, and P. C. Canfield, private communication.
64. E. Pellegrin, C. T. Chen, G. Meigs, R. J. Cava, J. J. Krajewski, and W. F. Peck , *Phys. Rev. B* **51,** 16,159 (1995).
65. V. Metlushko, U. Welp, A. Koshelev, I. Aronson, G. W. Crabtree, and P. C. Canfield, *Phys. Rev. Lett.* **79,** 1738 (1997).
66. M. Xu, B. K. Cho, P. C. Canfield, D. K. Finnemore, D. C. Johnston, and D. E. Farrell, *Physica C* **235&240,** 2533 (1994).
67. I. R. Fisher, J. R. Cooper, and P. C. Canfield, *Phys. Rev. B* **56,** 10,820 (1997).
68. E. Johnston-Halperin, J. Fiedler, D. E. Farrell, M. Xu, B. K. Cho, P. C. Canfield, D. K. Finnemore, and D. C. Johnston, *Phys. Rev. B* **51,** 12,852 (1995).
69. (a) M. Heinecke and K. Winzer, *Z. Phys. B* **98,** 147 (1995); (b) G. Goll, M. Heinecke, A. G. M. Jansen, W. Joss, L. Nguyen, E. Steep, K. Winzer, and P. Wyder, *Phys. Rev. B* **53,** 8871 (1996).
70. (a) C. Murayama, N. Mori, H. Takagi,H. Eisaki, K. Mizuhashi, S. Uchida, and R. J. Cava, *Physica C* **235&240,** 2545 (1994); (b) H. Schmidt and H. F. Braun, *Physica C* **229,** 315 (1994); (c) E. Alleno, J. J. Neumeier, J. D. Thompson, P. C. Canfield, and B. K. Cho, *Physica C* **242,** 169 (1995); (d) Y. Uwatoko, G. Oomi, P. C. Canfield, and B. K. Cho, *Physica B* **216,** 329 (1996); (e) T. Ishii, G. Oomi, Y. Uwatoko, P. C. Canfield, and B. K. Cho, *Physica B* **237&238,** 299 (1997).
71. C. Godart, Z. Hossain, L. Gaillet, R. Nagarajan, and L. C. Gupta, *Physica B* **223&224,** 76 (1996).
72. (a) U. Yaron, P. L. Gammel, A. P. Ramirez, D. A. Huse, D. J. Bishop, A. I. Goldman, C. Stassis, P. C. Canfield, K. Mortensen, and L. R. Eskilden, *Nature* **382,** 236 (1996); (b) M. R. Eskildsen, P. L. Gammel, B. P. Barber, A. P. Ramirez, D. J. Bishop, N. H. Andersen, K. Mortensen, C. A. Bolle, C. M. Lieber, and P. C. Canfield, *Phys. Rev. Lett.* **79,** 487 (1997); (c) M. R. Eskildsen, P. L. Gammel, B. P. Barber,

U. Yaron, A. P. Ramirez, D. A. Huse, D. J. Bishop, C. Bolle, C. M. LLieber, S. Oxx, S. Sridhar, N. H. Andersen, K. Mortensen, and P. C. Canfield, *Phys. Rev. Lett.* **78,** 1968 (1997); (d) M. R. Eskildsen, K. Harada, P. L. Gammel, A. B. Abrahamsen, N. H. Andersen, G. Ernst, A. P. Ramirez, D. J. Bishop, K. Mortensen, D. G. Naugle, K. D. D. Rathnayaka, and P. C. Canfield, *Nature* **393,** 242 (1998); (e) D. Paul McK, C. V. Tomy, C. M. Aegerter, R. Cubitt, S. H. Lloyd, E. M. Forgan, S. L. Lee, and M. Yethiraj, *Phys. Rev. Lett.* **80,** 1517 (1998).

73. Y. De Wilde, M. Iavarone, U. Welp, V. Metlushko, A. E. Koshelev, G. W. Aranson, G. W. Crabtree, and P. C. Canfield, *Phys. Rev. Lett.* **78,** 4273 (1997).
74. (a) J. W. Lynn, Q. Huang, S. K. Sinha, Z. Hossain, L. C. Gupta, R. Nagarajan, and C. Godart, *Physica B* **223&224,** 66 (1996); (b) J. W. Lynn, Q. Huang, S. K. Sinha, Z. Hossain, L. C. Gupta, R. Nagarajan, and C. Godart, *J. Appl. Phys.* **79,** 5857 (1996); (c) S. K. Sinha, J. W. Lynn, T. E. Grigereit, Z. Hossain, L. C. Gupta, R. Nagarajan, and C. Godart, *Phys. Rev. B* **51,** 681 (1995).
75. F. G. Aliev, Y. Gorelenko, V. V. Pryadun, S. Vieira, R. Villar, and J. Paredes, *Physica B* **194&196,** 171 (1994).
76. (a) M. El Massalami, M. B. Giordanengo, J. Mondragon, E. M. Baggio-Saitovitch, A. Takeuchi, J. Voiron, and A. Sulpice, *J. Phys. Condens. Matter* **7,** 10015 (1995); (b) P. C. Canfield, B. K. Cho, and K. W. Dennis, *Physica B* **215,** 337 (1995).
77. C. Detlefs, A. I. Goldman, C. Stassis, P. C. Canfield, B. K. Cho, J. P. Hill, and D. Gibbs, *Phys. Rev. B* **53,** 6355 (1996).
78. K. Tomala, J. P. Sanchez, P. Vulliet, P. C. Canfield, Z. Drzazga, and A. Winiarska, *Phys. Rev. B* **58,** 8534 (1998).
79. C. Detlefs, A. H. Z. M. Islam, I. Goldman, C. Stassis, P. C. Canfield, J. P. Hill, and D. Gibbs, *Phys. Rev. B* **55,** 680 (1997).
80. A. Kreyssig, J. Freudenberger, C. Sierks, M. Loewenhaupt, K. H. Muller, A. Hoser, and N. Stuesser, *Physica B* **259&261,** 590 (1999) and references therein.
81. (a) T. E. Grigereit, J. W. Lynn, Q. Huang, A. Santoro, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Phys. Rev. Lett.* **73,** 2756 (1994); (b) Q. Huang, A. Santoro, T. E. Grigereit, J. W. Lynn, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Phys. Rev. B* **51,** 3701 (1995).
82. (a) A. I. Goldman, C. Stassis, P. C. Canfield, J. Zarestky, P. Dervenagas, B. K. Cho, D. C. Johnston, and B.Sternlieb, *Phys. Rev. B* **50,** 9668 (1994); (b) J. P. Hill, B. J. Sternlieb, D. Gibbs, C. Detlefs, A. I. Goldman, C. Stassis, P. C. Canfield, and B. K. Cho, *Phys. Rev. B* **53,** 3487 (1996).
83. H. Schmidt, M. Weber, and H. F. Braun, *Physica C* **246,** 177 (1995).
84. E. Tominez, Ph.D thesis, Universite Paris XI, 1999.
85. C. Mazumdar, Ph.D thesis, IIT Bombay, 1995.
86. N. M. Hong, H. Michor, M. Vybornov, T. Holubar, W. Perthold, G. Hilscher, and P. Rogl, *Physica C* **227,** 85 (1994).
87. T. Kohara T. Oda, K. Ueda, Y. Yamada, A. Mahajan, K. Elankumaran, Z. Hossain, L. C. Gupta, R. Nagarajan, R. Vijayaraghavan, and C. Mazumdar, *Phys. Rev. B* **51,** 3985 (1995).
88. F. Borsa, Q. Hu, K. H. Kim, B. J. Suh, D. R. Torgeson, P. Canfield, D. C. Johnston, Z. R. Wang, M. Xu, and B. Zhong, *Physica C* **235&240,** 2547 (1994).
89. K. Elankumaran, A. V. Mahajan, L. C. Gupta, Z. Hossain, R. Nagarajan, and R. Vijayaraghavan, *Physica B* **223&224,** 90 (1996).
90. T. Oda, Y. Iwamoto, K. Ueda, T. Kohara, A. Mahajan, K. Elankumaran, Z. Hossain, L. C. Gupta, R. Nagarajan, R. Vijayaraghavan, and C. Mazumdar, *Physica B* **223&224,** 79 (1995).
91. D. W. Cooke, J. L. Smith, S. F. J. Cox, A. Morrobel-Sosa, R. L. Lichti, T. L. Estle, B. Hitti, L. C. Gupta, R. Nagarajan, Z. Hossain, C. Mazumdar, and C. Godart, *Phys. Rev. B* **52,** 3864 (1995).
92. (a) B. J. Suh, F. Borsa, D. R. Torgeson, B. K. Cho, P. C. Canfield, D. C. Johnston, J. Y. Rhee, and B. N. Harmon, *Phys. Rev. B* **53,** 6022 (1996); (b) B. J. Suh, F. Borsa, D. R. Torgeson, B. K. Cho, P. C. Canfield, D. C. Johnston, J. Y. Rhee, and B. N. Harmon, *Phys. Rev. B* **54,** 15,341 (1996).
93. D. R. Sanchez, H. Micklitz, M. B. Fontes, S. L. Bud'ko, and E. Baggio-Saitovitch, *Phys. Rev. Lett.* **76,** 507 (1996).
94. (a) P. Bonville, J. A. Hodges, C. Vaast, E. Alleno, C. Godart, L. C. Gupta, Z. Hossain, R. Nagarajan, G. Hilscher, and H. Michor, *Z. Phys. B* **101,** 511 (1996); (b) E. Alleno, P. Bonville, C. Godart, L. C. Gupta, G. Hilscher, J. A. Hodges, Z. Hossain, H. Michor, R. Nagarajan, and C. Vaas, *Hyperfine Interact. C* **1,** 171 (1996).
95. K. Levin, M. J. Nass, C. Ro, and C. S. Grest, *in* "Superconductivity in Magnetic and Exotic Materials" (T. Matsubara A. Kotani, Eds.), p. 104. Springer-Verlag, Berlin, 1984.
96. (a) I. Felner, C. Godart, and E. Alleno, *Physica C* **282&287,** 1317 (1997); (b) J. A. Hodges, P. Bonville, H. Takeya, C. Godart, E. Alleno, G. Hilscher, H. Michor, M. El-Hagary, and A. M. Mulders, *Eur. Phys. J. B* (1999), in press.
97. C. Detlefs, A. H. M. Z. Islam, T. Gu, I. Goldman, C. Stassis, P. C. Canfield, J. P. Hill, and T. Vogt, *Phys. Rev. B* **56,** 7843 (1997).
98. J. P. Sanchez, P. Vulliet, C. Godart, L. C. Gupta, Z. Hossain, and R. Nagarajan, *Phys. Rev. B* **54,** 9421 (1996).
99. Z. Q. Peng, K. Krug, and K. Winzer, *Phys. Rev. B* **57,** 8123 (1998).
100. (a) L. P. Le, R. H. Heffner, G. J. Nieuwenhuys, P. C. Canfield, B. K. Cho, A. Amato, R. Feyerherm, F. N. Gygax, D. E. Mac Laughlin, and A. Schenck, *Physica B* **206&207,** 552 (1995); (b) R. Nagarajan, E. Alleno, S. J. Blundell, C. Mazumdar, D. W. Cooke, S. P. Cottrell, S. F. J. Cox, C. Godart, L. C. Gupta, Z. Hossain, W. L. Hults, Jestadt Th, E. J. Peterson, F. L. Pratt, and J. L. Smith, *Physica B* **259&261,** 588 (1999).
101. A. M. Mulders, P. C. M. Gubbens, and K. H. J. Buschow, *Phys. Rev. B* **54,** 14,963 (1996).
102. (a) U. Gasser, P. Allenspach, A. Furrer, and A. M. Mulders, *J. Alloys Compd.* **275&277,** 587 (1998); (b) A. M. Mulders, P. C. M. Gubbens, U. Gasser, C. Baines, and K. H. J. Buschow, *J. Magn. Magn. Mater.* **177&181,** 555 (1998); (c) A. M. Mulders, P. C. M. Gubbens, U. Gasser, C. Baines, and K. H. J. Buschow, *Phys. Rev. B* **57,** 10,320 (1998).
103. E. Tominez, E. Alleno, and C. Godar, unpublished (1999).
104. V. Chechersky, A. Nath, and R. J. Cava, *Physica C* **303,** 91 (1998).
105. L. C. Gupta, R. Nagarajan, C. Godart, S. K. Dhar, C. Mazumdar, Z. Hossain, C. Levy-Clement B. D. Padalia, and R. Vijayaraghavan, *Physica C* **235&240,** 150 (1994).
106. M. D. Lan, T. J. Chang, and C. S. Miaw, *J. Phys. Chem. Solids* **59,** 1285 (1998).
107. K. Eversmann, A. Handstein, G. Fuchs, L. Cao, and K. H. Muller, *Physica C* **266,** 27 (1996).
108. Z. Hossain, R. Nagarajan, S. M. Pattalwar, S. K. Dhar, L. C. Gupta, and C. Godart, *in* "International Conference SCES 96, Zurich, Switzerland, August 19–22, 1996."
109. B. K. Cho, P. C. Canfield, and D. C. Johnston, *Phys. Rev. Lett.* **77,** 163 (1996).
110. Z. Hossain, R. Nagarajan, S. K. Dhar, and L. C. Gupta, *Physica B* **259&261,** 606 (1998).
111. L. C. Gupta, *Phil. Mag.* **77,** 717 (1998).
112. C. V. Tomy, G. Balakrishnan, and D. M. C. K. Paul, *Physica C* **248,** 349 (1995).
113. (a) A. K. Gangopadhay, A. J. Schuetz, and J. S. Schilling, *Physica C* **246,** 317 (1995); (b) Z. Zeng, D. E. Ellis, D. Guenzburger, and E. M. Baggio-Saitovitch, *Phys. Rev. B* **53,** 6613 (1996); (c) P. Ravindran, B. Johansson, and O. Eriksson, *Phys. Rev. B* **58,** 3381 (1998).
114. S. L. Bud'ko, M. Elmassalami, M. B. Fontes, J. Mondragon, W. Vanoni, B. Giordanengo, and E. M. Baggio-Saitovitch, *Physica C* **243,** 183 (1995).
115. C. K. Choi, E. S. Choi, J. H. Lee, Y. W. Park, and Y. S. Song, *Phys. Rev. B* **57,** 126 (1998).

116. M. El Massalami, R. E. Rapp, and G. J. Nieuwenhuys, *Physica C* **304,** 184 (1998).
117. A. Yatskar, S. L. Bud'ko, P. C. Canfield, W. P. Beyermann, G. M. Schmiedeshoff, M. S. Torkachvili, C. H. Mielke, and A. Lacerda, *Physica B* **230&232,** 876 (1997).
118. R. Sala, F. Borsa, E. Lee, and P. C. Canfield, *Phys. Rev. B* **56,** 6 (1995–1997).
119. R. Nagarajan, L. C. Gupta, S. K. Dhar, C. Mazumdar, Z. Hossain, C. Godart, B. Levy-Clement, D. Padalia, and R. Vijayaraghavan, *Physica B* **206&207,** 548 (1995).
120. (a) Z. Hossain, L. C. Gupta, C. Mazumdar, R. Nagarajan, S. K. Dhar, C. Godart, C. Levy-Clement, B. D. Padalia, and R. Vijayaraghavan, *Solid State Commun.* **92,** 341 (1994); (b) L. C. Gupta, R. Nagarajan, S. K. Dhar, C. Mazumdar, Z. Hossain, C. Godart, C. Levy-Clement, B. D. Padalia, and R. Vijayaraghavan, *in* "Proceedings of the International Conference on Physical Metallurgy," p. 494. Gordon and Breach, 1994.
121. D. T. Adroja, B. D. Rainford, A. V. Volkozub, and P. A. J. De Groot, *Physica C* **229,** 193 (1994).
122. Y. Y. Sun, I. Rusakova, R. L. Meng, Y. Cao, P. Gautier-Picard, and C. W. Chu, *Physica C* **230,** 435 (1994).
123. (a) H. Fujii, S. Ikeda, T. Kimura, S. I. Arisawa, K. Hirata, H. Kumakura, K. Kadowski, and K. Togano, *Jpn. J. of Appl. Phys.* **33,** 4B, L590 (1994); (b) S. Ikeda, H. Fujii, T. Kimura, H. Kumakura, K. Kadowaki, and K. Togano, *Jpn. J. Appl. Phys.* **33,** 7A, 3896 (1994).
124. (a) H. W. Zandbergen, T. J. Gortenmulder, J. L. Sarrac, J. C. Harrison, M. C. De Amdrade, J. Hermann, S. H. Han, Z. Fisk, M. B. Maple, and R. J. Cava, *Physica C* **232,** 328 (1994); (b) H. W. Zandbergen, E. J. Van Zwet, J. C. Sarrac, J. C. De Andrade, J. Hermann, S. H. Han, Z. Fisk, M. B. Maple, and R. J. Cava, *Physica C* **229,** 29 (1994).
125. (a) H. W. Zandbergen, W. G. Sloof, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Physica C* **226,** 365 (1994); (b) C. L. Jia, Y. H. Xu, M. Beyss, F. Peter, and K. Urban, *Physica C* **229,** 325 (1994).
126. V. Ström, K. S. Kim, A. M. Grishin, and K. V. Rao, *J. Appl. Phys.* **79,** 5860 (1996).
127. V. Ström, K. S. Kim, A. M. Grishin, and K. V. Rao, *J. Mater. Res.* **11,** 572 (1996).
128. E. Tominez, P. Berger, E. Alleno, B. Decamps, G. Schiffmacher, M. Bohn, and C. Godart *in* "International Conference ICFE3, Paris, Sept., 1997."
129. P. Berger and G. Revel, *Ann. Chim.* **19,** 283 (1994).
130. E. Tominez, P. Berger, E. Alleno, B. Decamps, G. Schiffmacher, M. Bohn, and C. Godart, *J. Alloys Compd.* **275&277,** 123 (1998).
131. P. Berger, C. Godart, E. Alleno, E. Tominez, L. Daudin, and J. P. Gallien, *in* "Proceedings ISBB99, 1999."
132. R. M. Kadam, M. D. Sastry, Z. Hossain, C. Mazumdar, R. Nagarajan, L. C. Gupta, C. Godart, and R. Vijayaraghavan, *Physica C* **232,** 359 (1994).
133. Y. Y. Xue, Y. Cao, R. L. Meng, C. Kinalidis, and C. W. Chu, *Physica C* **227,** 63 (1994).
134. O. M. Cappannini, C. O. Rodriguez, and N. E. Christensen, *Physica C* **306,** 101 (1998).
135. R. J. Cava, H. W. Zandbergen, B. Batlogg, H. Eisaki, H. Takagi, J. J. Krajewski, W. F. Peck, E. M. Gyorgy, and S. Uchida, *Nature* **372,** 245 (1994).
136. Q. Huang, B. C. Chakoumakos, A. Santoro, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Physica C* **244,** 101 (1995).
137. (a) H. Michor, R. Krendelsberger, G. Hilscher, E. Bauer, C. Dusek, R. Hauser, L. Naber, D. Werner, P. Rogl, and H. W. Zandbergen, *Phys. Rev. B* **54,** 9408 (1996); (b) H. Michor, G. Hilscher, R. Krendelsberger, P. Rogl, and F. Bouree, *Phys. Rev. B* **58,** 15,045 (1998).
138. R. J. Cava, B. Batlogg, T. Siegrist, J. J. Krajewski, W. F. Peck, S. Carter, R. J. Felder, H. Takagi, and R. B. Van Dover, *Phys. Rev. B* **49,** 12,384 (1994).
139. (a) R. J. Cava, B. Batlogg, J. J. Krajewski, W. F. Peck, T. Siegrist, R. M. Flemeing, S. Carter, H. Takagi, R. J. Felder, R. B. Van Dover, and L. W. Rupp, *Physica C* **226,** 170 (1994); (b) M. Buchgeister, G. Fuchs, J. Klosowski, U. Wiesner, and J. Zawadzki, *Physica C* **255,** 19 (1995).
140. F. S. Jeng, Y. B. You, H. C. Ku, and J. C. Ho, *Phys. Rev. B* **53,** 3492 (1996).
141. R. J. Cava, T. Siegrist, B. Batlogg, H. Takagi, H. Eisaki, S. A. Carter, J. J. Krajewski, and W. F. Peck, *Phys. Rev. B* **50,** 12,966 (1994).
142. J. Ye, T. Shishido, T. Sasaki, T. Takahashi, K. Obara, R. Note, T. Matsumoto, and T. Fukuda, *J. Solid State Chem.* **133,** 77 (1997).
143. T. Shishido, J. Ye, T. Sasaki, R. Note, K. Obara, T. Takahashi, T. Matsumoto, and T. Fukuda, *J. Solid State Chem.* **133,** 82 (1997).
144. J. Ye, T. Shishido, T. Matsumoto, and T. Fukuda, *J. Alloys Compd.* **275&277,** 76 (1998).
145. S. A. Carter, B. Batlogg, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Phys. Rev. B* **51,** 12,829 (1995).
146. K. Kadowaki, H. Takeya, K. Hirata, and T. Mochiku, *Physica B* **206&207,** 555 (1995).
147. F. M. Mulder, J. H. V. J. Brabers, R. Coehorn, R. C. Thiel, K. H. J. Buschow, and F. R. De Boer, *J. Alloys Compd.* **217,** 118 (1995).
148. H. Schmidt, M. Muller, and H. F. Braun, *Physica C* **235&240,** 779 (1994).
149. S. L. Bud'ko, B. Giordanengo, A. Sulpice, M. B. Fontes, and E. M. Baggio-Saitovich, *Solid State Commun.* **94,** 119 (1995).
150. C. C. Hoellwarth, P. Klavins, and R. N. Shelton, *Phys. Rev. B* **53,** 2579 (1996).
151. R. E. Rapp and M. El Massalami, *Phys. Rev. B* **60,** 3355 (1999).
152. L. Gao, X. D. Qiu, Y. Cao, R. L. Meng, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, *Phys. Rev. B* **50,** 9445 (1994).
153. X. D. Qiu, L. Gao, R. L. Meng, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, *Phys. Rev. B* **53,** 12,318 (1996).
154. A. K. Gangopadhyay and J. S. Schilling, *Phys. Rev. B* **54,** 10,107 (1996).
155. E. Z. Kurmaev, A. V. Ezhov, V. M. Cherkashenko, S. N. Shamin, S. Bartkowski, M. Neumann, and A. K. Gangopadhyay, *Solid State Commun.* **105,** 65 (1998).
156. (a) M. El Massalami, E. Baggio-Saitovitch, and A. Sulpice, *J. Alloys Compd.* **228,** 49 (1995); (b) L. J. Chang, C. V. Tomy, K. Mac Paul, N. H. Andersen, and M. Yethiraj, *J. Phys. Condens. Matter* **8,** 2119 (1996); (c) Q. Huang, J. W. Lynn, A. Santoro, B. C. Chakoumakos, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Physica C* **271,** 311 (1996); (d) M. El Massalami, M. S. Da Costa, M. A. Novak, and V. Barthem, *J. Magn. Magn. Mater.* **188,** 379 (1998); (e) X. Z. Zhou, H. P. Hunkel, J. A. Cowen, and G. Williams, *Physica B* **246&247,** 421 (1998); (f) Z. Hossain, R. Nagarajan, and L. C. Gupta, *J. Magn. Magn. Mater.* **184,** 235 (1998).
157. Q. W. Yan, B. G. Shen, Y. N. Wei, T. Y. Zhao, Y. S. Yao, B. Yin, C. Dong, F. W. Wang, Z. H. Cheng, P. L. Zhang, H. Y. Gong, and Y. F. Li, *Phys. Rev. B* **51,** 8395 (1995).
158. H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, *J. Solid State Chem.* **110,** 196 (1994).
159. Rukang Li, X. Chaoshui, Z. Hong, Bin Lu, and Y. Li, *J. Alloys Compd.* **223,** 53 (1995).
160. H. Kito, S. Ikeda, S. Takekawa, H. Abe, and H. Kitazawa, *Physica C* **291,** 332 (1997).
161. K. S. Kim, S. C. Yu, V. Ström, and K. V. Rao, *J. Magn. Magn. Mater.* **177&181,** 553 (1998).
162. H. Szillat, H. Kuhn, Schuster Th, P. Majewski, M. Seeger, F. Aldinger, and H. Kronmuller, *Physica C* **280,** 43 (1997).
163. W. Zhao, J. Tang, Y. Lee, and C. J. OConnor, *J. Appl. Phys.* **79,** 5870 (1996).
164. L. Paccard and D. Paccard, *J. Less-Common. Met.* **136,** 297 (1988).
165. T. Hufken, A. M. Witte, and W. Jeitschko, *J. Alloys Compd.* **266,** (1998).

166. A. D. Chinchure, S. K. Dhar, R. Nagarajan, V. R. Marathe, and L. C. Gupta, *J. Magn. Magn. Mater.* **195,** 43 (1999).
167. A. D. Chinchure, R. Nagarajan, and L. C. Gupta, *Solid State Commun.* **110,** 691 (1999).
168. L. C. Gupta, R. Nagarajan, Z. Hossain, C. Mazumdar, S. K. Dhar, C. Godart, C. Levy-Clement, B. D. Padalia, and R. Vijayaraghavan, *J. Magn. Magn. Mater.* **140&144,** 2053 (1995).
169. R. Nagarajan, L. C. Gupta, C. Mazumdar, Z. Hossain, S. K. Dhar, C. Godart, B. D. Padalia, and R. Vijayaraghavan, *J. Alloys Compd.* **225,** 571 (1995).
170. Z. Hossain, S. Dhar, R. Nagarajan, L. C. Gupta, C. Godart, and R. Vijayaraghavan, *in* "Intermag Conf. 95, Poster AQ12, San Antonio, Texas, 18–21 April, 1995."
171. K. Prassides, A. Lappas, M. Buchgeister, and P. Verges, *Europhys. Lett*. **29,** 641 (1995).
172. S. L. Bud'ko, M. B. Fontes, D. Aliaga-Guerra, and E. M. Baggio-Saitovitch, *Phys. Rev. B* **52,** 305 (1995).
173. Z. Hossain, L. C. Gupta, R. Nagarajan, S. K. Dhar, C. Godart, and R. Vijayaraghavan, *in* "International Conf. SCES 95, Goa, India, Sept. 27–30, 1995;" *Physica B* **223&224,** 99 (1996).
174. B. K. Cho, P. C. Canfield, and D. C. Johnston, *Phys. Rev. B* **52,** 3844 (1995).
175. P. Dervenagas, J. Zaretstky, C. Stassis, A. I. Goldman, P. C. Canfield, and B. K. Cho, *Physica B* **212,** 1 (1995).
176. R. J. Cava, H. Takagi, H. Eisaki, H. W. Zandbergen, T. Siegrist, A. B. Batlogg, J. J. Krajewski, W. F. Peck, S. Carter, K. Mizuhaski, J. O. Lee, S. Uchida, R. Felder, and R. B. Van Dover, *Physica C* **235&240,** 154 (1994).
177. G. Hilscher, T. Holubar, N. M. Hong, H. Michor, W. Perthold, M. Vybornov, and P. Rogl, *in* "Proceedings ICM 94, Warsaw, Poland, August 22–26 1994."
178. J. S. Kim, W. W. Kim, and G. R. Stewart, *Phys. Rev. B* **50,** 3485 (1994).
179. S. A. Carter, B. Batlogg, R. J. Cava, J. J. Krajewski, W. F. Peck, and H. Takagi, *Phys. Rev. B* **50,** 4216 (1994).
180. M. Baran, L. Gladczuk, J. Gorecka, H. Szymczak, R. Szymczak, Z. Drzazga, and H. Winiarska, *J. Magn. Magn. Mater.* **136,** L1 (1994).
181. H. W. Zandbergen, J. Jansen, R. J. Cava, J. J. Krajewski, and W. F. Peck, *Nature* **372,** 759 (1994).
182. Z. Hossain, R. Nagarajan, S. K. Dhar, and L. C. Gupta, *in* "Proceedings of Solid State Physics Symposium, Mumbai, India, Dec. 27–31, 1996," Vol. 39C, 56.
183. M. B. Fontes, J. C. Trochez, B. Giordanengo, S. L. Budko, D. R. Sanchez, E. M. Baggio-Saitovitch, and M. A. Continentino, *Phys. Rev. B* **60,** 6781 (1999).