行政院國家科學委員會補助專題研究計畫成果報告

過渡元素材料的電子結構及磁特性之研究

計畫類別：個別型計畫


執行期間：92年08月01日至95年10月31日

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執行單位：國立成功大學物理系

中華民國96年1月3日
We have performed a systematic study of Fe-doped MgB2 alloys using 11B NMR spectroscopy. The Knight shift, line shape, as well as spin-lattice relaxation time on each individual composition have been identified. The central transition and quadrupole line widths increase with Fe concentration, attributed to the effect of disorder on these measurements. The temperature independence of the central transition line width further confirms no magnetic moment associated with these dopants. In addition, the value of $T_1 T$ remains unchanged with Fe content, indicative of little or no effect on the B-2p Fermi level density of states (DOS) by substituting Fe in the Mg sublattice of MgB2. These observations clearly revealed that the drop of $T_c$ cannot be accounted for either by the pair breaking or by the electronic DOS reduction. It thus revealed the importance of the phonon contributions to the change of $T_c$, presumably due to the decreased phonon frequency and/or the reduced electron-phonon coupling strength through Fe-doping.

**Keywords:** NMR, Knight shift, quadrupole interaction, spin-lattice relaxation, Fermi-level density of states

There is general agreement from intense experimental and theoretical research that MgB2 is a two-gap superconductor associated with the coexistence of two-dimensional $\sigma$ bands and three-dimensional $\pi$ bands near the Fermi surface. Its peculiar superconducting features have been attributed to the different electron-phonon coupling strengths in both bands. Due to the simplicity in the chemical composition, a large number of efforts have been devoted to study the chemical substitutions of MgB2, focusing on the understanding of the nature of the parent compound as well as the possible improvement of application
potential. However, only Al replacing Mg and C replacing B had been possible for higher doping level. Other substitutions such as the transition metal elements in the Mg sublattice are limited to a very low concentration.

Among these substitutions, the Fe-substituted MgB$_2$ system is of particular interest owing to the presence of Fe ions in the samples. The suppression of critical temperature $T_c$ with Fe concentration is moderate (see Fig. 1) as compared with single crystal Mg$_{1-x}$Mn$_x$B$_2$ where the superconductivity is lost for $x = 0.02$. Although the polycrystalline samples exhibit a relatively slow decrease in $T_c$ with $x$, presumably due to an overestimate on the Mn content arising from incomplete solubility, the magnetic pair-breaking effect has been considered as a major source for the rapid $T_c$ drop in Mg$_{1-x}$Mn$_x$B$_2$. In this regard, it is important to examine whether Fe ions carry magnetic moments in Mg$_{1-x}$Fe$_x$B$_2$. Together with other origins such as electronic and phonon effects, a reliable interpretation for the observed $T_c$ variation is expected to be quite complicated.

Fig. 1

Polycrystalline Fe-doped MgB$_2$ compounds were synthesized as follows. The starting precursor powders for sample preparation are crystalline magnesium (99.8%, 325 mesh) from Alfa Aesar, amorphous boron (95 - 97%) from Fluka and nano particles of Fe2O3 (10 - 15 nm) from Pi-Kem. Nano Fe2O3 was used as opposed to Fe because (a) the nano-scale morphology of the Fe2O3 allowed for very uniform mixing, and (b) the presence of oxygen was not significant because it was already present in the Mg or B precursor. Appropriate amount of Mg and B in the stoichiometric proportion of 1:2 was first weighed and nano particles of Fe2O3 with wt % of 0, 0.5, 1.0, 2.0, and 5.0 % were then added accordingly. The powders were then well mixed and ground for 60 min. This was followed by pressing the resultant powder into pellets of 5 mm in diameter and about 4 mm thick. Each of the pellets was then wrapped in Ta foil with the presence of some Mg turnings and annealed at 900 C for 15 min with heating and cooling rate of 15 C/min.

Room-temperature x-ray diffraction taken with Cu Kα radiation on powder specimens was consistent with the C32
crystal structure. Strong reflections in these alloys could be indexed according to the expected structure with several weak peaks corresponding to the MgO phase which had little effect on the NMR measurements. Based on the atomic radii of Fe (0.14 nm) and Mg (0.15 nm), it is natural to conclude that Fe atoms substitute on the Mg site rather than the B (0.085 nm) site. As illustrated in Fig. 2, lattice parameters were found to decrease linearly up to 2% Fe2O3 in weight, indicating that the Mg site is successfully replaced by Fe atoms, according to the Vegard's law.

![Graph showing lattice parameter changes](image)

Fig. 2

NMR measurements were performed using a Varian 300 spectrometer, with a constant field of 7.05 T. A home-built probe was employed for both room-temperature and high-temperature experiments. Since the studied materials are metals, powder samples were used to avoid the skin depth problem of the rf transmission power. Each specimen was put in a plastic vial that showed no observable $^{11}$B NMR signal. The Knight shifts here were referred to the $^{11}$B resonance frequency of one molar aqueous NaBH4.

![Graph showing NMR signal changes](image)

Fig. 3

Within the C32 crystal structure for Mg$_{1-x}$Fe$_x$B$_2$, there is a single B site with D$_{3h}$ symmetry, leading to a symmetric one-site NMR powder pattern for each composition, as shown in Fig. 3. Here the central transition $^{11}$B NMR spectra were obtained from the Fourier transform (FT) of the solid echo pulse sequence. The $^{11}$B Knight shift here was determined from the position of the maximum of each spectrum with respect to an aqueous NaBH$_4$ solution reference. The observed Knight shifts are temperature independent in the normal state, a typical character for paramagnetic metals. A small Knight
shift of about 86 ppm was obtained for our MgB2, close to the values reported previously. Such a tiny shift has been attributed to few s-character electrons at the Fermi energy. The p-electrons also have little contribution to the Knight shift due to the low hyperfine field from p states, even though the B-2p Fermi level density of states N_{2p}(E_F) is relatively high in MgB2. Note that the value of the Knight shift remains constant with the present doping level, indicative of the minor influence on N_{2p}(E_F) by substituting Fe in the Mg sublattice of MgB2.

As mentioned, the substitution of Fe in MgB2 may produce the pair breaking effect, leading to a drop of Tc. Here the NMR line width could be employed to examine this magnetic effect on the resonance spectrum. The central transition line width, determined from the full width at half maximum (FWHM), is about 14 kHz for pure MgB2. The narrow width, mainly arising from the nuclear magnetic dipolar interaction, indicates good quality of this sample. However, as shown in Fig. 4, the line width tends to increase with Fe concentration but still remains small values (~ 35 kHz for Mg_{0.97}Fe_{0.03}B_2), which is not likely due to the strong local magnetism. Indeed, the line widths were found to be temperature independent for all studied compositions, definitely proving that no magnetic moment is associated with the Fe ions. Hence, the Fe impurities in MgB2 could not act as strong magnetic scattering centers, and the possibility for the Tc suppression arising from magnetic-induced pair breaking could be excluded. Such a finding agrees well with the recently theoretical result that predicted a non-magnetic character for Fe in MgB2.

As for the multi-band superconductor MgB2, scattering by nonmagnetic impurities should have a similar Tc suppression trend just as a pair breaking effect from magnetic impurities in conventional superconductors. For the present Fe-doping, the Fe ions which are magnetically inactive would behave like nonmagnetic impurities. Accordingly, with addition of Fe in MgB2, the degree of hyperfine field inhomogeneity enhances, resulting in a broader NMR spectrum as observed. Alternatively, such the blurred feature could be driven by distortions near the Fe sites leading to shorter B-B distances, which would result locally in an enhancement on the
dipolar interaction. This effect will also introduce a modification on the local electric field gradient (EFG), leading to a change on the quadrupole frequency \( v_Q \). However, as we will demonstrate below, this possibility should be ruled out since no visible change in \( v_Q \) has been found as increasing Fe concentration.

In Fig. 5, we show the low-frequency satellite line \( m = +1/2 \leftrightarrow +3/2 \) for each composition, obtained from the integration of spin echo signals. It clearly indicates that the quadrupole frequency of about 840 kHz is almost unaffected by Fe substitution, whereas the sharp satellite line edge gradually smears out as MgB2 deviates from its stoichiometry. This observation could be accounted for by the disorder effect which introduces a distribution of the local electric field gradient and thus broaden the features of the satellite line. Such a disorder effect appears to be significant with increasing doping concentration. As a matter of fact, the observed broadening in transition width increasing with Fe content could result from the same effect.

In principle, the first order quadrupole shift is the main effect shaping the satellite line, while the central line shape is affected by the second-order quadrupole interaction. Therefore, the effect of disorder should broaden both line shapes in a similar manner. To provide a convincing picture, we performed a shape function fitting with convolution to reproduce the synthetic spectra. For each individual composition, two broadening factors \( \delta_c \) and \( \delta_s \) were employed for the central transition and satellite line fittings, respectively. The best-simulated results (not shown here) yield the corresponding \( \delta_c \) and \( \delta_s \) values, which are plotted in the inset of Fig. 4 as a function of Fe concentration. As one can see, both factors correlate well with each other, indicating that the phenomena of the line broadening are essentially due to the same effect.

Band structure modifications due to disorder effect are very common in ordinary metals. Such an effect usually broadens the band width and/or shifts the Fermi energy, leading to a change of the Fermi-level density of states (DOS). In order to shed light on this scenario, we carried out the NMR spin lattice
relaxation time $T_1$ measurement which is known as a sensitive probe of the band structure near the Fermi level in non-magnetic metals. We measured each $T_1$ by centering the resonance frequency at $m = +1/2 \leftrightarrow -1/2$ transition line using the inversion recovery method. In these experiments, the relaxation process involves the adjacent pairs of spin levels, and the corresponding spin-lattice relaxation is a multi-exponential expression. To provide accurate values, each $T_1$ has been measured several times and the averaged $T_1$ for each temperature was displayed in Fig. 6.

![Figure 6](image)

In paramagnetic metals, the spin-lattice relaxation rate measurement is a direct probe of the Fermi surface. While the relaxation of nuclei in a metal is normally governed by their coupling to the spin of the s-character electrons, other mechanisms such as orbital and dipolar relaxation become important when the Fermi-contact term is essentially small. This would be appropriate for the case of MgB2. From the theoretical calculations, B-p bands are all at the Fermi level. On the other hand, only a few s boron electrons are close to the Fermi surface. The low $N_s(E_F)$ should have a minor contribution to the observed relaxation rate, in spite of the stronger hyperfine field for the B-s electrons at the Fermi level. This gives the dominant p-orbital and dipolar relaxation rates, and the experimental $T_1$ is mainly proportional to the square of the B-2p Fermi level DOS, $N_{2p}(E_F)^2$.

As indicated from Fig. 6, the $T_1$ results for all compositions exhibit the Korringa behavior, confirming a conduction-electron mechanism for the observed relaxation. However, the value of $1/T_1T$ is almost unchanged with Fe doping level, indicative of a negligible effect on $N_{2p}(E_F)$ as substituting Fe for Mg in MgB2, being consistent with the observations in the Knight shift measurement. In these regards, the plausible Tc suppression associated with the electronic DOS reduction is unlikely based on our NMR investigations.

The absence of DOS correction with Fe content in Mg$_{1-x}$Fe$_x$B$_2$ is quite different from that in the Mg$_{1-x}$Al$_x$B$_2$ system, which shows a progressive decrease of $N_{2p}(E_F)$ with increasing the Al doping level up to $x=0.5$. It is generally believed that the substitution of Al$^{3+}$ ions in MgB2 will dump electrons in the $\sigma$ bands of the Fermi
energy, leading to a reduction in the DOS. Such a band filling effect with the corresponding changes in the DOS seems to be sufficient to understand the drop of Tc as a function of Al concentration. For the case of Fe-doping, the dopants have been proposed to be trivalent ions. In that case, one would expect that the nonmagnetic Fe\textsuperscript{3+} ions in MgB\textsubscript{2} will act as electron donors and have an effect similar to those of Al\textsuperscript{3+} ions. However, no marked change in the DOS has been found from our T\textsubscript{1} analysis. Such a discrepancy may be qualitatively interpreted as follows: The disorder effect causes an E\textsubscript{F} shift to a higher DOS whereas the band filling effect reduces the DOS. As a consequence, the compensation between both mechanisms renders no visible modification in the DOS as evidenced by the present NMR measurements.

In conclusions, we have studied the influence of Fe substitution on the Tc suppression of MgB\textsubscript{2} by means of the \textsuperscript{11}B NMR measurement in the normal state. Results clearly revealed that the observed Tc variation cannot be accounted for either by the magnetic induced pair breaking or by the electronic DOS reduction. We thus point to the importance of the phonon contributions to the change of Tc, presumably attributed to the decreased phonon frequency and/or the reduced electron-phonon coupling strength through Fe doping.

**Note:** Publications under this project are as follows:


2. C. S. Lue, C. F. Chen, J. Y. Lin, Y. T. Yu, and Y. K. Kuo, 2007, Thermoelectric properties of quaternary Heusler alloys Fe\textsubscript{2}VAl\textsubscript{1-x}Si\textsubscript{x}, Phys. Rev. B (accepted). (SCI)

3. C. S. Lue, B. X. Xie, and T. H. Su, 2007, Effect of Zn doping on the spin gap characteristics of BaCu\textsubscript{2}V\textsubscript{2}O\textsubscript{8}: A \textsuperscript{51}V NMR study, J. Magn. Magn. Mater. (accepted) (SCI)


7. C. S. Lue, T. H. Su, B. X. Xie, and C. Cheng, 2006, Comparative NMR study of hybridization effect and structural
stability in D0_{22}-type NbAl_{3} and NbGa_{3}, Phys. Rev. B 74, 094101. (SCI)


17. Y. –K. Kuo, K. M. Sivakumar, C. R. Lin, C. S. Lue, and S. T. Lin, 2005, Electrical and thermal transport properties of icosahedral Al_{70}Pd_{22.5} (Re_{1-x}Mn_{x})_{7.5} quasicrystals, J. Appl. Phys. 97, 103717. (SCI)


19. C. S. Lue, H. D. Yang, and Y. K. Kuo, 2005, Low temperature specific heat enhancement in Fe_{2}VGa, Chin. J. Phys. 43, 775. (SCI)
20. **C. S. Lue** and B. X. Xie, 2005, NMR investigation of BaCu$_2$V$_2$O$_8$ in alternating-chain and dimer-chain models, Phys. Rev. B 72, 052409. (SCI)


27. **C. S. Lue** and Y. –K. Kuo, 2004, Thermal and transport properties of the Heusler-type compounds Fe$_{2-x}$Ti$_{1+x}$Sn, J. Appl. Phys. 96, 2681. (SCI)


30. 呂欽山、賴文振，2004, 核磁共振量測物質的微觀電磁性質, 物理雙月刊廿六卷三期, 519.