High-temperature ferromagnetism and superconductivity in new borides – mechanism and utilization

Abstract

In order to develop new superconducting borides, we have studied firstly the mechanism for high transition temperature in MgB$_2$ by intimate cooperation of experiment and theory. By using self-made high-quality single crystals, we measured upper critical fields and thermal conductivity in magnetic fields. We explain the characteristics in terms of interacting two-dimensional holes and three-dimensional electrons, both of which become superconducting. We have secondly made thin superconducting films of MgB$_2$ by electrophoretic method. Thirdly, we have found high-temperature superconductivity of 18K in cubic Y$_2$C$_3$. Our improved sintering method is essential in raising drastically the previously reported transition temperature of 11K. For magnetic materials, on the other hand, we have found colossal magnetoresistance in EuB$_6$ doped with Ca. The magnitude in similar to that in Mn oxides. Concerning high-temperature ferromagnetism in doped CaB$_6$, CaB$_2$C$_2$ and related materials, we find by $\mu$SR in CeB$_6$ small internal fields, and strange temperature dependence of NMR relaxation time in CaB$_2$C$_2$. However, we have not been able to characterize the condition of ferromagnetism.

keywords: borides, superconductivity, ferromagnetism, MgB$_2$, Y$_2$C$_3$

1 Introduction

Our NEDO program was motivated by two previous findings: superconductivity in MgB$_2$ and ferromagnetism in divalent hexaborides without magnetic elements. In 2001, one of our members (Akimitsu) found a new high-temperature superconductor MgB$_2$, which ignited intensive research on this and related materials. In our NEDO project, we have investigated its basic property by cooperation of theory and experiment for the purpose of clarifying the mechanism of high-temperature superconductivity. The large electron-phonon coupling in MgB$_2$ is due to the presence of two-dimensional $\sigma$-type holes. On the other hand, three-dimensional carriers, which are populated in the $\pi$ band, have a weaker tendency toward superconductivity. The unique properties of MgB$_2$ come from the coexistence of different characters of carriers. Tunnelling [1] spectroscopies have found
multiple gaps of different magnitudes. We have synthesized good single crystals of MgB$_2$, and measured various physical quantities ranging from thermal conductivity in magnetic fields, upper critical fields, to phonon and electron spectroscopies [2]. We have succeeded in explaining the peculiar temperature dependence of transport and specific heat in terms of the two-band picture.

Another motivation was the report by Ott and Fisk in 1999 that doped CaB$_6$ and related materials show high-temperature ferromagnetism. We have extended the possibility to CaB$_2$C$_2$ [3]. Although μSR and NMR show strange magnetic properties including small internal fields, our intensive research has not yet made it possible to control the condition for ferromagnetism. Hence the ferromagnetism may originate from tiny amount of Fe impurities. However, iron borides should not be the origin since intentional doping of Fe does not increase the ferromagnetism. In addition to CeB$_6$, we have studied various divalent and trivalent hexaborides. Among them, we found in Eu$_{1-x}$Ca$_x$B$_6$ drastic decrease of the electrical resistivity by magnetic field [4]. The ensuing colossal negative magnetoresistance has a magnitude comparable to Mn oxides. In the course of theoretical study, we considered a new mechanism of ferromagnetism in the two-band system where electrons and holes coexist. An exactly soluble two-band model with partially polarized ground state has been found in one-dimension [5].

We briefly explain below some selected results obtained within the NEDO program.

2 High-Temperature Superconductivity in MgB$_2$

As a result of our NEDO program, we established that MgB$_2$ is the first case where the superconducting properties are determined by coexistence of strongly two-dimensional $\sigma$ bands and three-dimensional $\pi$ bands. The direct evidence comes from measurement of transport and thermal properties in magnetic fields.

2.1 Thermal conductivity of MgB$_2$ with carbon doping

We have measured the thermal conductivity $\kappa$ in the basal plane of the hexagonal crystal lattice of MgB$_2$ [6]. The experiments were made on a single crystalline specimen with an average lateral dimension of 0.2 mm. The analysis of the $\kappa(T)$ data in zero magnetic field indicates that the superconducting state involves two different gaps with significantly different maximum values. The measurements of $\kappa(H)$ at constant temperature $T$ confirm this conclusion and they allow for a rather precise evaluation of the upper critical field for the chosen field orientations. The substitution of carbon for boron leads to a considerable reduction of the electronic heat transport, while the phonon thermal conductivity seems to be much less sensitive to impurities. The introduction of carbon enhances mostly the intraband scattering in the $\sigma$-band. In contrast to the previously observed anomalous behavior of pure MgB$_2$, the Wiedemann-Franz law is valid for Mg(B$_{0.94}$C$_{0.06}$)$_2$ at low temperatures. Figure 1 shows the thermal conductivity and the Wiedemann-Franz ratio normalized to the free-electron value. It is clear that carbon doping kills the anomalously large ratio.

2.2 Phonon anomaly in MgB$_2$

We have already reported that the temperature dependence of the integrated intensity of the generalized phonon density-of-states observed by inelastic neutron scattering measurements showed clear anomalous behavior, which increases with decreasing temperature
below $T_c$ in the energy range, close to $E_{2g}$ (B in-plane bond stretching) and $B_{1g}$ (B out-of-plane bond bending) phonon modes at $\Gamma$ point in the Brillouin zone. To clarify the contribution to the electron-phonon coupling strength from these phonons, we performed inelastic neutron scattering measurements using Al-doped MgB$_2$. The integrated intensity of the generalized phonon density-of-states gradually changes with increasing Al contents.

2.3 Electrophoretic synthesis of thin superconducting films

We made a new apparatus to make thin films of MgB$_2$ by electrophoretic synthesis. In this apparatus we can prevent oxidation of Mg, and use durable materials against strong acid or alkali. We can synthesize at wide range of temperatures because of build-in refrigerator. By this apparatus we are making high-quality superconducting films of MgB$_2$, which will be important for application.

2.4 Two-band theory for MgB$_2$

We have refined and completed the analysis of the anomalous behavior of the thermal conductivity as a function of temperature and magnetic field. The fits to the experimental data give clear evidence in favor of the two-gap model of the superconductivity. The two-band model we use includes intra-band coupling $V_\sigma$ for the two-dimensional band, $V_\pi$ for the three-dimensional band, and the interband coupling $V$ connecting $\sigma$ and $\pi$ bands. We find that the smaller superconducting gap due to three-dimensional electrons closes at the same upper critical field $H_{c2}$ as the larger gap closes. However, the smaller gap decreases much faster with small interband couplings. Since the smaller gap plays the role of the bottle neck for robustness against magnetic fields, the controls of the $\pi$ band is important in improving the material for practical application.

Figure 2 shows examples of our model calculation. With the ratio of coupling parameters shown in the figure, we find good overall agreement with experimental results. For example, at low temperatures $H_{c2}$ for fields along the $c$-axis is about $20\%$ of $H_{c2}^{a,b}$ perpendicular to the $c$-axis. This large anisotropy, however, decreases with increasing $T$. In the single-band BCS theory, the change of anisotropy in $H_{c2}$ cannot be explained. Our result shown in the left part Fig.2 nicely reproduces this behavior. The specific heat at the superconducting transition is rather peculiar. The jump $0.80$ of the specific heat at zero field is much smaller than the BCS value of $1.43$ in the unit of the figure, and becomes
even smaller with increasing field. We explain this peculiarity in terms of the two-band model. These results will be published soon.

3 New Superconducting Materials

New superconducting borides and carbides were found by our NEDO study. We find that W$_7$Re$_{13}$X (X=B or C) systems become superconductor around 7 K. The crystal structure is of cubic $\beta$-Mn type (space group: $P4_132$) where the Re atoms form the tilted octahedron. The magnetization curves show a typical type-II superconducting behavior, and the lower critical field, $H_{c1}(0)$, the upper critical field, $H_{c2}(0)$ and the Ginzburg-Landau (GL) parameter are 7.7 mT, 11.4 T, 54 for X=B and 4.0 mT, 12.6 T, 80 for X=C. From the specific heat measurement, the magnitude of superconducting gap is estimated to be $2/k_B T_c = 4.28$ and 4.02, respectively. We conclude that the symmetry of superconductivity in both compounds is isotropic s-wave from temperature dependence of specific heat below $T_c$. We conclude that this $\beta$-Mn type crystal structure can be stabilized by a small amount of B and C atoms.

We found [7] another high-temperature superconductivity at 18 K in an yttrium sesquicarbide system, Y$_2$C$_3$ by a magnetization measurement, although this material with a maximum $T_c$ of 11.5 K has already been investigated by Krupa et al. [J. Less-Common Met. 17 (1969) 91]. The crystal structure of Y$_2$C$_3$ is a cubic (Pu$_2$C$_3$-type) structure, and the lattice parameters are varied by heat treatment conditions. The magnetization curves of this compound show a typical type-II superconducting behavior, and the lower critical field, $H_{c1}(0)$, is 3.5 mT. The $T_c$ value in this system is changed in the range from 15 K to 18 K, depending on sintering conditions. The sintering conditions in this work are different from those in a previous work by Krupka et al. We successfully synthesized a new high-$T_c$ phase in Y$_2$C$_3$. The Pu$_2$C$_3$-type cubic structure shown in Fig.3. Also shown is the susceptibility indicating clearly the superconducting transition. Relationship between the slight change of structure and transition temperature is being studied by synchrotron radiation.

A protocol has been worked out for growth of high quality single crystals of the heavy Fermion YbAlB$_4$. We made crystals with resistance ratio of approximately 100. Pressure
Figure 3: Crystal structure of $Y_2C_3$ (left), and the magnetic susceptibility against temperature (right). The superconducting transition occurs at 18 K.

experiments are in progress for the study of quantum critical behavior in this boride.

4 Magnetic Properties of Divalent Hexaborides

4.1 Electronic structure of $CaB_6$

We have performed high-resolution angle-resolved photoemission spectroscopy (ARPES) on $CaB_6$. It was believed that the material is a semimetal or a small-gap semiconductor. The band structure determined by ARPES shows a 1 eV energy gap at the X point between the valence and the conduction bands. We found a small electron pocket at the X point, whose carrier number is estimated to be $(4 \sim 5) \times 10^{19}$ cm$^{-3}$, in good agreement with the Hall resistivity measurement with the same crystal. The experimental results are discussed in comparison with band structure calculations and theoretical models for the high-temperature ferromagnetism [2]. For example, the original semimetallic model for high-temperature ferromagnetism loses its validity.

4.2 Fe doping into divalent hexaborides

We have worked extensively on deliberate doping of $CaB_6$ with transition metals. We find that crystal growth from Al melts with Ca:Fe ratios of order 1:1 with excess B give weak ferromagnetism with $T_c < 50K$. The incorporation of Fe in the bulk of these crystals is at the 0.1 % level. We find similar results with Mn, Co and Ni in place of Fe in the growth melts. However, growths with small La additions (Ca:La of 1:0.005) again with Ca:Fe of order 1:1 show weak ferromagnetism present at 300 K. This result indicates that La is in some as yet unknown way enabling incorporation of Fe at low levels into the crystals such that the high temperature weak ferromagnetism exists. The saturation moment is of order 1 emu per mole $CaB_6$. With Co in place of Fe, there is no ferromagnetism at 300K. These experiments are now directing the experimental effort towards understanding the dependence of Fe uptake on La concentration.

4.3 Colossal magnetoresistance in $Eu_{1-x}Ca_xB_6$

Although both Eu and Ca enter as divalent cations and therefore the chemical substitution is isoelectronic, it appears that the concentration of itinerant charge carriers decreases
substantially with increasing Ca content. This is partly reflected in the low temperature behaviour of the electrical resistivity where with increasing Ca content, an enhanced residual resistivity is observed. This enhancement is, however, not due to disorder on the cation sublattice. By applying external magnetic fields these residual resistivities can be reduced by orders of magnitude. On an absolute scale, the resulting negative magnetoresistance grows with increasing content, at least up to $x = 0.75$. In particular, we have analyzed the available resistivity $\rho(T, H)$ and Hall constant $R_H(T, H)$ data for the compound with $x = 0.4$. Both parameters are significantly influenced by the bulk magnetization of the material. At low temperatures, the field induced reduction of $\rho$ is exponential in $M$, such that $\rho = \rho(0) \exp(-\beta M)$ over more than two orders of magnitude. The reduction ceases, once the disorder dominated value of $\rho$ is reached in high fields. This exponential dependence on $M$ suggests that some intrinsic spin valve process may dominate the low temperature electronic transport in this material. An unexpected universal dependence on the bulk magnetization has been found for the Hall constant in the form of $R_H = R_0 + R'[1 - \exp\{-\alpha(M-M_0)\}]\Theta(M-M_0)$. Here, $R_0$ is the high temperature normal Hall coefficient and $M_0$ a threshold magnetization. The physical reason for this feature, which is valid for temperatures between 2 and 200K and magnetic fields up to 70 kOe, has not yet been identified. Figure 4 shows the experimental results [8].

4.4 EPR and NMR on divalent hexaborides

A large variation in the size of the ordered moment has been variously reported by different groups. An EPR study we collaborated in has found that an EPR signal with $g = 2$ is found associated with the larger ordered moments, that this signal can be removed by chemical etching and that these apparent surface moments have their own ordering temperature which is approximately 450 K. The semiconductor like Kondo insulator SmB$_6$ has been carefully looked at for weak ferromagnetism. We have detected ferromagnetism in samples of SmB$_6$ through susceptibility measurements near 50 K, where the background magnetic susceptibility coming from Sm is smallest. The moment we found was of 1emu/mole.

High resolution NMR experiments on CaB$_6$ at one fixed field revealed a splitting of the central transition into two lines. Each of these two lines exhibits a magnetic shift of the order of 100 ppm but of opposite sign, barely varying with temperature between 300 and 7 K. Similar features were subsequently identified for BaB$_6$, which exhibits weak
ferromagnetic order at temperatures exceeding 300 K. The spin lattice relaxation rate is 
essentially constant with temperature for all studied MB$_6$-type materials, i.e., with M = Sr, Ca and Ba and low concentrations of defects. However, the relaxation very much depends on the magnitude of the external magnetic field, i.e., it decreases with increasing magnetic field approximately as $H^{-2}$. These features indicate that the relaxation is due to free magnetic moments, and from our data it may be concluded that even in the magnetically ordered state, not all of the magnetic degrees of freedom involving some localized moments have been quenched.

4.5 NMR on CaB$_2$C$_2$

We performed $^{13}$C NMR investigation of $^{13}$C isotope enriched CaB$_2$C$_2$ samples. The major advantage of $^{13}$C NMR is that $^{13}$C is spin $I = 1/2$, hence there are no complications by nuclear quadrupole interactions with electric field gradient. We found a major surprise in $^{13}$C NMR spin-lattice relaxation rate $^{13}(1/T_1)$. First, the temperature dependence of $^{13}(1/T_1)$ observed in high magnetic field of 9-Tesla is consistent with the typical correlated electron behavior in itinerant antiferromagnets. Second, we found a large magnetic-field dependence of $^{13}(1/T_1)$ between 0.35 Tesla and 9 Tesla. In 0.35 Tesla, the bulk magnetization measurements showed that the ordered moments are not saturated by magnetic field. Thus our observation of highly enhanced $^{13}(1/T_1)$ at 0.35 Tesla might point towards the presence of fluctuating moments in the bulk of the sample. Furthermore, the magnetic field dependence continues up to about 300 K. Since the energy scale of the 9-Tesla applied magnetic field is only 10 K, the field dependence of $^{13}(1/T_1)$ is not consistent with a scenario that $^{13}(1/T_1)$ below 300 K is simply dominated by paramagnetic impurities. Instead, our results suggest that certain collective effects of magnetic moments are involved in spin fluctuations of CaB$_2$C$_2$.

4.6 Uranium doping of CaB$_6$

Replacing U for Ca in semiconducting CaB$_6$ at the few at.% level induces metallic behaviour and Kondo-type phenomena at low temperatures, a rather unusual feature for U impurities in metallic hosts. For Ca$_{0.999}$U$_{0.008}$B$_6$, the resistance minimum occurs at $T = 17$ K. The subsequent characteristic logarithmic increase of the resistivity with decreasing temperature merges into the expected $T^2$ dependence below 0.8 K. Data of the low-temperature specific heat and the magnetization are analyzed by employing a simple resonance-level model. These results are shown in Fig.5 [9]. Analogous measurements on LaB$_6$ with a small amount of U revealed no traces of Kondo behavior, above 0.4 K.

5 Multipole Moments in Trivalent Hexaborides

LaB$_6$ is the reference compound for trivalent hexaborides. As compared with divalent hexaborides such as BaB$_6$, one more conduction electron per site makes the system from intrinsic semiconductor to metal. Thus comparison between divalent and trivalent hexaborides should contribute to deeper understanding of hexaborides. Besides, LaB$_6$ is known as the best electron emission material because of its low work function and high melting temperature. As the atomic number of rare-earth element increases, finite number of $f$ electrons are introduced in the system. The orbital and spin degrees of freedom of $4f$ electrons adds rich features in the system such as the quadrupole order and other electronic orders of even higher multipoles. In our NEDO project, we studied mainly CeB$_6$ both experimentally and theoretically.
5.1 Neutron and $\mu$SR measurements of magnetic properties of CeB$_6$ and Ce$_{1-x}$La$_x$B$_6$

We reported previously that polarized neutron study for CeB$_6$ reveals the presence of a significant amount of localized spin density between the nearest neighbor boron atoms. However, more careful neutron experiments demonstrated that the observed magnetic form factor was distorted by the extinction effect. After correcting the extinction effect, we got a proper magnetic form factor.

The order parameter in phase IV in Ce$_{1-x}$La$_x$B$_6$ remains to be identified. The magnetic properties of Ce$_{0.7}$La$_{0.3}$B$_6$ single crystal have been studied by muon spin relaxation ($\mu$SR) [10]. The absence of a clear muon spin precession under zero external field in phase IV indicates that no commensurate long-range magnetic order is present in this phase. Moreover, the time spectra under a longitudinal field strongly suggests that there are two sources of local fields exerting coherently on muons in phase IV. It was inferred from the muon Knight shift under a transverse field that the direction of the effective internal magnetic field probed by muon exhibits a marked change between phase III and IV.

5.2 Intersite multipolar interactions for the complicated ordering pattern

We introduced the pseudo-dipolar interaction between next-nearest neighbors and explained the stability of the peculiar ordering pattern of CeB$_6$ [11]. The pseudo-dipolar interaction was first introduced phenomenologically, but detailed microscopic calculation has confirmed the presence of this term in the model including the proper orbitally degeneracy [12].

5.3 Octupole ordering model in Ce$_{1-x}$La$_x$B$_6$

Possible order parameters of the phase IV in Ce$_x$La$_{1-x}$B$_6$ have been discussed with special attention to the lattice distortion recently observed. We have proposed a $\Gamma_{5u}$-type octupole order with finite wave number as the origin of the distortion along the [111] direction. The $\Gamma_8$ crystalline electric field level splits into three levels by a mean field with the $\Gamma_{5u}$ symmetry. The ground and highest singlets have the same quadrupole moment, while the intermediate doublet has an opposite sign. It is shown that any collinear order of $\Gamma_{5u}$-type
octupole moment accompanies the $\Gamma_{5g}$-type *ferro-quadrupole* order, and the coupling of the quadrupole moment with the lattice induces the distortion. The cusp in the magnetization at the phase transition is also reproduced [13]. The octupole model is further supported by recent experiment using uniaxial pressure and resonant X-ray scattering.

6 Summary

In summary, achievements of our NEDO project dealing with superconductivity and magnetism in borides include:

* Establishing the two-band superconductivity in MgB$_2$,
* Drastically increasing the superconducting transition temperature in Y$_2$C$_3$,
* Finding new superconductors W$_7$Re$_{13}$X (X=B or C),
* Finding colossal magnetoresistance in Eu$_{1-x}$Ca$_x$B$_6$,
* Finding Kondo effect in Ca$_{1-x}$U$_x$B$_6$,
* Proposing octupole ordering in Ce$_{1-x}$La$_x$B$_6$.

Although the research on superconductivity was very successful, we could not attain the initial goal concerning the high-temperature ferromagnetism. As a byproduct with potential future application, however, we found colossal magnetoresistance in a related divalent hexaboride.

In the course of our NEDO project, international cooperation including both experimentalists and theoreticians was very useful. We sincerely thank NEDO for giving us this wonderful opportunity.

References


List of other most important papers and patents

Papers


Patents
