TOPICAL REVIEW

Prospects for improving the intrinsic and extrinsic properties of magnesium diboride superconducting strands

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Abstract

The magnetic and transport properties of MgB₂ films present performance goals yet to be attained for powder-processed bulk samples and conductors. Carbon-doped films have exhibited upper critical fields, $\mu_0H_{c2}$, as high as 60 T and a possible upper limit of more than twice this value has been predicted. Very high critical current densities, $J_c$, have also been measured for films, e.g. 25 MA cm⁻² in the self-field and 7 kA cm⁻² in 15 T. Such performance limits are still out of reach for even the best MgB₂ magnet wire. In discussing the present status and prospects for improving the performance of powder-based wire we focus attention on (1) the intrinsic (intragrain) superconducting properties of MgB₂—$H_{c2}$ and flux pinning, and (2) the factors that control the efficiency with which current is transported from grain to grain in the conductor, an extrinsic (intergrain) property. With regard to item (1), the role of dopants in $H_{c2}$ enhancement is discussed and examples presented. On the other hand their roles in increasing $J_c$, both via $H_{c2}$ enhancement as well as via direct fluxoid/pinning center interaction, are discussed and a comprehensive survey of $H_{c2}$ dopants and flux pinning additives is presented. Dopant selection, chemistry, methods of introduction (inclusion), and homogeneity of distribution (via the rounding of the superconducting electronic specific heat transition) are considered. Current transport through the powder-processed wire (an extrinsic property) is partially blocked by the inherent granularity of the material itself and the chemical or other properties of the intergrain surfaces. Overall porosity, including reduced density and intergranular blocking, is quantified in terms of the measured temperature dependence of the normal-state resistivity compared to that of a clean single crystal. Several experimental results are presented in terms of per cent effective cross-sectional area for current transport. These and other such results indicate that in many cases less than 15% of the conductor’s cross-sectional area is able to carry transport current. It is pointed out that densification in association with the elimination of grain-boundary blocking phases would yield fivefold-to-tenfold increases in $J_c$ in relevant regimes, enabling the performance of MgB₂ in selected applications to compete with that of Nb₃Sn.

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1. Introduction

The initial announcement of superconductivity below a $T_c$ of about 40 K in MgB$_2$ by Akimitsu in 2001 [1] triggered extensive research on its preparation in film, bulk, and wire forms as well as its electrical, magnetic, and mechanical properties. Already by June of that year more than 250 research papers had been published and by November 2001 MgB$_2$ was the subject of a comprehensive review by Buzea and Yamashita [2]. With upper critical fields, $H_{c2}$, no higher than about 18 T in single crystals, bulks, and wires, and with critical current densities, $J_c$, mostly less than about $10^4$ A cm$^{-2}$ at 5 K, 5 T, MgB$_2$ tended to be of scientific rather than practical interest. But it was the report of very high $H_{c2}$ in alloyed ('dirty') thin films, accompanied by promisingly high $J_c$s by Eom et al in May 2001 [3], along with the subsequent reports of $H_{c2}$s of more than 70 T by Braccini et al [4] in 2005, that alerted the community to the possibility of wide-spread practical applications if such properties could be transferred to tapes and wires on a large scale. Subsequent years have seen the establishment of commercial companies dedicated to the manufacture of bulk MgB$_2$ objects and long lengths of MgB$_2$ tapes and wires. At the same time steady improvements in $H_{c2}$ and $J_c$ have been reported. As a result MgB$_2$ is on the threshold of wide-spread practical application, an important example being magnets for magnetic resonance imaging. But to take the next step, whether we are interested in high field 4 K operation, or in the more energy efficient 20 K temperature regimes well out of the range of the present NbTi and Nb$_3$Sn wires, further improvement of the in-field $J_c$ is needed. In addressing this issue we must recognize two classes of properties (what might be termed 'intrinsic' and 'extrinsic', respectively) that are in urgent need of fundamental research. Below, we summarize some of the key issues that need to be addressed.

1.1. Intrinsic properties
The essential intrinsic (i.e. intragranular) properties of polycrystalline MgB$_2$ are $H_{c2}$ and flux pinning (or, alternatively, intragrain $J_c$). Increases in the former are always welcome, but the already measured $H_{c2}$s of more than 33 T [5] are usefully high provided they are homogenous. That this is not yet the case is all too evident in experimental results to-date. We must also consider the anisotropy of the superconducting properties, as manifested particularly in the $H_{c2}$ values for field along the basal plane as compared to those along the $c$-axis. This anisotropy can be addressed at an intrinsic level by dopant selection, as some dopants modify this intrinsic anisotropy. Anisotropy also has implications for grain-to-grain current flow in untextured polycrystalline materials, but this is better addressed as a kind of effective connectivity within the extrinsic group of properties.

Beyond this, there must be a satisfactorily high level of flux pinning. Such is not the case at present; flux pinning centers yielding high bulk pinning forces, $F_p$, with maxima located at fields much higher than the existing 4–5 T at 4 K (i.e., at about 20% of the irreversibility field, $H_{irr}$) are preferred. Extensive research has already been carried out on the effects of dopant additions on $H_{c2}$ and $J_c$. Indeed, numerous metallic elements, borides, carbides, oxides, and even organic compounds have been added. This research needs to be continued on a rational scientific basis and redirected if MgB$_2$ is to operate successfully at higher fields and temperatures. Necessary to generate improved properties is the presence of suitably chosen combinations of dopants (elements in substitutional solid solution) plus nano-size flux pinning additions (e.g. [6]). However, as will be argued below, the two most crucial improvements needed to significantly enhance MgB$_2$ performance are: (i) homogeneous dopant induced $H_{c2}$ enhancement, and (ii) large increases in connectivity (the removal of intergrain resistive boundaries). Texturing (or anisotropy reduction) and flux pinning, while important, will not influence final transport $J_c$, as strongly as those properties. While homogeneous doping and $H_{c2}$ enhancement can be considered intrinsic properties, connectivity is an inherently extrinsic property.

1.2. Extrinsic properties—connectivity and porosity issues
In addition to intrinsic-property improvement substantial across-the-board increases in $J_c$ will accompany increases in the superconductor-material’s effective cross-sectional area for the conduction of transport current. The possibility of ‘cross-sectional deficiency’ was first recognized by Rowell [7, 8] who noted that the normal-state electrical resistivities of some polycrystalline thin film samples of MgB$_2$ could be as high as 500 $\mu$Ω cm—well beyond the regime of metallic conductivity. Not only normal-current flow, but supercurrent flow is also expected to be reduced by this cross-sectional deficiency, removal of which is estimated to increase the $J_c$ of a given polycrystalline sample by factors of five to ten. Although grain boundaries as such do not impede supercurrent flow [9], the observed intergranular partial coatings of insulating MgO or amorphous Bo, [10] will certainly do so. Formation of the coating, an interesting problem in solid state chemistry, is an area of active study. Research is focusing on the possibility of reducing or eliminating it [11] leading to improved intergranular connectivity.

Magnesium diboride wires are made by powder-in-tube processes, either ex situ in which ready-made MgB$_2$ powder is packed into a tubular jacket and drawn down or in situ in which the jacketed elemental Mg and B ingredients are reacted together at final wire size. Although the ex situ wire is subject to the porosity expected of any powder-processed body, the in situ wire filling is made even more...
porous by the voids remaining from the prior Mg particles after the Mg + 2B → MgB₂ reaction. Various consolidation techniques are beginning to be introduced in attempts to reduce porosity in bulk samples and wires. Different reaction routes to MgB₂ formation that will lead directly to reduced porosity are also being studied [12].

2. Intrinsic properties of MgB₂ conductors

The very high \( H_{c2} \)s reported for dirty films ([3] and subsequently [4]) which alerted the community to the possibility of high field and other practical applications, continue to serve as useful references against which the \( H_{c2} \)s of evolving MgB₂ conductors can be compared. Likewise the high \( J_c \)s of dirty films can be seen as goals, bearing in mind that although films are not immune to connectivity problems, at least they are not porous.

2.1. Upper critical fields and irreversibility fields and their enhancement by dopant induced impurity scattering

2.1.1. Theory. For dirty, non-paramagnetically limited, single-band, low temperature superconductors the following well known expression for 0 K upper critical field, \( H_{c2} \), can be obtained by starting with Maki’s dirty-limit \( H_{c2} \) and inserting an expression for the 0 K thermodynamic critical field, \( H_{c0} \), thus:

\[
\rho_0 = \frac{3.27 \times 10^{-5}}{\gamma} \left( \frac{H_{c20}}{T_c} \right) = \frac{2.23 \times 10^{-5}}{\gamma} \left( \frac{-dH_{c2}}{dT} \right)_{T_c}
\]

where \( \rho_0 \) is the impurity resistivity and \( \gamma \) the electronic specific heat coefficient. Equation (1) indicates that the value of \( H_{c2}(T) \) at 0 K and its slope at \( T_c \) are proportional to \( \rho_0 \) (alternatively, inversely proportional to the charge-carrier diffusivity, where \( 1/\rho_0 = e^2 N_c D_e \)). Increases in \( H_{c20} \) would be expected to follow directly from the introduction of charge-carrier-scattering impurities into the superconductor’s lattice structure—a rule that has guided the design of low temperature superconductors over the years. But this simple rule is no longer obeyed for MgB₂, for which there is no direct relationship between \( H_{c20} \) and \( \rho_0 \) [13].

In the compound MgB₂ the presence of Mg stabilizes the B sublattice in the form a honeycomb-like stack of hexagonal networks, essentially a new allotropic of B. The B honeycomb dominates the electronic structure which can be thought of as deriving from \( \sigma \) bonding within the B plane (leading to a ‘\( \sigma \) band’) and \( \pi \) bonding both in and out of the plane (leading to a ‘\( \pi \) band’) [14]. The bands have their individual Fermi densities-of-state, superconductive energy gaps, and scattering relation times, \( D_\sigma \) and \( D_\pi \), respectively [15]. In clean MgB₂ (e.g. undoped monocrystals) electron–phonon coupling in the \( \sigma \) band (see section 4.1) and hence \( H_{c2} \) has been shown to be strongly affected by the application of external pressure [16]. Accordingly it has been suggested that internal pressure administered by atomic disorder at grain boundaries or around dopant particles could also be responsible for \( H_{c2} \) enhancement. On the other hand in dirty MgB₂ typified by the bulk pellets and wire considered here it is recognized that charge-carrier scattering dominates the normal—and superconducting properties.

With reference to a copious body of experimental upper critical field results comparable to that of figure 1, Gurevich et al. [17, 18] have been able to illustrate and explain MgB₂’s unusual critical field temperature dependence in terms of the electronic diffusivities (\( D_\sigma \) and \( D_\pi \)) associated with its two-band conductivity:

\[
\sigma = e^2 (N_\pi D_\pi + N_\sigma D_\sigma).
\]

The introduction of two diffusivities results in pronounced departures from the single-band predictions; in particular, \( H_{c2(\text{near } T_c)} \) and \( H_{c20} \) respond individually to \( D_\sigma \) and \( D_\pi \). Thus, according to Gurevich et al [17] and to a first approximation:

\[
H_{c2(\text{near } T_c)} \propto \frac{1}{\lambda_1 D_\sigma + \lambda_2 D_\pi}
\]

(3)

(in which the \( \lambda \)s are appropriate functions of the intraband and interband electron–phonon coupling constants [17], see also section 4.1.2) and

\[
H_{c20} \propto \frac{1}{\sqrt{D_\sigma D_\pi}}.
\]

(4)

Simply stated, near the critical temperature \( H_{c2(\text{near } T_c)} \) varies inversely as the weighted arithmetic mean of \( D_\sigma \) and \( D_\pi \), while \( H_{c2(\text{near } 0 \text{ K})} (H_{c20}) \) varies inversely as their geometric mean. Thus while increasing impurity scattering is beneficial to \( H_{c2} \) over the entire temperature range for both single-band and double-band superconductors, in the latter case (and recognizing the independence of \( D_\sigma \) and \( D_\pi \)) it allows \( H_{c20} \) to diverge to very large values in response to decreases in either \( D_\sigma \) or \( D_\pi \).

\( H_{c2} \) at ‘high temperatures’. Suppose, as has turned out to be the case for dirty MgB₂ films, \( D_\pi \ll D_\sigma \) (i.e., \( \pi \) scattering much stronger than \( \sigma \) scattering) equation (3) approximates to

\[
H_{c2(\text{near } T_c)} \propto \frac{1}{\lambda_1 D_\sigma}.
\]

(5)
H\textsubscript{c20} at ‘low temperatures’. Referring to equation (4) in which $D_\sigma$ and $D_\pi$ are tied together as a product (even though $D_\pi$ is the ‘dominant’ component), it would seem that manipulation of either of them would influence $H_{\text{c20}}$. But examination of the $H_{\text{c20}}$ relationship in more detail reveals that for very different diffusivities

\[ H_{\text{c20}} \propto \frac{1}{D_\sigma} \quad D_\sigma \ll D_\pi \] (6)

\[ H_{\text{c20}} \propto \frac{1}{D_\pi} \quad D_\pi \ll D_\sigma \] (7)

so the $H_{\text{c20}}$ is controlled by the smaller of the two diffusivities—e.g., the $D_\sigma$ in dirty MgB\textsubscript{2}. As pointed out by Gurevich [18] $H_{\text{c20}}$ close to the BCS paramagnetic limit of $H_0 = 65$ T (see figure 1 [19]) are already being attained in MgB\textsubscript{2}. Furthermore, given that BCS underestimates $H_\pi$ by the factor $(1 + \lambda)$ where $\lambda$ is some global electron–phonon coupling constant, values as high as 130 T may in principal be achievable. Based on the spectacular thin film results Gurevich et al [17] pointed out that the use of MgB\textsubscript{2} will open a ‘new domain of application for superconducting magnets’, one that is outside the reach of NbTi and to some extent NbSn, implying that in general enhancements to the $H_{\text{c20}}$ will follow the judicious introduction of scattering impurities.

2.1.2. Selection of dopants for $H_{\text{c20}}$ optimization. It has been suggested that: (i) macroscopic particles that contribute to lattice distortion enhance both $\pi$ and $\sigma$ scattering, (ii) disorder on the Mg sublattice (e.g. by Al addition) can increase the $\pi$ scattering, (iii) oxygen when substituting for B was expected to provide strong $\sigma$ scattering; so also was C [17]. By now a multitude of papers have described the benefits of adding C in one form or another to the MgB\textsubscript{2} lattice. Carbon has been added in elemental form (microspheres, nanotubes, nanodiamond) or by way of C-containing compounds such as SiC, TiC, B\textsubscript{4}C, organic compounds, and so on (see below). The work has been largely semi-empirical in nature albeit related to and guided by the principles outlined above.

Although C when doped into the B lattice might be expected to increase $\sigma$ scattering (as predicted by recent electronic-structure calculations [20]), Angst et al [21] and more recently Gurevich [18] have offered experimental evidence in support of a $\pi$-scattering mechanism. These authors agree that the upward curvature of the low temperature $H_\text{c(2)w}$, field parallel, or at least its lack of negative curvature, see figure 1, points to the dominance of $\pi$-band scattering. Although dopant induced buckling of the $a$–$b$ (Mg) planes has been suggested as a mechanism for the enhanced $\pi$ scattering [18, 21] the latter authors have concluded that it is in fact an intrinsic result of C substitution but for reasons that are not fully understood [18, 21].

In selecting dopants, reaction chemistry is an important consideration. The success of SiC as a dopant for C [22] relies on the fact that, during in situ processing, the Mg decomposes SiC and releases atomic C before the onset of the Mg + 2B $\rightarrow$ MgB\textsubscript{2} reaction. This is clearly demonstrated in the results of differential scanning calorimetry (DSC), figure 2. All DSC data depicted there were collected with a TA Instruments DSC2920 under argon flow, using an Fe pan. Three different runs were made: (1) the first with Mg only (solid line) exhibits the endothermic peak associated with Mg melting at about 650°C. (2) A run made just with mixed SiC and Mg powders (the dashed line) evinces the reduction of SiC by Mg at 524°C again followed by Mg melting at 650°C. (3) The third curve (dash–dot) shows the response of a sample of mixed Mg and amorphous B (99+% pure) powders. It depicts the exothermic surface reaction described in [23] as well as the onset of MgB\textsubscript{2} formation at 615°C below the Mg’s 650°C melting point [23].

Since dopant concentrations are generally small, attention must be given to ensuring that they are uniformly distributed and/or incorporated into the lattice. Thinking along these lines, Ribiero et al [24] selected B\textsubscript{4}C as a source of C doping reckoning that the C and the B were already mixed on an atomic-length scale. A similar strategy, and other considerations, also guided the selection of the diborides TiB\textsubscript{2}, ZrB\textsubscript{2}, and NbB\textsubscript{2} as potential $H_{\text{c20}}$-enhancing dopants [5]. Of these, ZrB\textsubscript{2} was the most potent, and with an $H_{\text{c20}}$ of 29 T, became the subject of more detailed study [25], figure 3. Two bulk samples were made, the first with binary stoichiometric MgB\textsubscript{2} and the second with 7.5 mol% ZrB\textsubscript{2} addition. They were prepared by the in situ reaction of a stoichiometric mixture of 99.9% pure Mg and amorphous B (99+% pure) powders after SPEX milling and compacting into pellets. Critical field measurements were performed resistively at 4 K, and magnetically at higher temperatures [25]. In figure 3, the filled triangles give the $H_{\text{irr}}$ versus $T$ for binary MgB\textsubscript{2}, the filled circles give the response of the ZrB\textsubscript{2}-doped sample, and the open triangles represent the percentage increase in $H_{\text{irr}}$.
resulting from that doping. Based on XRD measurements, which showed increases in both the c- and a-lattice parameters, we deduced that Zr was substituting on the Mg site. Thus, we might expect the dopant to be effective primarily at lower temperatures (assuming π-band scattering). It is interesting to note that the increase for ZrB₂ [25] is not very different from that contributed by SiC doping [22]. Additionally, even with substitutional doping the possibility of unreacted residues cannot be ignored. Although they were not present as a result of ZrB₂ doping, they were observed with NbB₂ doping [25] and are known to be present after SiC doping [22].

Of course, the unreacted residue is not necessarily inert, and may contribute flux pinning centers, or indirectly increase either π and σ scattering via lattice distortion and in that way increase \( H_{\text{irr}} \). However, although numerous dopants (including metallic elements, borides, carbides, oxides, and organic compounds) have been added to MgB₂ little direct attention has been paid to the possible existences of such dual doping mechanisms.

2.2. Critical current density and its enhancement by doping and flux pinning

2.2.1. Doping in general. In considering the \( J_c \)s attainable in MgB₂ bulk samples we turn again, as a first basis of comparison, to the results of thin films measurements, with reference to the work of Eom et al [3] and many subsequent researchers. Figure 4 displays the \( J_c \)s of MgB₂ films made by various techniques—e-beam evaporation, thermal co-evaporation, hybrid physical–chemical vapor deposition, and pulsed-laser deposition (PLD). There are two versions of PLD—‘in situ’ in which the MgB₂ is directly deposited and ‘ex situ’ in which a PLD-deposited B layer is exposed to Mg vapor, although in practice, some post-deposition of Mg seems to be needed even in the ‘in situ’ case.

These thin film ‘reference \( J_c \)s’ are compared to those of commercially processed binary MgB₂ powder-in-tube (PIT) wires. They typically achieved 4 K \( J_c \)s of \( 10^5 \) A cm\(^{-2}\) at 4.5–5 T, and \( 10^4 \) A cm\(^{-2}\) at 8 T, about an order of magnitude below the best thin film data. We go on to show some incremental improvements in \( J_c \) that result from: (i) the introduction of even more Mg and (ii) the doping of the excess-Mg strand with SiC particles, figure 6. For this sample set the best results (\( 10^5 \) A cm\(^{-2}\) and \( 10^4 \) A cm\(^{-2}\) at 6 T and 11.5 T, respectively) are found when the excess-Mg level is raised to 15% and SiC is added. Still further improvements are depicted in figure 7 which emphasizes the effectiveness of
Table 1. List of dopants added to MgB$_2$.

| Nitrides      | Borides       | Silicides       | Carbon and carbon inorganics | Metal oxides | Metallic elements | Organic compounds |
|---------------|---------------|-----------------|------------------------------|--------------|-------------------|------------------|
| Si$_3$N$_4$ [46–48] | WB [49]      | ZrB$_2$ [5, 44] | C nanotubes [54–57]          | D$_2$O$_3$ [69] | Ti [75–77]       | Sugar [86]        |
|               |               | TiC [60, 61]    |                              | HfO$_2$ [70]  | Zr [77]          | Malic acid [87]   |
|               |               | TiB$_2$ [5]     | SiC [38, 42, 62–65]          | Al$_2$O$_3$ [71] | Mo [78]         | Maleic anhydride [41] |
|               |               | NB$_2$ [5]      | B$_4$C [40, 66, 67]          | MgO [45]      | Fe [79]         | Paraffin [88]     |
| CaB$_6$ [50]  |               |                 | Na$_2$CO$_3$ [68]           | Pr$_6$O$_{11}$ [73] | Co [80]       | Toluene [89]      |
| WSi$_2$ [51–53] |               |                 |                               | SiO$_2$ [74]  | Ni [80]        | Ethanol [89]      |
| ZrSi$_2$ [51, 52] |               |                 |                               |               | Cu [81]       | Acetone [89]      |
|               |               |                 |                               |               | Ag [82]       | Tartaric acid [90] |
|               |               |                 |                               |               | Al [83]       | Ethyltoluene [91] |
|               |               |                 |                               |               | Si [84]       |                  |
|               |               |                 |                               |               | La [85]       |                  |

The C-containing dopants e.g. maleic anhydride, SiC, and C itself when appropriately introduced. On the best of such samples the $10^4$ A cm$^{-2}$ $J_c$ is obtained at a field as high as 13 T. Although this result could be said to be about a factor of three off from the best thin film data reported at these fields, there is in fact a paucity of data in this regime, some of the best performing films having been measured only at lower fields.

Over the years some 40-odd dopant species have been introduced into MgB$_2$, table 1. It is possible to discern a few guiding principles that may have governed their selection. The inclusion of the metallic elements and metal oxides were clearly attempts to introduce normal flux pinning centers. The borides, nitrides and C-containing dopants were added to increase $H_{c2}$ and hence to increase the effectiveness of already present pinning centers as described below. Some additions likely played a dual role—decomposing to partially substitute into the MgB$_2$ lattice while leaving a flux pinning particulate residue.

In concluding this section on $J_c$ enhancement it is important to note that: (i) The primary purpose of a few of the compositional modifications and/or dopant additions (e.g., CaC$_6$) is to reduce grain-boundary contamination and improve connectivity, the subject section 3 of this paper. (ii) Although useful as interim goals, the thin film $J_c$s of figures 4–7 are not the ultimate ‘gold standards’: essential to the Rowell connectivity analysis [7, 8] was the fact that even polycrystalline films are subject to intergrain transport degradation. Even so, it is important to make and then measure films out to high fields at 4 K to explore the potential of MgB$_2$ in this field regime.

2.2.2. Flux pinning and doping mechanisms. Apart from pure single crystals all MgB$_2$ samples—films, bulks, and wires—are polycrystalline in the as-prepared state and hence tend to be moderately well grain-boundary pinned. The introduction of dopants can have one or more effects which may combine to increase the bulk pinning strength: (1) by increasing the crystal’s $H_{c2}$ and $H_{irr}$; (2) by forming a wide distribution of point pinning centers each described by an elementary pinning force $f_p$; (3) by producing localized lattice strains which also contribute to flux pinning. The magnitude and behavior of $J_c$ in an applied field $H$ is described by a bulk pinning function, $F_p$, which represents an appropriate summation of the elementary
pinning forces, \( f_p \) [92–94]. Summation leads to expressions for the bulk pinning force density originally written in the form:

\[
F_p = H_{c2}^m f(h) \quad \text{where } h = H/H_{c2}
\]

recognizing that for MgB\(_2\) with an \( H_{irr} \) (the actual field at which \( F_p \) vanishes) that is significantly less than \( H_{c2} \) we need to define \( h = H/H_{irr} \). Although part of the prefactor in the expression for \( F_p \) derives from the field-normalization step, it is significant that another component comes from a condensation energy. Its presence indicates that dopants added to increase \( H_{c2} \), although not pinning centers themselves, serve to increase the measured \( F_p \) of already pinned samples.

The bulk pinning force field dependence, which generally rises to a maximum at some \( h = h_{max} \), may be expressed in normalized form \( F_p(h)/F_p(h_{max}) \). This, for a given type of pinning center, is independent of temperature, a property known as scaling. The quotient \( F_p/F_{p, max} \) is of the general form

\[
f(h) \propto h^b (1 - h)^c.
\]

As pointed out by Dew-Hughes [92] various classes or types of pinning by ‘normal’ (non-superconducting) objects can be distinguished by the values assigned to the index \( p \) (with \( q = 2 \) for all normal pins), thus

\[
\begin{align*}
&h^b (1 - h)^c \rightarrow \text{normal volume pinning } \quad d < a, b, c \\
&h^{1/2} (1 - h)^2 \rightarrow \text{normal surface (grain boundary) pinning } \quad d < a, b \\
&h^1 (1 - h)^2 \rightarrow \text{normal point pinning } \quad d > a, b, c
\end{align*}
\]

where \( a, b, c \), characterize the dimensions of the pin and \( d \) is the fluxoid spacing; \( d^2 = 1.15(\phi_0/B) \). Normal surface and point pinning can also be distinguished in terms of the corresponding values of \( h_{max} \), namely 0.2 and 0.33, respectively. Examples of the above normal pinning functions together with pinning force data for a SiC-doped MgB\(_2\) sample are given in figure 8 in which the normalizing field, \( H_{irr} \), was based on a 100 A cm\(^{-2}\) criterion. This figure displays pronounced departures from scaling. The generally expected characteristic of grain-boundary pinning is seen for temperatures between 10 and 20 K, while in the 20–30 K range it appears that point pinning is beginning to dominate.

2.3. Electronic specific heat and compositional inhomogeneity

In selecting and introducing potential \( H_{c2} \)-enhancing dopants it is important to be alert to the likelihood of compositional inhomogeneity in the resulting doped sample. In adding small fractions of dopant to a sample it is difficult to guarantee that the starting particles are uniformly dispersed. Even if they are, during reaction heat treatment the existence of finite diffusion distances will essentially guarantee a certain levels of inhomogeneity. Such will manifest themselves in terms of deviations from expected pinning curves—difficult to deconvolute and separate from the effects of mixed pinning centers. However, analysis of the electronic specific heat jump of a superconducting material in the vicinity of its \( T_c \) can provide a sensitive quantitative measure of its degree of compositional homogeneity. The total low temperature specific heat of a metal (\( C_e \)) is the sum of a lattice (phononic) component, \( C_l \), given by:

\[
C_l = 9Nk \left( \frac{T}{\Theta} \right)^3 \int_0^{\Theta_B/T} \frac{x^4 \exp(x)}{(e^x - 1)^2} dx
\]

in which \( N = \) Avogadro’s number, \( k = \) Boltzmann’s constant (hence \( Nk = 8.31 \) J mol\(^{-1}\) K\(^{-1}\)) and an electronic component, \( C_e \), given by \( \gamma T \) for a normal metal and \( \gamma(T_c a \exp(-b/T)) \) for a superconductor below its transition temperature where \( a \) and \( b \) are metal specific constants. At temperatures around the \( T_c \) of MgB\(_2\)-C\(_e\) is negligible compared to \( C_l \) (cf figures 9(a) and (b)). This has two consequences: (1) The specific heat data can be fitted to equation (10) enabling a calorimetric-\( \Theta_0 \) to be extracted. (2) A special technique must be invoked to expose the electronic component. On the assumption that the lattice specific heat is magnetic field independent the superconductive \( C_e \) and its jump at \( T_c \) can be revealed and expanded after the in-field-measured specific heat is subtracted from the zero-field data. For this purpose a PPMS machine was used to take measurements in a magnetic field of 9 T over the temperature range 20–40 K. Figure 9(a) shows the results of \( C_p \) measurements on bulk samples of (i) binary stoichiometric
are attributed to the presence of impurities [95, 96] and in our case to the presence of dopants. The breadths of the superconducting jumps in figure 9(b) contain information about the distribution of transition temperatures. No attempt is made here to fit the data to such a distribution although it is possible to do so using standard techniques [97–99]. Nevertheless the presence of compositional inhomogeneities in the heavily doped MBTi700 and MBSiC700 is at least revealed qualitatively in the figure.

3. Extrinsic properties of polycrystalline MgB$_2$

3.1. Porosity

Randomly packed similar spheres will occupy space to a volume density of about 65% (although spheres of mixed sizes will fill the space more efficiently) for which reason compacted-powder pellets and the cores of PIT wires are inherently porous, e.g. figure 10. Thus the packing densities of ex situ-processed bulks and wires, based geometrically on the packing densities of powders, will be around 65%. Those of in situ-processed bulks and wires are complicated by shrinkage associated with the Mg + 2B \rightarrow MgB$_2$ reaction, but can be estimated using the data from table 2. Our limiting estimates are based on two model scenarios.

**Model-(1):** one mole of MgB$_2$ produced in situ within a fixed-volume enclosure from a mixture of equi-sized Mg and B particles packed to a volume density-factor $P_i$.

From table 2 the volume ratio $([\text{final}(\text{MgB}_2)/\text{initial}(\text{Mg} + 2\text{B})] = 17.2/23.0 = 0.75$. It follows that if the initial packing density is $P_i$ then the final density is $P_f = 0.75P_i$. For example an initial mixed-powder close-packing of 65% leads to an MgB$_2$ powder density of 49%.

**Model-(2):** one mole of MgB$_2$ produced in situ within a fixed-volume enclosure from coarse Mg particles imbedded in
recognized by Rowell [7, 8] who noted that the normal-state electrical resistivities of some polycrystalline thin film samples of MgB₂ could be as high as 500 μΩ cm—well beyond the regime of metallic conductivity. Supercurrent flow is also expected to respond to this same cross-sectional deficiency, which causes the measured extrinsic $J_c$ of a polycrystalline sample to be very much less than its intrinsic value.

3.2. General connectivity

Since the effect of general porosity can be regarded as a geometrical phenomenon it is postulated that normal-state resistivity can be used as a measure of effective cross-sectional area for transport in both the normal and superconducting states. Our connectivity analysis, which uses a modification of the Rowell approach [7, 8], requires a detailed resistivity temperature dependence measurement but in response yields some additional information relevant to the sample’s superconducting properties. We begin with an expression for the measured total resistivity:

$$\rho_m(T) = \rho_{0,m} + \rho_{i,m}(T) = F[\rho_0 + \rho_i(T)]$$  (11)

in which $\rho_{0,m}$ is the measured residual resistivity and $\rho_{i,m}(T)$ is the measured ideal (phononic), component. Finally, on the right-hand-side the terms within the brackets, $\rho_0$ and $\rho_i(T)$, are the intragrain residual- and ideal (phononic) resistivities, respectively, and the prefactor, $F > 1$, represents the observed resistivity enhancement due to the reduced effective transport cross-sectional area. Our approach consists in replacing the previously assumed universal $\rho_i(T)$ with the Bloch–Grüneisen function, thus:

$$\rho_m(T) = F \left[ \rho_0 + \frac{k}{\theta_D} \left( \frac{T}{\theta_D} \right)^5 \int_0^{\theta_0/T} \frac{e^{-z^2} \, dz}{(e^z - 1)^2} \right]$$  (12)

in which $\theta_0$ is the Debye temperature and $k$ is a ‘materials constant’ which we evaluate by fitting equation (12) to a published set of $a$–$b$ textured, fully connected, single crystal data for which $F \approx 1$. Fits of equation (12) to the measured resistivity data then yield the following information: (1) the $F$-factor (leading to a per cent connectivity, $K$) which enables the true intragrain $J_c$ to be determined from the results of an accompanying $J_c$ measurement; (2) the intragrain residual resistivity, $\rho_i$; (3) a resistive Debye temperature, $\theta_R$, available for comparison to its calorimetrically measured counterpart, $\theta_D$, see below.

By way of example we draw on the results of resistivity measurement on three pellets measured above for heat capacity; one binary stoichiometric sample, one doped with 7.5% TiB₂, and another doped with 10% SiC. The results

![Figure 11. Packing density of MgB₂ formed from equi-sized Mg and B particles, model-(1), and that formed from large Mg particles imbedded in fine B powder, model-(2).](image)

![Figure 12. Schematic illustration of the combined presence of pores and intergranular film showing general porosity or general lack of connectivity.](image)
shown in figure 13 after fitting to equation (12) and correcting for the estimated effect of grain anisotropy as described by Yamamoto et al [10] (see footnote to table 3), yielded the values of $\rho_0$, $\theta_E$, $F$, and per cent connectivity, $K$, that are listed in table 3.

Connectivity is the most practically significant result of the resistivity experiment. In table 3 we note that the connectivities of the polycrystalline grains of the unalloyed and doped MgB$_2$ pellets vary from 17 to 37%. If these materials are representative of PIT wire cores, as no doubt they are, we can expect substantial increases in $J_c$, e.g. (by factors of 6.0 and 2.7, respectively) beyond the values presented in Figure 7 in response to increases in connectivity.

4. Discussion

The potential ‘reach’ of MgB$_2$ is subject to: (i) the optimization of $H_{c2}$ and $J_c$ through selected dopant additions, and (ii) increasing connectivity and minimizing porosity.

4.1. Intrinsic properties

4.1.1. Electronic properties. Measurements on doped (‘dirty’) thin films at liquid-He temperatures have demonstrated the attainment of $H_{c2,0}$ approaching the BCS paramagnetic limit of $H_p = 65$ T (e.g. [18, 19]). Furthermore, given that BCS underestimates $H_p$ by the factor $(1 + \lambda)$, values as high as 130 T may in principal be achievable [18]. The spectacular thin film results have inspired researchers to seek equally high $H_{c2,0}$ in bulk pellets and wires, to achieve which suitable dopants need to be found and suitably dispersed. Likewise the high $J_c$’s encountered in some thin film samples have provided goals for $J_c$ development in wires. Progress has been reported in recent years such that, through the use of carefully selected dopants, wire $J_c$’s are already on the threshold of the film values. Dopant selection is critical; they should have at least the following properties: (i) They should be able to be uniformly dispersed at an appropriate size scale. (ii) If unreactive with MgB$_2$ or its precursors, their distribution should be such that they ideally interact with the coherence length of MgB$_2$. (iii) If the dopants react with MgB$_2$ or its precursors their products should either modify the Fermi surface of MgB$_2$ so that the critical fields are increased or the reaction products should follow the criteria established in (i). Table 1 summarizes a survey of the several classes of dopants that have been added to the binary base. Of them C, the only element that has so far been substituted for B, has turned out to be the most potent. Although it has been introduced in many forms—elemental C, C-containing inorganic and organic compounds, the most effective medium has been SiC, which is decomposed into Si + C by Mg prior to the Mg + 2B $\rightarrow$ MgB$_2$ reaction. Carbon, which produces strong impurity scattering (hence high normal-state resistivity) in the $\sigma$-band (as well as the $\pi$-band)—cf equation (7)—is responsible for the upturn in $H_{c2}$ at low temperatures [18]. It is important to note that whereas in dirty MgB$_2$ below $T_c$ both the $\sigma$- and $\pi$-bands support superconductivity (mediated by the electron–phonon coupling constants $\lambda_{\sigma\sigma}, \lambda_{\pi\pi}, \lambda_{\sigma\pi}$, and $\lambda_{\pi\sigma}$) above $T_c$ strong impurity scattering in the $\pi$-bands shunts normal transport current into the $\sigma$ band [101].

4.1.2. Lattice and related properties. Although the $\sigma$- and $\pi$-bands play different roles above and below $T_c$ this difference does not invalidate the use of normal-state resistivity as a measure of superconducting state connectivity. Thus the BG-based resistivity analysis has provided an effective cross-sectional area for general current transport as a measure of connectivity. As well as quantifying the connectivity of powder-formed MgB$_2$ superconductors the BG-based resistivity analysis yielded values for the intragrain residual resistivity, $\rho_0$ (not just its $F$-enhanced value). The increase in $\rho_0$ that accompanied the substitution of SiC (hence C) into MgB$_2$ (table 3) indicates increased scattering in the $\sigma$ band, the primary conveyer of normal-state current, in agreement with the results of thermal transport measurements on C-doped MgB$_2$ [102]. Deduced from the results of magnetic measurements [18, 21] (but not observed resistively for the above reason) C doping also enhances scattering in the $\pi$-band.
band and hence elevates the low temperature \( H_{c2} \) following equation (7). Thus C doping enhances scattering in both the \( \sigma \) and \( \pi \) bands, for which reason the observed increase in \( \rho_0 \) from 11.3 to 38.6 \( \mu \Omega \) cm is indirectly related to a corresponding increase in \( H_{c2} \) of from 21 to more than 33 T [5].

The BG analysis also yields resistive Debye temperatures, \( \theta_k \). For our three bulk samples, both undoped and doped (average value 680 K), the values obtained are significantly lower than the deduced \( \theta_k \)s of a pair several dense samples (\( \theta_k \sim 850 \) K) and a single crystal (950 K). From this we deduce that in the present set of samples granularity and porosity disturb the phonon spectrum more strongly than sample chemistry. To confirm the resistively measured \( \theta_k \) values the lattice specific heats of MB700, MBTi800, and MBSiC700 were measured at temperatures up to 300 K. The results (figure 9(a)) were in satisfactory agreement with published data including those of Wälti et al [95] who, in a paper dedicated to the specific heat of MgB\(_2\), reported a value of 34 J mol\(^{-1}\) K\(^{-1}\) at 200 K, cf 37.9 J mol\(^{-1}\) K\(^{-1}\) from figure 9(a). The PPMS machine’s internal software fitted the collected data to a standard Debye function and provided values of the calorimetric Debye temperatures, \( \theta_D \). By so doing it ignored the electronic component of total specific heat which, however, contributed less than about 2% to the lattice specific heat at 300 K. The values of \( \theta_D \) so obtained, averaging ~670 K, agreed rather well with the resistive results. Wälti et al obtained a \( \theta_D \) of 750 K on a pressed and sintered pellet of \textit{ex situ} MgB\(_2\) powder heat treated for 72 h at 500°C, and Bud’ko et al [96] obtained 750 ± 30 K on a pellet prepared \textit{in situ} for 2 h at 950°C. It is likely that these differences in \( \theta_D \) respond to the differences in sample preparation conditions.

Given a measured \( T_c \), e.g. from the electronic specific heat transition depicted in figure 9(b) and either the measured transport- or calorimetric Debye temperature, \( \theta_k \) or \( \theta_D \), an electron–phonon coupling constant, \( \lambda \), can be directly obtained via the following McMillan expression [103, 104]

\[
T_c = \frac{\theta_k}{1.45} \exp \left[ -1.04(1 + \lambda) \left( \frac{\lambda}{\mu^*} (1 + 0.62\lambda) \right) \right]. \tag{13}
\]

In selecting a value for \( \mu^* \), the Coulomb repulsion parameter or ‘psuedopotential’, a survey of the literature ([105–112], but see in particular [111]) yielded \( \mu^* = 0.10 \pm 0.02 \) (actually equal to the 0.1 estimated for most metals [111]). Presented in table 4, the results of our analysis provided \( \lambda = 0.98 \) for the sintered binary pellet and 0.89 and 1.02 for the doped ones. The value for our binary MgB\(_2\) lies within the range of reported values [101, 105–110, 112–114], namely 0.84 ± 0.21.

What emerges from the specific heat experiment is a global average coupling parameter, \( \lambda \), which according to [115] is related to the intraband and interband components, \( \lambda_{\sigma\sigma} \), \( \lambda_{\pi\pi} \), \( \lambda_{\sigma\pi} \), and \( \lambda_{\pi\sigma} \), by:

\[
\lambda = \frac{\lambda_{\sigma\sigma} + \lambda_{\pi\pi}}{2} + \frac{\sqrt{\left( \lambda_{\sigma\pi} - \lambda_{\pi\sigma} \right)^2 + 4 \lambda_{\sigma\pi} \lambda_{\pi\sigma}}}{2}. \tag{14}
\]

It is widely recognized (e.g. [106, 113]) that electron coupling to the so-called B\(_{2g}\) phonon mode that represents

| Sample        | Onset \( T_c \) (K) | \( \theta_k \) (K) | \( \theta_D \) (K) | \( \lambda (\mu^* = 0.10) \) |
|---------------|---------------------|-------------------|-------------------|-----------------------------|
| MB700 (binary)| 38.0                | 677               | 653               | 0.98                        |
| MBTi800 (TiB\(_2\)) | 36.5        | 764               | 745               | 0.89                        |
| MBSiC700 (SiC) | 35.5              | 593               | 600               | 1.02                        |

4.2. Extrinsic properties

In general, current transport in all kinds of polycrystalline MgB\(_2\) samples tends to be partially blocked by pores and grain-boundary precipitates such that the effective transport cross-sectional area is less than the conductor’s geometrical cross-sectional area by a large factor, \( F > 1 \). Based on the assumption that both superconducting- and normal-state electrical current transport are moderated by the same effective cross-sectional area the result of a normal-state electrical resistivity temperature dependence, \( \rho_m(T) \), measurement can be manipulated so as to provide a value for \( F \) and hence a ‘per cent connectivity’, \( K = 146/F \). This quantity is important to the development of practical MgB\(_2\) conductors since it leads to estimates of the projected \( J_S \) of microstructurally optimized materials quite apart from any improvements that might be expected to accompany the introduction of \( H_{c2} \)-enhancing and flux pinning dopants. In Rowell’s seminal articles on the subject [7, 8], \( F \)-values for fairly clean MgB\(_2\) were derived on the assumption of a universal ideal resistivity \( \rho_0(T) \) for all samples.

We have confirmed the validity of this approach for a pair of binary MgB\(_2\) samples but have gone on to show that it may break down for heavily doped ones. The breakdown has to do with a sample-to-sample variation of Debye temperature, \( \theta_D \). In order to take this into account we have replaced the invariant \( \rho_0(T) \) with its Bloch–Grüneisen (BG) counterpart. As a result excellent fits were obtained for the \( \rho_m(T) \) of three in-house-prepared samples as well as five published sets of \( \rho_m(T) \) data, as reported elsewhere [116]. The deduced values of \( F \) for our bulk powder-processed samples, after correcting for grain anisotropy following [10], yielded connectivities, \( K \), of from 17 to 37%. Comparable results are expected for \textit{in situ} PIT-processed wires indicating that increases in their \( J_S \) by factors of 6.0–2.7 would accompany the establishment of full connectivity.
It is important to note that $F_p$ curves reported to-date combine the effects of flux pinning and connectivity, the material’s real $F_p$ being obscured by deficient connectivity. While it is useful to compare the $J_c$ values of various classes of superconductor (e.g., MgB$_2$, YBCO, and Nb$_3$Sn), it is essential to de-convolute the connectivity from the $F_p$. Doing so enables us to define the essential properties in need of improvement. Figure 14 compares the 4 K $F_p$'s of an MgB$_2$ strand (actual and projected) with that of an ‘internal-Sn’ Nb$_3$Sn strand. As a starting point we compare the experimental $F_p$ for the MgB$_2$ strand (based on the $I_c$ of the powder core divided by the internal cross-sectional area of the sheath or stabilizer) with that of the Nb$_3$Sn strand (based likewise on its ‘non-Cu $J_c$’). Clearly MgB$_2$ cannot compete with Nb$_3$Sn within the liquid-H$_e$ temperature range depicted here.

Next, let us for a moment assume that a well connected MgB$_2$ strand could be made, such that (based on the bulk-material data of table 3) its $F_p$ is enabled to increase by factors of 2.7 or 6.0. As illustrated in figure 14 its 4 K $F_{p,\text{max}}$ would increase into the range of 26–57 GN m$^{-3}$ (cf that of Nb$_3$Sn which, however, occurs at a higher applied field). An even higher value of $F_{p,\text{max}}$, (namely 90 GN m$^{-3}$) was estimated by Matsumiya et al for their bulk MgB$_2$ sample assuming full connectivity [10, 117]. Not shown in the figure are the even greater enhancements of overall $F_p$ that would result from: (i) increases in $H_{c2}$ and the associated $H_{irr}$ that would follow the addition of suitably chosen dopants especially if they were homogeneously distributed or (ii) the shift to higher fields of the position of the $F_{p,\text{max}}$ in response to the inclusion of point pinning centers.

In displaying figure 14, we in no way aim to minimize the difficulty of achieving the projected $F_p$ goals, or even assert their inevitable attainment. Indeed, while we may surely expect improvements in both intrinsic and extrinsic properties, the degree to which we will be able to approach full connectivity is at present unknown. Similarly, we are constrained in the level of achievable homogeneity in $H_{c2}$ not only by the need to dope uniformly, but also to reduce the anisotropy, or to texture the material. The main point of figure 14 is to draw attention to the properties most in need of improvement. While flux pinning in MgB$_2$ is already relatively strong (comparable to that of Nb$_3$Sn) connectivity and doping homogeneity are the properties most in need of improvement and control.

5. Conclusion

The prospects for improving the properties of MgB$_2$ in wire form and rendering it suitable for numerous practical applications have been discussed from two essential standpoints, one dealing with the properties of the MgB$_2$ crystal or grain (the intrinsic properties) and the other having to do with ensuring that the intragranular properties are replicated in the material in strand form (the extrinsic aspect of the problem). Regarding intrinsic properties, published thin film results indicate that the true potential of MgB$_2$ can be approached by the inclusion in it of carefully selected dopants that: (i) increase $H_{c2}$ and associated $H_{irr}$, (ii) increase the volume pinning strength, $F_p$, and especially shifting its maximum to higher reduced fields by augmenting the present grain-boundary pinning with point pinning, (iii) and associate the foregoing with attention to dopant homogeneity, texturing (or, alternatively, anisotropy reduction). But in addition to the incremental improvements that are already being made to the intrinsic properties, spectacular increases in $J_c$ (hence $F_p$) over all fields and temperatures will accompany reductions in porosity and increases in connectivity. Porosity in in situ and ex situ-processed materials has been discussed and a new resistivity-based approach to overall connectivity measurement described. It has been estimated that full densification and the removal of intergranular blocking phases could yield across-the-board increases in $J_c$ of up to an order of magnitude. Thus, while all of the parameters listed above are important and will continue to demand attention, the issue of most pressing urgency is connectivity enhancement.

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