The theory of hole superconductivity explains high temperature superconductivity in cuprates as driven by pairing of hole carriers in oxygen $p\pi$ orbitals in the highly negatively charged $Cu-O$ planes. The pairing mechanism is hole undressing and is Coulomb-interaction driven. We propose that the planes of $B$ atoms in $MgB_2$ are akin to the $Cu-O$ planes without $Cu$, and that the recently observed high temperature superconductivity in $MgB_2$ arises similarly from undressing of hole carriers in the planar boron $p_{x,y}$ orbitals in the negatively charged $B^-\cdots$ planes. Doping $MgB_2$ with electrons and with holes should mirror the behavior of underdoped and overdoped high $T_c$ cuprates respectively. We discuss possible ways to achieve higher transition temperatures in boron compounds based on this theory.

I. INTRODUCTION

Superconductivity with a remarkably high transition temperature ($\sim 40 K$) has recently been discovered in $MgB_2$ [1]. It has been proposed that it results from strong electron-phonon interaction and high phonon frequency due to the light ionic masses [2], and indeed measurement of an isotope effect has been reported [3]. Here we propose instead that the phenomenon is another clear example of the mechanism of hole superconductivity at work [3]. The theory of hole superconductivity proposes that this is the universal mechanism of superconductivity in solids [3].

No measurement of the Hall coefficient of $MgB_2$ has yet been reported in the literature to our knowledge. The Hall coefficient for other metal diborides with the same crystal structure ($YB_2$, $TiB_2$, $VB_2$, $ZrB_2$, $NbB_2$, etc.) has been measured and found to be negative [2,6,7]. Correspondingly we expect no superconductivity in those compounds (no superconductivity in those compounds has ever been detected to our knowledge). Instead, we expect the Hall coefficient of $MgB_2$, certainly for transport in the planes, to be positive, indicating the dominant role of hole carriers in the normal state transport expected for superconductors within our theory. In other words, we expect the family of metal diboride compounds to be another clear example of the Chapnik-Feynman empirical rule [8–10] that superconductivity exists when the normal state transport is hole-like and does not exist when it is electron-like.

In the theory under consideration here [4–6], superconductivity is an ‘undressing’ transition, and it can only be driven by carriers in bands that are almost full. It is argued that the dressing of quasiparticles in an electronic energy band, due to electron-electron interactions, is an increasing function of the electronic band occupation. When the Fermi level is near the top of the band, the carriers (hole carriers) are most heavily dressed, and the normal state transport is largely incoherent; when these heavily dressed hole carriers pair they partially undress, and this is the driving force for superconductivity. The superconducting condensation energy is kinetic in origin, as undressed carriers have a lower effective mass. Similarly, undressing also occurs upon hole doping a nearly full band in the normal state. If the Fermi level is not close to the top of the band, carriers are not as heavily dressed in the normal state and do not gain enough by pairing to overcome Coulomb repulsion, and superconductivity disappears.

II. WHAT MAKES $MgB_2$ A HIGH TEMPERATURE SUPERCONDUCTOR

The crystal structure of $MgB_2$ is the so-called $AlB_2$ structure: honeycomb layers of boron atoms alternate with hexagonal layers of $Mg$ atoms. $B$ atoms in different planes are on top of each other, and the $Mg$ atoms are at the center of the hexagons defined by the $B$ atoms. It was proposed long ago that in metal diborides the boron atoms accept electrons from the metal, and the boron planes become negatively charged [11]. The simplest ionic picture would suggest that in $MgB_2$ the $Mg^{2+}$ donates two electrons to the $B$ planes, and the ionic compound $Mg^{2+}(B^-)_2$ results, which will be metallic due to boron band overlap. This picture is supported by band structure calculations.

Within the theory of hole superconductivity what drives superconductivity in the cuprates is hole transport through the planar oxygen $p\pi$ orbitals [12]. That band is full in the undoped cuprates, and we have proposed that when the materials are hole doped, hole carriers will go predominately into that band (although transport through the $O\,p\sigma$-$Cu\,d_{x^2-y^2}$ orbitals may also occur [13]). For the electron-doped cuprates, we have proposed that holes in the planar $O\,p\pi$ orbitals are induced by electron
doping \[14\] and that they become mobile when oxygen is removed through annealing in a reducing atmosphere \[15\].

Band structure calculations for the doped cuprates are complicated due to the strong Coulomb repulsion on the Cu atoms, and so far they have not shown evidence that the Fermi level cuts an oxygen \(p\pi\) band near its top. In contrast, band structure calculations for \(MgB_2\) are simpler and expected to be accurate, and several calculations have been reported in the literature, using different methodologies, that are in essential agreement \[16\]–\[18\], \[2\].

Figs. 1 and 2 show band structure calculation results of Armstrong et al for \(MgB_2\) \[16\] and \(AlB_2\) \[19\] respectively. The essential fact that makes \(MgB_2\) a superconductor, according to our theory, is that the Fermi level at the \(\Gamma\) point cuts two bands right near the top, as seen in Fig. 1 (bands 3 and 4 in the terminology of Armstrong et al \[16\]). These two bands give rise to nearly cylindrical hole-like Fermi surfaces around the \(\Gamma\) point (see also Fig. 3 of Ref. 2), indicating that the transport from these hole carriers will be dominantly in-plane. The atomic states giving rise to these bands are dominantly boron planar \(p_{x,y}\) orbitals \[3\]–\[6\]. Within the theory of hole superconductivity, it is those heavily dressed hole \(p_{x,y}\) carriers that give rise to the high temperature superconductivity of \(MgB_2\). As emphasized by Armstrong et al, the main difference between \(MgB_2\) and \(AlB_2\) is that in the latter compound these \(p_{x,y}\) orbitals are completely filled and do not contribute to conduction. The conduction in \(AlB_2\) is mainly electron-like, as suggested by Fig. 2 and by the measured negative Hall coefficient of the similar compound \(YB_2\) \[1\]. Hence \(AlB_2\) is not a superconductor.

The existence of a hole-like Fermi surface is a necessary condition for superconductivity within our model. However to obtain high temperature superconductivity the presence of negatively charged conducting structures is also found to be favorable, as negative ions give rise to larger values of the parameter \(\Delta t\) that drives superconductivity \[20\]. Thus the fact that the boron planes in \(MgB_2\) are essentially \(B^-\), i.e. highly negatively charged, naturally fits within this picture. The same situation is found in the high \(T_c\) oxides, where the \(Cu\) \(-\) \(O\) planes are also highly negatively charged, with two extra negative charges per unit cell (\(Cu^{++}(O^-)2\)).

Figure 3 shows the generic behavior of \(T_c\) versus hole concentration predicted by our theory \[1\]–\[14\]. The magnitude of the parameter \(\Delta t\) used, that drives superconductivity in our model, is \(\Delta t \sim 0.37eV\) for the case of Fig. 3, well within the range obtained from first-principles calculations of this parameter for \(p\)-orbitals and negatively charged ions \[20\]. According to the Mulliken population analysis of Armstrong and Perkins \[16\] the hole occupation in the boron \(p_{x,y}\) orbitals in \(MgB_2\) is 0.07. Although the position of the maximum \(T_c\) in our model can vary somewhat with parameters, it generally occurs for lower hole concentrations, as seen in the example in Fig. 3. This would imply that \(MgB_2\) is slightly overdoped, so that a small decrease in the hole carrier concentration would increase \(T_c\) up to a maximum of around 50\(K\). Doping with electrons, for example in a compound \(M_{1-x}Al_xB_2\) (assuming it forms with the same structure) would bring \(T_c\) over the maximum and drive it to zero in the underdoped regime. Doping with holes, for example with \(M_{1-y}Na_yB_2\) (assuming it forms with the same structure) would drive \(T_c\) to zero in the overdoped regime.

The theory of hole superconductivity predicts a crossover from strong to weak coupling regimes as the hole concentration increases \[20\], a scenario which is in qualitative agreement with observations in the cuprates. We may expect to see a similar scenario (although less pronounced) in the doped magnesium diborides. In the underdoped regime (\(M_{1-x}Al_xB_2\)) increasingly incoherent transport and higher resistivity, decreasing coherence length and increasing gap ratio as \(x\) increases, possibly even pseudogap behavior and charge inhomogeneity. This should only occur for a small range of \(x\) however, after which the \(p_{x,y}\) bands will become full and the behavior will change sharply for larger \(x\): superconductivity will disappear, the Hall coefficient will become negative, the transport will become coherent, and the resistivity will decrease as \(x\) increases further with increasing electron carriers. The lattice stability should also increase in this regime of large \(x\). In contrast, in the overdoped regime (\(M_{1-y}Na_yB_2\)) we expect increasingly coherent behavior as \(y\) increases, with lower resistivity, increasing superconducting coherence length diverging as \(T_c\) approaches zero, and gap ratio close to the BCS weak coupling value. The London penetration depth should decrease monotonically as the hole concentration increases from underdoped to overdoped \[22\].

### III. EFFECT OF PRESSURE

Within our theory a decreasing \(B - B\) intraplane distance should increase \(T_c\) \[1\], as seen in Fig. 3. Similarly we have argued that in high \(T_c\) oxides the intrinsic effect of increase of \(T_c\) with pressure is caused by decreasing intraplane \(O - O\) distance \[23\]. This is because superconductivity is driven by the correlated hopping parameter \(\Delta t\) that depends exponentially on interatomic distance. Hence we expect application of pressure in the plane direction in \(MgB_2\) will increase \(T_c\). Hydrostatic pressure should also increase \(T_c\) assuming it leads to a decrease in the \(B - B\) intraplane distance. However the situation could be more complicated if charge transfer between the \(B\) planes and the metal occurs under pressure, in which case the sign and magnitude of the change in \(T_c\) would depend on the sign of the charge transfer, whether the system is in the overdoped or underdoped regime, and on the relative weight of the change induced by charge transfer and change induced by changing interatomic distances. All of these effects could be disentangled by mea-
suring changes in lattice constants and Hall coefficient under pressure.

IV. HOW TO ACHIEVE HIGHER $T_c$'S IN THE DIBORIDES

Various calculations of band structures in diborides suggest that a rigid band picture works reasonably well [14,16,19,24]. In the transition metal diborides it is found that the Fermi level states are dominantly of metal 3$d$ character [24], in contrast to the main group diborides where the boron $2p_{x,y}$ orbitals dominate the Fermi level states. According to the theory discussed here, the latter situation is the favorable one for superconductivity, and the position of the Fermi level in $MgB_2$ is close to optimal. Hence what remains to be optimized is the interatomic distances, which may be achieved by 'chemical pressure'.

Consider the compound $BeB_2$ [23,24]. Its structure is similar although not identical to that of $MgB_2$, however the interatomic distances should be significantly smaller than those in $MgB_2$ due to the smaller size of the $Be$ atom. The lattice constants for $BeB_2$ obtained by averaging experimental data over a larger unit cell have been inferred to be $a = 2.94\text{Å}$, $c = 2.87\text{Å}$ [27], while those of $MgB_2$ are $a = 3.084\text{Å}$, $c = 3.522\text{Å}$ [3]. Hence the crucial $B - B$ intra-plane distance should be about 5% shorter in $BeB_2$, allowing in principle for considerably higher $T_c$.

However even though $Be$ and $Mg$ are both nominally divalent the ionization potentials of $Be$ are significantly larger: the first and second ionization potentials are $E_1 = 9.32\text{eV}$, $E_{11} = 18.21\text{eV}$ for $Be$, and $E_1 = 7.64\text{eV}$, $E_{11} = 15.03\text{eV}$ for $Mg$ [28]. Hence the charge transfer from $Be$ to $B$ in $BeB_2$ will be less than that from $Mg$ to $B$ in $MgB_2$, and the Fermi level in $BeB_2$ will be lower than shown in Fig. 1, probably beyond the regime where superconductivity occurs. Hence the system $BeB_2$ needs to be doped with electrons, and we suggest to achieve that through the compound $Be_{1-x}Al_xB_2$. If this compound forms in the $AlB_2$ structure, we predict that with increasing $x$ the $T_c$ versus $n_h$ curve of Fig. 3 will be mapped from overdoped to underdoped, with a maximum $T_c$ significantly larger than in the $MgB_2$ structure.

Similarly a $LiB_2$ or $NaB_2$ compound with the same structure and doped with electrons, e.g. $Li_{1-x}Al_xB_2$, would map the $T_c$ versus $n_h$ curve, for larger values of $x$ ($x > 1/2$). The $Li$ case should yield higher $T_c$'s than the $Na$ case due to the smaller interatomic distances.

Finally we comment on the transition metal diborides. Several compounds of the form $MB_2$ form with the $AlB_2$ structure, e.g. $M = Sc,Ti,V,\ldots,Zr,Nb,Mo,Hf,Ta,W$ [14,18,24]. All are reported to have negative Hall coefficient [18,24] and the transport is dominated by carriers in the metal $d$ orbitals [18,24]. The band structure calculations of Armstrong [24] show that the Fermi level is above the $\Gamma_5$ point in Figure 1, and approaches that point as one moves to the right and down in the periodic table. Doping these materials with holes, for example by forming intermetallic compounds where transition metals are partially substituted by alkali or alkali earths, should bring the Fermi level down to the $B\ p_{x,y}$ bands and give rise to superconductivity. However these cases should be like the two-band situation of ref. [3], where the hole carriers drive the system superconducting in the presence of a large number of electron carriers, and $T_c$'s should be considerably lower than in $MgB_2$.

V. ISOTOPE EFFECT

The presence of an isotope effect is usually considered evidence that electron-phonon coupling drives superconductivity. However, an isotope effect is also expected in the mechanism considered here. The parameter that drives superconductivity, $\Delta t$, depends sensitively on interatomic distances, as does the single particle hopping $t$. Let us assume we have

$$t(q) = t + \gamma q$$  \hspace{1cm} (1a)

$$\Delta t(q) = \Delta t + \gamma' q$$  \hspace{1cm} (1b)

where $q$ is an optic phonon mode, and $\gamma' = \gamma \Delta t/t$. The zero-point motion of the atoms will yield a small increase in the effective $\Delta t$, that depends on the ionic mass:

$$\Delta t_{eff} = \sqrt{<\Delta t>^2} = \Delta t + \gamma' q$$  

$$<q^2> = \Delta t$$  \hspace{1cm} (2)

Using $<q^2> = \hbar \omega/2K$, with $\omega$ the phonon frequency and $K$ the force constant, we find that if the ionic mass $M$ changes by $\delta M$, the parameter $\Delta t_{eff}$ changes by

$$\delta(\Delta t_{eff}) = \frac{\alpha^2}{4K} \frac{\Delta t}{t^2} \frac{\hbar \omega \delta M}{M}$$  \hspace{1cm} (3)

Finally, with $D = 2zt$ the bandwidth ($z$ the number of nearest neighbors) and $\lambda = \gamma^2/KD$ the dimensionless electron-phonon coupling we have

$$\delta(\Delta t_{eff}) = z \lambda \frac{\Delta t \hbar \omega \delta M}{t^2 M}$$  \hspace{1cm} (4)

and the change in $T_c$ is given by

$$\frac{\partial \ln T_c}{\partial \ln M} = \frac{\partial \ln T_c}{\partial \ln \Delta t} \times \frac{z \lambda \hbar \omega}{2t}$$  \hspace{1cm} (5)

For the parameters used in Figure 3, $\partial \ln T_c/\partial \ln \Delta t = 14.5$, $t \sim 0.63eV$, and using $\omega = 750K$ as an estimate of the phonon frequency [3] we find for the isotope coefficient...
so that to reproduce the measured isotope shift $\alpha_B \sim 0.26$ \cite{2} would require a rather small $\lambda$, $\lambda \sim 0.12$. The estimated value of $\lambda$ in ref. \cite{2} is much larger, $\lambda \sim 0.7$.

While the calculation discussed here is not expected to be very accurate, it illustrates the fact that the mechanism of hole superconductivity is very sensitive to ionic vibrations and generically leads to a positive isotope effect due to the increased effective $\Delta t$ from larger zero-point vibrations. Eq. (6) and the measured isotope shift suggest that the actual $\lambda$ in the material may be substantially smaller than estimated in ref. \cite{2}. Alternatively, the isotope shift estimate Eq. (6) may be reduced by the fact that a smaller ionic mass would also be expected to lead to a slightly larger average interatomic distance, an effect which would partially compensate the increase in effective $\Delta t$ estimated here.

VI. CONCLUSIONS

We have proposed here an interpretation of the observed high temperature superconductivity in MgB$_2$ based on the theory of hole superconductivity. According to this theory, the essence of high $T_c$ cuprates is metallic oxygen, more specifically holes conducting through nearly full oxygen $p\pi$ planar orbitals in the highly negatively charged Cu – O planes \cite{1}. Similarly, holes in nearly filled boron planar $p_{x,y}$ orbitals in the negatively charged $B^-$ planes should drive superconductivity in MgB$_2$. In this sense, MgB$_2$ is then a beautiful realization of the essential physics of superconductivity in cuprates, without the complications of Cu $d_{x^2−y^2}$ orbitals, antiferromagnetism, chains, etc., that we have argued obscure the physics and are non-essential in the cuprates \cite{1}. Already in our early work we noted in connection with high $T_c$ cuprates “a moment on the cation (like Cu$^{2+}$) is not needed, in particular a closed shell should do”, and “The high $T_c$ oxide structures with Mg in place of Cu, if they formed, would be excellent candidates to support our picture and rule out other mechanisms” \cite{1}. Remarkably, the band structure calculations in the borides and their interpretation \cite{3,4} directly support the scenario expected in our theory to be favorable for hole superconductivity.

We expect that the various effects predicted by the theory of hole superconductivity for the cuprates \cite{3,4} should exist, and be of appreciable magnitude in MgB$_2$, due to its high $T_c$, in particular: (1) tunneling asymmetry of universal sign, i.e. larger current for negatively biased sample; (2) charge imbalance of quasiparticle excitations (quasiparticles have a net positive charge), resulting in particular in positive thermopower for NIS and SIS tunnel junctions; (3) apparent violation of low energy conductivity sum rule, i.e. a larger $\delta$-function weight (smaller London penetration depth) than expected from the missing area in the low frequency conductivity; (4) color change, i.e. transfer of optical spectral weight from high frequencies, up to the visible range, down to low frequencies upon onset of superconductivity; (5) evidence for ‘undressing’ in angle-resolved photoemission \cite{28}, i.e. emergence of a sharp quasiparticle peak in the superconducting state from a weaker peak and an incoherent background in the normal state, as well as evidence of increased coherence upon hole doping in the normal state.

Furthermore, as discussed in previous sections, we expect $T_c$ to be an increasing function of pressure applied in the plane direction, positive Hall coefficient for MgB$_2$, and $T_c$ versus hole concentration of the generic form given by Figure 3, with strong coupling to weak coupling crossover in various properties as function of increasing hole doping in the various diboride compounds discussed in the text. As we noted in earlier work \cite{14,31}, the same generic $T_c$ versus hole concentration behavior is seen in transition metal alloys, a phenomenon known as “Matthias’ rules” \cite{32}.

Of course there will be other theories proposed to explain the superconductivity of MgB$_2$ and related compounds, and in particular an electron-phonon one has already been advanced \cite{2}. Even though an isotope effect may appear to favor such a theory, we have pointed out here that such an effect is also expected within the theory of hole superconductivity. Fortunately all theories should not yield identical predictions as to which other diborides should give rise to high temperature superconductivity, nor about what their properties are. Spelling out such predictions clearly, preferably before the experiments are performed, should make it easier to ascertain the relative merits of the various theories.

In closing we remark that the theory of superconductivity through hole undressing discussed here predicts the symmetry of the superconducting state for all superconductors to be s-wave. We suggest that the apparent evidence for d-wave superconductivity in the cuprates may be connected to the presence of Cu $d$ orbitals near the Fermi level. Since no such orbitals exist in MgB$_2$ we expect that clear evidence for s-wave superconductivity will be experimentally found.

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FIG. 1. Results of band structure calculation for MgB$_2$ in the plane directions reproduced from Ref. 16 by Armstrong et al. Note the hole pockets at the Γ point no longer exist as the Γ$_5$ point is considerably below the Fermi level. The Fermi surface for this case is predominantly electron-like.

FIG. 2. Band structure calculation results for AlB$_2$ in the plane directions reproduced from Ref. 19 by Armstrong et al. In contrast to Figure 1, the hole pockets at the Γ point no longer exist as the Γ$_5$ point is considerably below the Fermi level. The Fermi surface for this case is predominantly electron-like.

FIG. 3. $T_c$ versus hole concentration $n_h$ in the model of hole superconductivity for a two-dimensional case. This behavior is generic for this model. Values for the bandwidth, correlated hopping parameter, on-site and nearest neighbor repulsion used were $D = 5eV$, $\Delta t = 0.3725eV$, $U = 5eV$, $V = 0$ respectively. The dashed line indicates the behavior expected under application of physical or chemical pressure, with the parameter $\Delta t$ increased to $0.375eV$.
