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Raman study of element doping effects on the superconductivity of MgB$_2$

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The influences of phonon frequency and unit cell volume on the superconductivity of element-doped MgB$_2$ are discussed with reference to a Raman study on SiC, C, Mn, and Al-Ag-doped Mg-B materials. A phenomenon has been found in the doped samples, in that the phonon frequency changes to counteract the crystal lattice variation to keep the system stable within a Grüneisen parameter of 2.0–4.0. The chemical doping effects on phonon frequency and unit cell volume can be explained by the harmonic-anharmonic competition in the compounds. A decreased electronic density of states is responsible for the depression of superconductivity that is seen in doped MgB$_2$. The possibility of a high critical temperature, $T_c$, in the Mg-B system exists if the material can possess both a high phonon frequency and a big unit cell volume at the same time, as indicated by the isotope effect and hydrogenation experiments.

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The discovery of superconductivity at 40 K in MgB$_2$ (Ref. 1) has attracted intense scientific interest towards modifying the structural and electronic properties of this material to improve its critical transition temperature $T_c$. Although some possible routes to increase the $T_c$, such as increasing the phonon frequency, increasing the density of states, and expanding the unit cell volume, have been employed in the Mg-B system, all attempts to modify the MgB$_2$ host lattice to further increase $T_c$ have failed. It seems that most factors which influence the superconductivity of MgB$_2$ have already been optimized in the pure Mg-B system. Chemical substitution, a method to change several physical properties, such as the electron density, crystal lattice parameters, and the disorder effect, has been well investigated by different groups. On the fact of $T_c$ depression, Takenobu et al. and Lee et al. explain it as due to crystal lattice contraction, electron doping induced electronic structure variation, and the disorder effect arising from substitution, while Cortus et al. ascribe the $T_c$ depression to band filling and interband scattering effects. It should be noted that Kazakov et al. have suggested that the main issue is the competition between the effects of atomic size disorder, which causes the $T_c$ to decrease, and those of crystal lattice expansion, which tends to increase $T_c$, which is in agreement with the positive $T_c$ dependence on unit cell volume for MgB$_2$ samples under pressure, as estimated by Deemyad et al. However, in the case of Ag and Al codoped MgB$_2$ [Mg$_{1-2x}$Ag$_x$Al$_x$B$_2$], the $\alpha$-axis and $\gamma$-axis parameters increase with doping, and the volume $V$ also increases, while the $T_c$ decreases with doping. The authors attribute these characteristics to a disorder effect caused by the chemical substitution. In a phonon-mediated superconductor, it is well known that the $T_c$ is proportional to the averaged phonon frequency $\langle \omega \rangle$, according to the McMillan formula. Factor group analysis predicts four modes at the $\Gamma$ point of the Brillouin zone for the $P6/mmm$ space group in MgB$_2$: a silent $B_{1g}$ mode, the $E_{2g}$ Raman mode, and the infrared active $E_{1u}$ and $A_{2u}$ modes. Only the $E_{2g}$ mode is Raman active and strongly coupled to the electronic conduction $\sigma$ bands. The high $T_c$ for MgB$_2$ is partially attributed to the strong intensity of electron-phonon coupling due to the high frequency of the $E_{2g}$ phonon mode.

Chemical substitution is expected to modify the phonon spectrum, by diversifying the phonon frequency and electron-phonon coupling strength. Carbon substitution effects on the superconductivity have been studied widely, because carbon is believed to be one of the most effective elements for incorporation into the MgB$_2$ lattice. The $E_{2g}$ phonon peak shifts to the higher energy side, and the peak is narrowed with increasing $x$ in Mg(B$_{1-x}$C$_x$)$_2$. The increased $E_{2g}$ peak energy and narrowing of the peak width suggests the weakening of electron-phonon coupling by C substitution. The effects of C substitution are an increase in impurity scattering and band filling, which reduces the density of states and alters the shape of the Fermi surface. The decrease in $T_c$ in C-doped samples is mainly attributed to the decreased density of states and changes in phonon modes, while the increased scattering also contributes to the $T_c$ reduction, mainly at low doping concentrations. As a carbon source, nano-SiC has proved to be one of the most effective substitution dopants for improving the critical current density $J_c$, irreversibility field $H_{irr}$, and upper critical field $H_{c2}$ in MgB$_2$ since the discovery of superconductivity in this material. In spite of intensive studies on the transport properties of SiC-doped MgB$_2$, the mechanism explaining why SiC doping is special remains unclear, especially since there has not been adequate research on its effects on the superconductivity. In this work, the $T_c$ dependence on the phonon frequency and unit cell volume is researched systematically to explain the mechanism responsible for the superconductivity depression with different SiC doping levels in MgB$_2$. Furthermore, to find out how variation of the unit cell volume and the frequency of the $E_{2g}$ mode affect the superconductivity in doped MgB$_2$ and to further explore the mechanism of superconductivity, the influence of the phonon frequency and lattice parameters on $T_c$ for SiC-doped MgB$_2$ is compared with previous work on carbon, Mn, and Al-Ag-doped MgB$_2$. Then the possible origin of high $T_c$ in this material is proposed, based on the isotopic effects and hydrogenation experiments.

MgB$_2$ superconductor bulks were prepared by an in situ...
reaction process, using mixed powders of micron size magnesium (99%) and nanosized amorphous boron (99.99%), with different levels of 0, 5, 10, and 15 wt% nanosized SiC (99%). The mixtures were ground sufficiently, using an agate mortar in an argon gas filled glove box, and pressed into bulks with dimensions of 10 mm diameter and about 5 mm thickness under a pressure of ~600 MPa. Then the samples were sintered in a tube furnace at 750 °C for 30 min, at a heating rate of 5 °C/min, and furnace-cooled to room temperature. High purity argon gas flow was maintained throughout the sintering process. A pure MgB₂ sample was synthesized using 10 hours of sintering at 800 °C in high purity argon atmosphere. Part of the sample was hydrogenated in 30 atm H₂ atmosphere at 500 °C for 2 h to compare the superconductivity, phonon frequency, and unit cell volume.

All samples were characterized by x-ray diffraction (XRD; D:\\max-2000), and the lattice parameters were refined with the aid of JADE 5.0 software. The Raman scattering was measured using a confocal laser Raman spectrometer (Renishaw inVia plus) with a 100× microscope. The 514.5 nm line of an Ar⁺ laser was used for excitation, with the laser power maintained at about 20 mW, measured on the laser spot on the samples, in order to avoid laser heating effects on the studied materials. Several spots were selected on the same sample to collect the Raman signals, in order to make sure that the results were consistent. The magnetoresistivity, $\rho(H,T)$, was measured, with $H$ applied perpendicular to the current direction, using the four probe method in the temperature range from 4.2 K to 300 K and a field range from 0 T to 9 T [in a physical properties measurement system (PPMS: Quantum Design)]. The $T_c$ values were deduced from the $\rho(H,T)$ curves. The $T_c$ values of the sample before and after hydrogenation were determined by ac susceptibility measurements executed on the PPMS.

The Raman spectra of pure MgB₂ and SiC-doped MgB₂, measured at ambient temperature with an excitation wavelength of 514.5 nm, are shown in Fig. 1. Two broadbands centered at about 600 and 800 cm⁻¹ are observed for all materials. In pure MgB₂, the most prominent phonon peak located at lower frequency (centered at ~566 cm⁻¹) is assigned to the $E_{2g}$ mode. The high frequency Raman band [centered at 759 cm⁻¹ and marked as phonon density of states (PDOS) in Fig. 1] has also been observed earlier in MgB₂, and attributed to phonon density of states PDOS due to disorder. This second peak is responsible for the asymmetric profiles generally reported in the $E_{2g}$ mode frequency region in MgB₂. The Raman spectra of MgB₂ preserve their main characteristics as the SiC concentration increases, except that there is a new low frequency peak centered at 250 cm⁻¹. This peak arises from the Raman active $E_{2g}$ mode in the cubic structure of Mg₅Si, which is described by the Fm̅3m space group, and its intensity is enhanced with the increasing Mg₅Si content in the compounds. However, the $E_{2g}$ peak of the SiC-doped samples shifts to higher frequency, and its relative intensity and full width at half maximum (FWHM) decrease considerably, as shown in Figs. 1 and 2. At the same time, the peak centered at about 780 cm⁻¹ gradually becomes the most prominent feature in the Raman spectrum at higher doping levels. The FWHM of the $E_{2g}$ peak in pure MgB₂ exceeds 200 cm⁻¹, which is attributed to the presence of strong electron-phonon coupling and phonon-phonon interaction (anharmonicity). The latest calculations demonstrate that the Raman data can be explained if dynamical effects beyond the adiabatic Born-Oppenheimer approximation and electron lifetime effects are included in the phonon self-energy, without invoking anharmonicity. This result is consistent with the harmonic phonon dispersion results measured by inelastic x-ray scattering. As for the 5 wt% SiC-doped sample, its Raman spectrum shows little difference from that of the pure MgB₂.
MgB$_2$ because of the low level of both the Mg$_2$Si inclusions and C substitution for the boron. In the range up to 15 wt % in SiC-doped samples, the $E_{2g}$ peak shifts from 566 cm$^{-1}$ in pure MgB$_2$ to 622 cm$^{-1}$, while the PDOS peak gradually shifts from 759 cm$^{-1}$ to 788 cm$^{-1}$, as shown in Fig. 2. This behavior indicates that the band structure of MgB$_2$ shows a high phonon vibration frequency with the increasing SiC doping levels. This transformation has also been found in C-doped MgB$_2$ systems and is explained by the C substitution for B in the MgB$_2$, which causes a lattice relaxation around the C impurity atom because the C-B bond length, about 1.71 Å, is smaller than the B-B bond length (~1.78 Å). However, the SiC-doped MgB$_2$ shows a sharper rate of increase than in the C- doped samples. This is because the C atoms in SiC are easier to incorporate into the MgB$_2$ lattice than those from carbon black or graphite. According to the dual reaction model, SiC reacts with Mg to release highly reactive C at a low temperature, which is exactly the formation temperature of MgB$_2$. As a result, the C incorporation into the lattice and the inclusion of nanoparticles of Mg$_2$Si impurity in MgB$_2$ grains take place simultaneously. The actual carbon substitution level reached 3.2 at % at the 15 wt % doping level, whereas the actual C substitution from a comparable doping level of nanoparticles of carbon is less than 2 at %, which is also reflected in the smaller variation of the $a$-axis lattice parameter. Similar behavior was observed earlier in Mg$_{1-x}$Al$_x$B$_2$ superconductors in the high aluminum content region, because of the Al substitution induced lattice shrinkage.

Although it seems that SiC-, C-, or Al-doped MgB$_2$ should actually show higher $T_c$ than the pure sample, due to the strong electron-phonon coupling induced by the high phonon frequency, $T_c$ depression occurs in all the small size atom-doped systems. In contrast to SiC-, C-, and Al-doped MgB$_2$, with Al-Ag codoping, the $E_{2g}$ mode shifts to low frequency as the Al-Ag content increases, as observed from Raman spectroscopy. The $E_{2g}$ frequency in Al-Ag codoped MgB$_2$ decreases from 560 cm$^{-1}$ in pure MgB$_2$ to about 540 cm$^{-1}$ in Mg$_{0.97}$Al$_{0.03}$B$_2$. The $T_c$ of element doped MgB$_2$ deteriorates as the doping level is increased, regardless of the hardening or softening of the frequency of the $E_{2g}$ mode, and is lower than that of the pure MgB$_2$, 39.4 K, as shown in Fig. 3(a).

The analysis of lattice parameters shows a great constriction of the unit cells after SiC substitution, as shown in Table I, which is in accordance with previously reported carbide doped systems. This constriction due to chemical substitution corresponds to an application of hydrostatic pressure of 3.5–4.0 GPa. Due to the negative pressure coefficient, $dT_c/dP=-1.03-2.0$ K GPa$^{-1}$, the lattice shrinkage degraded the $T_c$, in a similar way to applying ambient pressure on the MgB$_2$. The frequency of the $E_{2g}$ mode under high pressure shows the same trend as for small size atom element doped MgB$_2$. To overcome the influence of the negative pressure coefficient on the superconductivity, the unit cell volume can be expanded via the substitution of atoms with a larger ionic radius, which would be expected to increase the $T_c$. Although Mn doping can increase the crystal cell volume, $T_c$ decreases sharply with a much more sensitive response than in the cases of C- and Al-doped samples.

![Raman study of element doping effects on the...](image_url)

**FIG. 3.** (Color online) $T_c$ dependence on (a) the frequency of the $E_{2g}$ mode, and (b) the unit cell volume for SiC-, carbon-, and Al-Ag-doped MgB$_2$, and for Mg$_{10}$B$_2$. The SiC-doped samples were sintered at 750 °C for 30 min. The carbon-doped samples were sintered at 900 °C for 2 h. The Al-Ag-doped MgB$_2$ was sintered at 950 °C for 2 h, while the magenta lines shows the $T_c$ and unit cell volume value of pure MgB$_2$ in Ref. 1.

The $E_{2g}$ peak remains almost un-changed as the Mn content is experimentally increased to 1 wt %. The authors believe that the Mn substitution does not weaken the electron-phonon coupling for the stable phonon frequency, but rather, electron pairs were destroyed by the magnetism of the Mn atoms. To keep the electronic structure and carrier concentration stable, while expanding the crystal unit cell volume, Al and Ag codoping effects with the same stoichiometric ratio have been explored. The crystal lattice expands along both the $a$- and $c$-axis directions, because the average ionic size, 0.843 Å for both Al and Ag, is larger than the ionic size of Mg (0.720 Å), but the $T_c$ is depressed as the doping levels increase. According to the $T_c$ dependence on the unit cell volume, both the volume contraction in SiC- and C-doped...
MgB$_2$, and the volume expansion in Al-Ag codoped MgB$_2$ cannot induce $T_c$ enhancement in the doped system, as shown in Fig. 3(b). Deemyad et al. have estimated the $T_c$ dependence on unit cell volume for MgB$_2$ samples under pressure as $T_c(V) = d\ln T_c/d\ln V_{0} = 0$ (Ref. 1) $= +4.18$ using the bulk modulus $B = 147.2$ GPa, $T_c(0) = 39.1$ K, and $dT_c/dP = -1.11$ K/GPa. As for the chemical doping effects, the SiC- and C-doped MgB$_2$ shows higher $T_c$ values, from +4.5 at low doping levels to +12 at high doping levels, due to the extra electrons. Although the Al-Ag codoped MgB$_2$ keeps the system in electron balance, its Fermi surface, $M$ is the mass of the atom, and $(\omega^2)$ is the average value of the square of a characteristic phonon frequency. Deemyad et al. have deduced $T_c(V)$ on the basis of Eqs. (1) and (2),

$$
\frac{d\ln T_c}{d\ln V} = -\gamma - \Delta_1 \left( \frac{\partial \ln \mu^2}{\partial \ln V} + \Delta_2 \left( \frac{\partial \ln \eta}{\partial \ln V} + 2\gamma \right) \right),
$$

where $\omega_{E_{2g}}$ is the vibration frequency, $V$ is the relevant unit cell volume, $d\omega_{E_{2g}}$ and $dV$ are the variations in $\omega_{E_{2g}}$ and $V$ due to the substitutions, and $\gamma$ is the Grüneisen parameter. Figure 4 plots the relationship between the frequency of the $E_{2g}$ mode and the unit cell volume for the SiC-, carbon-, and Al-Ag-doped MgB$_2$. The undoped samples processed under different conditions show different unit cell volumes and phonon frequencies. The unit cell volume of pure MgB$_2$ in Ref. 1, 29.06 Å$^3$, is also shown in Fig. 4 for comparison. The SiC-doped samples show high Grüneisen parameters because both carbon substitution and inclusions can cause great crystal distortion. The C-doped samples show slowly increased phonon frequency with decreased unit cell volume. An approximately linear variation with the Grüneisen parameter, $\gamma = 2.0 - 4.0$, can be deduced for the doped MgB$_2$, which is consistent with the values for pure MgB$_2$ under high pressure that were measured by Goncharov et al., $\gamma = (K_n \ln \omega / dP) = 2.9 \pm 0.3$, but larger than the results of Martinho et al. $\gamma$ = $\gamma = 2.0 - 4.0$

For the strong electron-phonon coupling superconductors, the $T_c$ can be predicted by the McMillan equation, as modified by Allen and Dynes:

$$
T_c = \frac{\langle \omega \rangle}{1.2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^2(1 + 0.62\lambda)} \right),
$$

where $\langle \omega \rangle$ is the averaged phonon frequency, $\lambda$ is the electron-phonon coupling constant, and $\mu^2$ is the Coulomb pseudopotential. The electron-phonon coupling constant can be written as $\lambda = N(E_f)/(\Gamma^2(M(\omega^2)))^{-1}$, where $N(E_f)$ is the density of electron states at the Fermi energy $E_f$. $\Gamma^2$ is the square of the electron-phonon matrix averaged over the Fermi surface, $M$ is the mass of the atom, and $(\omega^2)$ is the average value of the square of a characteristic phonon frequency. Deemyad et al. have deduced $T_c(V)$ on the basis of Eqs. (1) and (2),

$$
\frac{d\ln T_c}{d\ln V} = -\gamma - \Delta_1 \left( \frac{\partial \ln \mu^2}{\partial \ln V} + \Delta_2 \left( \frac{\partial \ln \eta}{\partial \ln V} + 2\gamma \right) \right),
$$

where $\eta = N(E_f)/(\Gamma^2)$ is the McMillan-Hopfield parameter given by the product of the electronic density of states and

![FIG. 4. (Color online) Dependence of the frequency of the $E_{2g}$ mode on the unit cell volume for SiC-, carbon black, and Al-Ag-doped MgB$_2$, for Mg$_{10}$B$_2$, and for hydrogenated MgB$_2$. The SiC-doped samples were sintered at 750 °C for 30 min. The carbon-doped samples were sintered at 900 °C for 2 h. The Al-Ag-doped MgB$_2$ was sintered at 950 °C for 1 h. The Mg$_{10}$B$_2$ sample was sintered at 950 °C for 2 h. The dashed black lines are guides for the Grüneisen relationship between the normal MgB$_2$ and Mg$_{10}$B$_2$, and the magenta line (dash-dotted-dash-dotted) shows the unit cell volume value of pure MgB$_2$ in Ref. 1. The hydrogenated MgB$_2$ was processed in 30 atm H$_2$ atmosphere at 500 °C for 2 h. The shaded area is the predicted higher $T_c$ position.](094517-4)
the average squared electronic matrix element, while the dimensionless prefactors \( \Delta_1 = 1.04 \mu^*(1 + \lambda)(1 + 0.62\lambda)/[\lambda - \mu^*(1 + 0.62\lambda)^2] \) and \( \Delta_2 = 1.04(1 + 0.38\lambda)/[\lambda - \mu^*(1 + 0.62\lambda)^2] \) are calculated using the values of \( \lambda \) and \( \mu^* \) at ambient pressure. The differences in the \( d \ln T_c/d \ln V \) values between the \( V \) increasing and \( V \) decreasing systems [as calculated from Fig. 3(a)] is dominated by \( \eta \) for small changes of \( \mu^* \) and \( \gamma \) in the doped MgB\(_2\). This is similar to the explanation for the absence of superconductivity in LiB (Ref. 49) and Li\(_2\)BC,\(^{50}\) which is attributed to a reduction in the electronic density of states that is driven by the lattice structure vibration. This means that the chemical doping effects will decrease the electronic density of states for alien atom invasion, and this is the reason why the superconductivity cannot be increased solely by enhancing the phonon frequency and lattice parameters.

Of itself, the chemical doping tends to increase anharmonicity in the lattice, but the changes in the electronic density of states compensate for this, so that the harmonic-anharmonicity balance is maintained. Although the chemical doping effect on superconductivity is disappointing, there are possible methods to break through this harmonicity-anharmonicity obstacle, which are hinted at by the isotope effect.\(^{51}\) Mg\(^{10}\)B\(_2\) shows a higher \( T_c \) of 40.2 K than that of Mg\(^{11}\)B\(_2\) at 39.2 K, while its cell volume, 30.11\( \text{Å}^3 \), is nearly 0.1% larger in the sample sintered under hydrogen. The lattice parameter \( a \) was nearly 0.1% larger in the sample sintered under hydrogen than in the sample sintered under argon. The \( T_c \) for the hydrogenated sample was \( \sim 0.6 \) K higher.\(^{52}\) The results of this work are in agreement with theirs. The phonon frequency of the \( E_{2g} \) mode for the hydrogenated MgB\(_2\) as measured from the Raman spectra increases, as shown in Fig. 5. The \( E_{2g} \) mode is dominant in the normal MgB\(_2\), because the long sintering makes the main

![FIG. 5. (Color online) Normalized Raman spectra for MgB\(_2\) before and after hydrogenation in 30 atm H\(_2\) atmosphere at 500 °C for 2 h. The baselines have been subtracted from the patterns. The inset shows the ac susceptibility of pure MgB\(_2\) before and after hydrogenation, respectively.](image-url)
between the $E_{2g}$ mode and the other modes. Although the crystal distortion is obviously reflected by the strong PDOS peak in the Raman spectrum of the hydrogenated MgB$_2$, the high frequency and strong FWHM of the $E_{2g}$ mode indicates that the interstitial H atoms can strengthen the electron-phonon coupling at the same time. On the fact that the superconductivity is absent in most compounds with typical graphitelike structures, such as AlB$_2$, ZrB$_2$, NbB$_2$, MoB$_2$, YB$_2$, TaB$_2$, TiB$_2$, HfB$_2$, VB$_2$, and CrB$_2$, Calandra et al. believe that even small variations in the valence or mass of the intercalant or in the structural parameters of the boron layers are sufficient to considerably alter the $\sigma$ or $\pi$ and positions or the shape of their Fermi surfaces and consequently destroy superconductivity. \(^{49}\) In contrast with the other chemical doping effects, H atoms do not substitute into the lattice positions of either Mg or B, where the dopant atoms lead to the formation of secondary phase particles and cause significant anharmonicity and distortion in the crystal lattice, which in turn reduce the $T_c$. \(^{54}\) MgB$_2$H$_x$ keeps the shape of the Fermi surface and the $N(E_f)$ with the absence of band filling. Furthermore, it shows strong electron-phonon coupling related to the increased frequency and linewidth of the $E_{2g}$ mode. On the basis of hydrogenation experiments and the isotope effect, it is believed that the MgB$_2$ will have higher $T_c$ if the values of the phonon frequency and the unit cell volume coincide with the shaded area in Fig. 4.

In summary, the doping effects of SiC, C, Mn, and Al-Ag on the $T_c$ of MgB$_2$ strongly depend on the harmonicity-anharmonicity competition in the compounds. The phonon frequency changes to counteract the crystal lattice variation to keep the system stable within a Grüneisen parameter of $\gamma=2.0$–4.0. Namely, the phonon frequency decreases as the unit cell volume is expanded, and vice versa. It is concluded from the $T_c(V)$ analysis that the decreased electronic density of states is responsible for the $T_c$ depression in the doped MgB$_2$. The $T_c$ for pure MgB$_2$ can be improved by 0.4 K by hydrogenation in 30 atm H$_2$ atmosphere at 500 °C for 2 h. The interstitial H atoms in the MgB$_2$ lattice do not alter the shape of the Fermi surface and the density of electron states at the Fermi energy $N(E_f)$ due to the absence of element substitution for Mg or B. However, they enhance the $E_{2g}$ mode and the intraplane B interaction. The strong increase in frequency and linewidth of the $E_{2g}$ mode and the expanded unit cell volume of MgB$_2$H$_x$ are responsible for the $T_c$ increase in the material, which is different from the case of the other doped systems, where strong electron-phonon coupling and a large unit cell volume cannot coexist. Although extensive research has not found an effective way to enhance the $T_c$ dramatically in the Mg-B system, there is reason to believe that it is possible to break through the harmonic-anharmonicity obstacle and thus achieve high $T_c$ MgB$_2$ compounds with both high phonon frequency and an expanded unit cell volume.

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RAMAN STUDY OF ELEMENT DOPING EFFECTS ON THE…