MgB$_2$ under pressure: phonon calculations, Raman spectroscopy, and optical reflectance

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The effect of pressure on optical phonon frequencies of MgB$_2$ has been calculated using the frozen-phonon approach based on a pseudopotential method. Grüneisen parameters of the harmonic mode frequencies are reported for the high-frequency zone-center $E_{2g}$ and $B_{1g}$ and the zone-boundary $E_{2u}$ and $B_{2u}$ modes at A. Anharmonic effects of phonon frequencies and the implications of the calculated phonon frequency shifts for the pressure dependence of the superconducting transition temperature of MgB$_2$ are discussed. Also reported are Raman and optical reflectance spectra of MgB$_2$ measured at high pressures. The experimental observations in combination with calculated results indicate that broad spectral features we observed in the Raman spectra at frequencies between 500 and 900 cm$^{-1}$ cannot be attributed to first-order scattering by zone-center modes, but originate in part from a chemical species other than MgB$_2$ at the sample surface and in part from a maximum in the MgB$_2$ phonon density of states. Low-temperature Raman spectra taken at ambient pressure showed increased scattering intensity in the region below 300 cm$^{-1}$.

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I. INTRODUCTION

Magnesium diboride, MgB$_2$, was recently discovered to exhibit a superconducting transition at 39 K [3], which is by far the highest $T_c$ for a binary compound. The light atomic masses in MgB$_2$ enhance the phonon frequencies which set the scale for $T_c$ in BCS theory. A variety of experimental observations (e.g., isotope effects [2] and scanning tunneling measurements of the superconducting gap [3]) indicate phonon-mediated (BCS) superconductivity, and theory finds medium or strong electron-phonon coupling [4]. The coupling is predicted to be particularly strong for the zone-center optical phonon of $E_{2g}$ symmetry and the related phonon branch connecting to the zone-boundary $E_{2u}$ mode at the A point (direction along the $c$ axis of the AlB$_2$-type structure) [5,6].

The effect of pressure on the superconducting properties of MgB$_2$ has been studied by several groups. [10–15] While there is some scatter in the experimental pressure coefficients all studies show a decrease of $T_c$, at rates between 0.7 and 2.0 K/GPa. Lattice parameters under pressure have been determined by neutron and x-ray diffraction [14,15]. An ab initio calculation of the pressure-volume relation and the optimized c/a axial ratio under pressure [2] is in good agreement with the experimental data. It was concluded that the decrease in $T_c$ is not driven by a change in the electronic density of states near $E_F$ but by an increase in phonon frequencies, specifically of the strongly coupled $E_{2g}$ mode [20].

The frequency of the $E_{2g}$($\Gamma$) phonon is expected between 470 and 665 cm$^{-1}$, according to recent calculations [12,22–24]. So far, this phonon mode has not been identified unambiguously by neutron inelastic scattering [22] or in Raman experiments [19,23,24]. A Raman spectrum by Bohnen et al. [23] indicates a broad asymmetric feature near 580 cm$^{-1}$, while other authors [19,22–24] report an even broader feature (260–300 cm$^{-1}$ width) centered near 620 cm$^{-1}$. Contradictorily, compliance with the selection rules for a $E_{2g}$ mode has been reported [22] as well as complete breakdown of the same, attributed to resonance effects [2]. The 620-cm$^{-1}$ feature was observed to increase in frequency under pressure, with an unusually large Grüneisen parameter [19]. It was generally assigned to first-order zone-center phonon scattering, highly broadened by strong electron-phonon coupling or anharmonic effects, but other interpretations were also considered.

In this paper we present a theoretical investigation of the pressure dependence of phonon frequencies of MgB$_2$. As no phonon has been, so far, unambiguously identified experimentally, the theoretical methods gain in importance – in particular the ab initio approaches, such as the frozen phonon method which is employed in this work. Compared to linear response theory, the frozen phonon method has the disadvantage that it is not very efficient in generating an overall picture of the phonon dispersions throughout the Brillouin zone, but is restricted to calculation of a few high-symmetry modes. One of the advantages of the frozen phonon method, however, is that it yields a clear picture of anharmonic effects, which in earlier calculations [3] were found to be particularly large for the atomic displacements corresponding to the $E_{2g}$ mode of MgB$_2$. The immediate interest in the shifts of phonon frequencies is in the context of interpreting the pressure dependence of $T_c$. Furthermore, the calculated pressure dependences of phonon frequencies can in principle be useful for the identification of spectral features in Raman spectra.

We also report here Raman and optical reflectance measurements of MgB$_2$ as a function of pressure at room temperature. Based on the pressure dependence of Raman spectra and the optical reflectance and by taking
into account the results of the phonon frequency calculations we argue that the observed Raman features are not due to zone-center first-order Raman scattering from MgB$_2$. The interpretation we suggest for our Raman results considers a superposition of a density-of-states peak of MgB$_2$ and scattering by a different chemical species present at the surface of as-grown samples. We also take a look at zero-pressure Raman spectra measured as a function of temperature in order to check whether it is possible to observe a pair-breaking excitation below $T_c$.

The paper is organized as follows: the symmetry analysis in Section II. Details of the theoretical method and the calculated results are presented and discussed in Section III. Experimental details and results are given in Section IV, followed by conclusions in Section V.

II. SYMMETRY ANALYSIS

The frozen phonon calculations described below require knowledge of the phonon displacement patterns. We thus start with the symmetry analysis of the vibrational spectra. The point group of the AlB$_2$ structure is $D_{4h}$. A factor-group analysis yields the decomposition of the coordinate representation

$$B_{1g} + E_{2g} + 2A_{2u} + 2E_{1u} \text{ at } \Gamma$$  \hspace{1cm} (1)

and

$$A_{1g} + E_{1g} + A_{2u} + B_{2u} + E_{1u} + E_{2u} \text{ at } A$$  \hspace{1cm} (2)

with, at the point $\Gamma$, one $A_{2u}$ and one $E_{1u}$ referring to the rigid translations ($\omega = 0$). Constructing then projection operators we find the bases spanning the irreducible representations in Eqs. 1 and 2 – i.e., the respective phonon displacement patterns at $\Gamma$ and $A$, respectively. They are shown in Figs. 1 and 2, with the modes arranged (columnwise) in the order of decreasing MgB$_2$ eigenfrequencies (which are obtained later, in Section II.C). At high pressures this ordering may, of course, be altered. The patterns in Fig. 2 are arranged so as to be the “end-points” of those $\Gamma$–$A$ branches of the phonon dispersion that start with the corresponding pattern in Fig. 1. This means that e.g. the three patterns in the last column of Fig. 2 are the end-points of the acoustic branches.

The patterns at $A$ alternate the $+u$ and $-u$ displacements from one layer to another. In addition, for the two highest frequency modes we notice that (within the $\pm$ alternation) the patterns of a layer are the same as at $\Gamma$.

III. CALCULATIONS

A. Theoretical Method

The frozen phonon approach starts from the $ab$ initio evaluation of the total energy $E^{tot}$ of the solid with frozen-in atomic displacements. The energy is evaluated using the density functional theory (DFT) within the generalized gradient approximation (GGA) [28]. We work in a plane-wave basis and use pseudopotentials. For the actual calculations we employed the VASP codes [29] [32] and the ultra-soft Vanderbilt-type pseudopotentials [33] were supplied by Kresse and Hafner [34]. The pseudopotential we chose for Mg treats the semicore states explicitly, i.e., Mg is represented with 8 valence electrons $2p^63s^2$, and the non-linear core correction (NLCC) [36] is applied as well. The calculations are carried out with the plane-wave cutoff energy of 33.6 Ry, and the Brillouin zone sampling is based on $\Gamma$-centered uniform meshes $16 \times 16 \times 14$ or $16 \times 16 \times 8$ – the latter one applied in the calculations with the doubled unit cell for frozen phonons at the Brillouin zone boundary. As the system is metallic, the $\vec{k}$-space integration with the incompletely filled orbitals uses the tetrahedron method [35] with Blöchl’s corrections [37]. The above meshes divide the Brillouin zone into 21504 or 12288 tetrahedra; the number of irreducible tetrahedra is lower by a factor 2 to 6, depending on the symmetry of the frozen-in phonon.

B. Structural Properties

For eleven volumes between 25.0 Å$^3$ and 29.6 Å$^3$, we calculated $E^{tot}(V)$ with different $c/a$ values while keeping the volume $V$ constant and, for every chosen $V$, found the optimized structure, i.e. the corresponding $a(V)$, $c(V)$, $c/a(V)$, and $E(V)$. The latter data were fitted by the Murnaghan relation for $E(V)$ [38] which provided the static equilibrium [39] as well as the bulk modulus $B_0$ and its pressure derivative $B'$. The results are summarized in Table I. The calculated equilibrium volume $(V_0 = 28.663$ Å$^3$) compares well with the experimental value $V_0 = 28.917(1)$ Å$^3$ (Ref. [18], at 37 K) meaning that we are -0.9% off in $V_0$. The individual lattice parameters are -0.6% off the experiment for $a_0$, +0.2% for $c_0$, and +0.8% for $c_0/a_0$. The variation of $c/a$ under pressure has been translated into a quadratic function of $(1 - V/V_0)$ and its coefficients are given in Table I as well. The present results are also in good agreement with those of a previous calculation [21] (see Table I).

A limited testing of different pseudopotentials revealed that treating the magnesium $2p^6$ electrons as valence states is not essential for getting the correct equilibrium, but using the GGA (rather than the LDA) is [21]. With the value of $c/a = 1.14$ the MgB$_2$ is well inside the stability region of the AlB$_2$ structures [11]. A rather
high pressure would probably be required to induce a phase transition, possibly towards the UHg$_2$-type structure (isostructural to AlB$_2$, but c/a less than $\sim$ 0.8) or a variant thereof, as is observed in other AlB$_2$-type intermetallic compounds [2].

The subsequent calculations of phonon frequencies are performed at the calculated equilibrium, and at volumes related to pressure by the Murnaghan relation

$$P(V) = \frac{B_0}{B'} \left( \frac{V}{V_0} \right)^{-B'} - 1,$$

which uses the calculated $V_0, B_0, B'$ quoted in Table I.

C. Phonon frequencies

In this work we are mainly concerned with the two highest frequency modes $B_{1g}(\Gamma)$ and $E_{2g}(\Gamma)$ and their $A$-point counterparts $B_{2u}(A)$ and $E_{2u}(A)$. For comparison with previous works we calculated the $A_{2v}(\Gamma)$ and $E_{1u}(\Gamma)$ as well. The branch $E_{2g}(\Gamma) - E_{2u}(A)$ in the phonon dispersion is the one that exhibits the strongest electron-phonon coupling [8], and the $B_{1g}(\Gamma)$ is the $z$-displacement analogue of the $E_{2g}(\Gamma)$.

We determine the vibrational eigenfrequencies using the frozen phonon method [23], while paying particular attention to obtaining the harmonic part of the ab initio calculated energy differences that, inevitably, have to be probed by finite displacements $u$. Thus for each pattern, atoms are given 5 different displacements ranging from $u/a = 0.010$ to 0.035, and the (six) calculated energy values $E(u)$ are fitted with a quartic polynomial yielding

$$\Delta E_{tot}(u) = a_2(u/a)^2 + a_3(u/a)^3 + a_4(u/a)^4$$

As an example we show in Fig. 3 the variation of $E_{tot}(u)$ for the $E_{2g}(\Gamma)$ mode [24]. The harmonic part of $\Delta E_{tot}$ is then retained for determination of the phonon energy:

$$\frac{\omega^2}{2} \sum M_k u_k^2 = E^{harm}(u \neq 0) - E^{harm}(u = 0)$$

For the four phonons listed above the procedure is repeated at various volumes. Although straightforward, this procedure calls for a few explanations.

The frozen-in phonon displacements of Fig. 4 conserve the translational symmetry of the elementary unit cell defining the MgB$_2$ structure. With the zone boundary modes given in Fig. 2 the total energy calculations as a function of displacement $u$ are to be done on a unit cell obtained by doubling the elementary cell (viz. along the [001] direction), which then comprises two formula units of MgB$_2$. The frozen-in displacements also lower the rotational symmetry of the system: starting from the $D_{6h}$, which is the point-group of the MgB$_2$ lattice, we end with, respectively, $D_{3d}$, $D_{2h}$, $C_{2h}$ when the $B_{1g}(\Gamma)$, $E_{2g}(\Gamma)$-(a,b) displacements are imposed, and $D_{3h}$, $D_{2h}$, $D_{2h}$ with the $B_{2u}(A)$, $E_{2u}(A)$-(a,b) displacements, respectively.

As the displacements $u$ are finite, a larger or smaller degree of anharmonicity will always be present, but some restrictions on the latter can be read out from symmetry. With all patterns at the zone boundary, replacing $+u$ by $-u$ has the same effect as shifting the phonon distorted structure by the lattice constant $c$, and it leaves the $E(u)$ invariant. Consequently, the cubic (and, generally, odd-power-) anharmonicity is forbidden in all zone-boundary modes. Inspecting, in turn, the $\Gamma$-displacement patterns we realize that for nearly all modes the $+u \leftrightarrow -u$ substitution is equivalent to applying a mirror reflection or $C_2$ rotation – an operation which, in spite of the lower symmetry, is still present in the point groups of the phonon-modulated structures and which thus leaves invariant the structure and its energy $E(u)$. This forbids the cubic term in the expansion of $E(u)$ as well. Among the 9 modes in Fig. 3 the $E_{2g}(\Gamma)$-(a) pattern is the only one in which all anharmonic terms are allowed and in which the cubic anharmonicity is to be expected.

For evaluation of phonon frequencies from $\Delta E_{tot}(u)$ we used the atomic masses of B and Mg that correspond to the natural isotope distribution: 10.8 and 24.3 a.m.u.; this is the usual approach in the spirit of the virtual crystal approximation. We may keep in mind that for a $^{10}$B-enriched sample the frequencies of all the modes involving boron would be higher by 4%.

Table I summarizes the results of our frozen phonon calculations at different volumes: the variations with volume or pressure are described by the mode Gr"uneisen parameter $\gamma_0 = -[d \ln \omega/d \ln V]/\omega_0$ or the coefficients $a$ and $b$ of a quadratic fit (see the caption). Figure 4 shows the calculated phonon frequencies as a function of volume.

We estimate that the calculated harmonic frequencies are uncertain to $\sim$1–3% (depending on the mode); this is the “instrumental precision” of the determination of total energies and the uncertainty following from the error analysis in fitting the variations $E(u)$ by polynomials.

D. Anharmonicity and the $E_{2g}(\Gamma)$ mode

We note that the five displacements $u/a$ quoted above range from one half to approximately the double of the r.m.s. displacement [24], and one expects vibrations in both harmonic and anharmonic regimes. The effort of removing from $\Delta E_{tot}$ the anharmonic contributions yields, in turn, an insight into the anharmonicities.

The phonons exhibiting the strongest electron-phonon coupling are those of the $E_{2g}(\Gamma) - E_{2u}(A)$ branch [8]. The $E_{2g}(\Gamma)$ has already received considerable attention [24,25,26,28]. Being doubly degenerate, it is materialized
by two distinct displacement patterns which are labeled (a) and (b) in Fig. 1. They both should lead to the same eigenfrequency (the same coefficient \(a_2\) in Eq. 4) and, in this sense, they are equivalent – as long as we stay within the harmonic approximation, i.e., within the standard group-theory reasonings. Once we step out of the harmonic approximation, the displacements (a) and (b) will become two unrelated patterns which are described by different anharmonic coefficients. This gets confirmed by numerical calculations and we obtained \(a_2 = 107\) eV/cell with both (a) and (b) patterns and, somewhat unexpectedly, also \(a_4 = 45800\) eV/cell equal in both patterns. The two modes are nevertheless distinct in the cubic term, which is absent in the (b) pattern \((a_3 = 0)\) and given by \(a_3 = -1644\) eV/cell in the (a)-pattern.

It is not difficult to understand why the mode \(E_{2g}(\Gamma)\) - (a) exhibits a strong cubic anharmonicity: giving the boron atoms a \(+u\) or \(-u\) displacement, the main contribution to \(\Delta E_{\text{tot}}\) comes from stretching or compressing the B–B bonds – which, obviously, has very different energetic cost. In the calculations, the cubic anharmonicity of the mode is dealt with easily: after obtaining the \(\Delta E_{\text{tot}}\) with the displacements \(+u\) and \(-u\) we take an average, and are left with \(\Delta E_{\text{tot}}\) carrying quartic anharmonicity only. Using the pattern (b) instead of (a) is technically somewhat simpler, because the averaging of the contributions from the stretched and compressed bonds is “built in” within the same displacement pattern.

A striking feature of the \(E_{2g}(\Gamma)\) mode (one which already has been noticed by other authors) is its strong anharmonicity \(a_4\); it is larger by an order of magnitude than that of the \(B_1g(\Gamma)\) mode. This is equally true for the corresponding mode \(E_{2u}(A)\) at the Brillouin zone boundary and, apparently, holds for the whole branch \(E_{2g}(\Gamma) - E_{2u}(A)\). The ratio of the quartic and harmonic energies, at any given displacement \(u\), is \(a_4/a_2^2 = 4\) eV\(^{-1}\) for \(E_{2g}(\Gamma)\) and 3.5 for \(E_{2u}(A)\). Yildirim et al. \(^[9]\) arrived at an even stronger anharmonicity of the \(E_{2g}(\Gamma)\) mode: \(a_4/a_2^2 \approx 8\) eV\(^{-1}\).

Large anharmonicity is consistent with a strong variation of the phonon frequency with volume and the mode Grüneisen parameters of \(E_{2g}(\Gamma)\) and \(E_{2u}(A)\) turn out to be much larger than those of the other modes (see Table II) – and, in any case, unusually large: 2.5 and 2.8, respectively. The corresponding frequency shifts \(\Delta \omega \propto \gamma \omega\) are approximately the same, which means that the whole branch \(E_{2g}(\Gamma) - E_{2u}(A)\) is shifting “rigidly” when compressed – unlike the branch \(B_{1g}(\Gamma) - B_{2u}(A)\) which becomes more dispersive under pressure.

It is interesting to note that for the \(E_{2g}(\Gamma)\) and \(E_{2u}(A)\) modes the quartic coefficient \(a_4\) of Eq. 4 (not given in Table II) turns out to be approximately constant and independent of volume, in the entire range of volumes shown in Fig. 6; this means that, under pressure, the quartic energy goes as the inverse fourth power of the lattice constant \(a\).

A well known effect of anharmonicity is in broadening the spectral features in phonon spectroscopies and in shifting them by some amount \(\Delta(\omega)\) with respect to the ideal \(\delta(\omega’ - \omega)\)-like response of the perfectly harmonic system. The intricate details of the variation \(\Delta(\omega)\) are beyond the scope of this work. Yildirim et al. \(^[9]\) report that for the \(E_{2g}(\Gamma)\) mode the \(\Delta(\omega)\) amounts to a frequency shift by 17 - 25% above the harmonic frequency. The estimate is based on their results for \(a_2, a_4, \omega(E_{2g}(\Gamma)) = 486\) cm\(^{-1}\) and employs two different ways of “renormalizing” the harmonic frequency. Taking into account that the anharmonic shift, in the lowest order of perturbation theory, is proportional to the ratio \(a_4/a_2^2\) and to the phonon energy \(\hbar \omega\) itself \(^[13]\), a simple rescaling of the Yildirim et al. results suggests, for our case, a 9 to 13% upshift of the \(E_{2g}(\Gamma)\)-frequency; similarly, the shift in \(E_{2u}(A)\) can be estimated at 7 to 10% (see the hatched areas in Fig. 6). Treating in the same way also the calculated harmonic phonon frequencies in compressed unit cells we estimate that these shifts reduce the Grüneisen parameters of the two modes from 2.5 and 2.8 to \(\gamma_0 = 2.0 - 2.2\) and \(\gamma_0 = 2.3 - 2.5\), respectively.

E. Comparison with other calculations

There have been several calculations of zone-center vibrations \(^[8,22]\) and phonon dispersion \(^[8,22]\). The results obtained for modes at \(\Gamma\) are compared in Table II. The most conspicuous feature of the comparison is the large spread of the results for the \(E_{2g}(\Gamma)\) mode – the calculated frequency varies from 470 cm\(^{-1}\) to 665 cm\(^{-1}\) – although otherwise good agreement between different authors is found for the other \(\Gamma\) modes.

Bohnen et al. \(^[23]\) attribute the disagreement in the frequency of the \(E_{2g}(\Gamma)\) mode to an insufficiently converged \(k\)-point sampling in some of the calculations. In our case we have ensured that full convergence is reached.

Large anharmonicity of the \(E_{2g}(\Gamma)\) was proposed as a possible cause of the discrepancies by Yildirim et al. \(^[9]\). The proper “separation” of the harmonic part in the calculated \(\Delta E_{\text{tot}}\) indeed matters: evaluating the frozen phonon energy at \(u = 0.057\) Å (=the r.m.s. displacement) we obtain, for the \(E_{2g}(\Gamma)-(a)\) mode, the harmonic term in Eq. 4 of 37.84 meV, the cubic 10.57 meV and the quartic 3.33 meV. Billing the quartic contribution into the harmonic energy would shift the frequency up by as much as 7%, assuming that the cubic term has been correctly eliminated (else the frequency would be shifted by another \(\pm 14\%)\).

When linear response theory is used for calculation of phonon frequencies the results are free of anharmonic contributions by construction. Nevertheless the results of Refs. \(^[22,23]\) for the \(E_{2g}(\Gamma)\) mode show a large spread, too (cf. Tab. II).
We note that there is still another factor which can be a source of considerable discrepancies. The large mode Grüneisen parameter implies a high sensitivity of the calculated $E_{2g}(\Gamma)$ phonon frequency to the (equilibrium) volume used. Some authors choose to perform the phonon calculations at the experimental equilibrium $V_0^{\exp}$ rather than at the calculated equilibrium $V_0^{th}$. Both choices are legitimate and, as a rule, they do not lead to any marked disagreements; the modes with large $\gamma$ may nevertheless constitute an exception. Our present calculations refer to the calculated equilibrium $V_0^{th}$ and the $E_{2g}(\Gamma)$ frequency at the experimental $V_0^{\exp}$ would be only 12 cm$^{-1}$ lower; the difference however becomes 35 cm$^{-1}$ in Ref. \cite{23} where the authors were careful enough to determine two sets of frequencies for all $\Gamma$-point phonons, viz. one at the theoretical and one at the experimental equilibrium. Generally, the existence of two results (one at $V_0^{th}$ and one at $V_0^{\exp}$) is an intrinsic uncertainty underlying the concept of frozen phonons itself and, in a sense, it can be thought of as a consequence of the DFT-LDA. If we estimate that, in a typical DFT-LDA calculation, the $V_0^{th}$ is between 1 and 3\% under the experimental value $V_0^{\exp}$, and with the Grüneisen parameter of the order $\gamma = 2.5$, the two calculations of frequencies of $E_{2g}(\Gamma)$ can differ by as much as 2.5 to 7.5\% (≈ 40 cm$^{-1}$).

Another possible source of discrepancies between frozen-phonon results are the errors of statistical nature that relate to the details of the fitting of Eq. (3) e.g., the choice of the degree of the polynomial and the selection of the displacements $u$ for which the $E(u)$’s are calculated and the polynomial then fitted. Even if the consequent differences are relatively small, both choices should be clearly stated for the sake of reproducibility.

The $E_{2g}(\Gamma)$ mode is, apparently, very sensitive to all details of the calculation. Besides the convergence with the plane-wave cutoff, the $k$-point sampling, and the technique used for dealing with the incompletely filled orbitals (the “metallic sampling” algorithm) – which are amenable to quantitative testing – still another source of divergences between different calculations is in the choice of the pseudopotentials or of the method for determination of the total energy. The consequent uncertainties are difficult to estimate though.

Considering the large spread, among different authors, in the calculated values of the $E_{2g}(\Gamma)$ mode frequencies, experimentally, one might attempt to discern this mode from the other ones by its unusually large value of the Grüneisen parameter $\gamma$ rather than by its frequency.

F. Mode Grüneisen parameters and pressure dependence of $T_c$

The whole optical phonon branch connecting the $E_{2g}(\Gamma)$ and the $E_{2u}(A)$ modes was shown to exhibit strong electron-phonon coupling \cite{23}. Within a medium or strong coupling scenario it is considered to largely determine the superconducting properties of MgB$_2$. Based on early calculations of the electron-phonon coupling constant \( \lambda \approx 0.7 \), an assumed mode Grüneisen parameter $\gamma = 1$, and a calculated pressure dependence of the density of states at the Fermi level of $d\ln N(0)/dP = -0.31\%/$GPa, the pressure dependence $d\ln T_c/dP$ of the critical temperature was estimated to fall in the range $-2.3$ to $-3.6\%/$GPa \cite{20}. The estimate compared well with experimental data and thus supported the notion of BCS superconductivity in MgB$_2$. The pressure-induced increase in characteristic phonon frequency was identified as the dominant cause of the decrease of $T_c$ under pressure.

With a refined calculated value of $\lambda = 0.87$ \cite{8}, $\omega_0 = 500$ cm$^{-1}$, and a typical Coulomb pseudopotential of $\mu^* = 0.1$ we obtain $T_c, P=0 = 36.7$ K based on the McMillan expression in the form given in Ref. \cite{24}. Following the analysis of Ref. \cite{21} but using an average $\gamma = 2.3$ for the $E_{2g}(\Gamma)$–$E_{2u}(A)$ phonon branch (taking into account anharmonicity) and a bulk modulus $B_0 = 145$ GPa as calculated above, as well as $d\ln N/dP = -0.31\%/$GPa \cite{20}, we estimate $dT_c/dP \approx -1.8$ K/GPa. Experimental values of $dT_c/dP$ in the range $-0.7$ to $-2.0$ K/GPa have been reported \cite{14}. The large spread of experimental data was, at least in part, attributed to differences in the samples studied \cite{14}. Our estimate of the pressure dependence of $T_c$ is close to the upper limit of the experimental values. This, however, is not surprising because we used the large Grüneisen parameter of the dominant $E_{2g}(\Gamma)$–$E_{2u}(A)$ phonon branch. Non-negligible contributions from other vibrational modes with smaller pressure dependences are expected to reduce the pressure shift of $T_c$ compared to our estimate.

Other effects may also be of relevance, especially a possible pressure dependence of the electron-ion matrix element $I$ which enters the electron-phonon coupling constant $\lambda$ and was assumed to be constant here. Nevertheless, the present results (in particular the large mode Grüneisen parameter of the phonon branch with the strongest electron-phonon coupling) underline the dominant role of the pressure dependence of the phonon spectrum with regard to $T_c$.

IV. EXPERIMENTS

A. Experimental Details

Polycrystalline MgB$_2$ was prepared from stoichiometric mixtures of Mg (Johnson Matthey Inc., 99.98\%) and natural Boron powder (≈325 mesh, 99.99\%, Aldrich). The reaction was carried out at 850°C for two days using sealed Ta capsules under Ar atmosphere that were in turn encased in evacuated silica tubes. After grading
under Ar, the sample was annealed at the same temperature for one day. The x-ray powder diffraction pattern showed a single phase sample with $a = 308.63(3)$ pm and $c = 352.34(3)$ pm. In susceptibility measurements the superconducting transition was observed at $T_c = 38.2(1)$ K.

For the high-pressure experiments at ambient temperature small amounts of the powder samples were placed into gasketed diamond anvil cells (DACs). The remainder of the sample cavity was filled with KCl as a quasi-hydrostatic pressure medium. The sample was in direct contact with the diamond window through which the Raman and reflectance spectra were taken.

High-pressure Raman spectra were excited at 633 nm employing a long-distance microscope objective. They were recorded in back-scattering geometry using a single-grating spectrometer with a multi-channel CCD detector and a holographic notch filter for suppression of the laser line (Dilor LabRam). For the Raman experiments the DAC was equipped with synthetic diamonds (Sumitomo type IIa) which emit only minimal luminescence. Optical reflectivity spectra of MgB$_2$ in the energy range 0.6–4.0 eV were measured using a micro-optical setup described in Ref. [13]. Pressures were measured by the ruby luminescence method [14–19]. Low-temperature Raman spectra of MgB$_2$ were excited with the 647-nm line of a Kr-ion laser. The scattered light was analyzed by a triple-grating spectrometer (Jobin-Yvon T64000) in combination with a multi-channel CCD detector. A DAC with synthetic diamonds was used as a low-luminescence container for the powder sample.

**B. Optical reflectance under pressure**

We first take a brief look at the optical reflectance spectra of MgB$_2$, because they provide some information for understanding the evolution of the Raman spectra under pressure. At low pressures, a low reflectance is observed throughout the spectral range from 0.6 to 4 eV [Fig. 3(a)]. At higher pressures the NIR reflectance increases and above 10 GPa we observe a Drude-like edge characteristic of a metallic sample. This edge then remains present even upon pressure release from 25 to 1 GPa. This observation indicates that the grains of the MgB$_2$ powder may be covered with some non-metallic surface layer which is, at least partially, removed by the deformation of the grains upon compression. X-ray photoemission studies have indeed shown that MgB$_2$ samples which have been exposed to air are covered with surface layers of B$_2$O$_3$ [28] and possibly MgCO$_3$ or Mg(OH)$_2$ [29]. Werheit et al. concluded that samples of boron-rich compounds in general tend to be covered with surface contaminants which are not transparent near 500 nm [22]. Consequently, Raman spectra of such compounds excited in the visible spectral region may be dominated by contributions from the surface layer rather than the bulk material.

The energetic position of the Drude edge uncovered by pressure cycling is probably determined by the onset of strong interband absorption at energies around 2 eV. The fact that the edge shows a small red shift of less than 10 meV/GPa on releasing the pressure from 25 to 1 GPa indicates a small change of the related interband absorption threshold. We have calculated the interband contributions $\varepsilon_{zz}^{\omega} (\omega)$ and $\varepsilon_{xx}^{\omega} (\omega)$ to the imaginary part of the dielectric function of MgB$_2$ [see Fig. 3(b)] using the WIEN97 code [30] with parameters as described in Ref. [21]. Without going into details here, we just note that the calculated $\varepsilon_{zz}^{\omega} (\omega)$ indeed shows a threshold at 2.1 eV, which shifts under pressure to higher energy at a rate of 8 meV/GPa. These interband transitions may result in resonance effects in Raman scattering.

**C. Raman spectra under pressure**

Figure 3 shows ambient-temperature Raman spectra of MgB$_2$ recorded at increasing pressures in the range 0–14 GPa and decreasing pressures of 15–0 GPa. In between the pressure was increased to $\sim$20 GPa. The 0.6-GPa spectrum of Fig. 3(a), consisting of a broad peak near 600 cm$^{-1}$ with a high-energy shoulder, is representative for the ambient-pressure Raman spectra of numerous samples we have investigated. It is also quite similar to an ambient-pressure Raman spectrum of MgB$_2$ reported by Bohnen et al. [23]. With increasing pressure the shoulder gains intensity and the spectrum exhibits two clearly resolved peaks. The enhanced intensity of the higher-energy peak persisted upon pressure release until the cell was opened and the sample was exposed to air [Fig. 3(b)].

Neither of the observed peaks can be attributed to the Raman-active $E_{2g} (\Gamma)$ mode nor to the silent $B_{1g} (\Gamma)$ mode. The observed pressure-induced peak shifts [Fig. 3, Tab. IV] translate to mode Grüneisen parameters of $\gamma_1 = 0.27$–0.45 and $\gamma_2 = 0.8$–1.2 for peaks (1) and (2), respectively, using $\omega_0 = 145$ GPa. Hence, the calculated Grüneisen parameter of the $E_{2g} (\Gamma)$ phonon and the experimental value for peak (1) differ by a factor of ~6. Similarly, for peak (2) the mode Grüneisen parameter and the 0-GPa frequency differ by a factor 2.3 and $>200$ cm$^{-1}$, respectively, from the values calculated for the $E_{2g} (\Gamma)$ mode. The pressure-induced peak shifts appear not to be fully reversible. This may, at least in part, be attributed to difficulties in determining the exact peak positions because of an intense nonlinear background that changes with pressure. It does not, however, compromise the above conclusion.

Tentatively, we attribute the higher-energy mode (2) with $\omega_0 = 750 \pm 20$ cm$^{-1}$ to a well-defined peak in the phonon density of states near 730 cm$^{-1}$ according to calculations by Kong et al. [8] and Bohnen et al. [23] as well as inelastic neutron scattering data by Osborn et al. [24].
Observation of this density-of-states peak in our spectra implies a violation of the momentum conservation for the Raman scattering process which may originate from disorder of the sample and/or the small optical penetration depth of the laser light into the metallic sample. A violation of the momentum conservation would not lead to spectral features near the frequency of the $E_{2g} (\Gamma)$ mode, as there is no density-of-states peak at this frequency $\approx 2\hbar k B_T$.

By taking into account the observations made in reflectance measurements we conclude that only the higher-energy peak (2) in our Raman measurements originates from MgB$_2$ which is uncovered from surface layers through the application of high pressure. The lower-energy peak (1) which is the dominant feature of the Raman spectra of MgB$_2$ at ambient conditions is attributed to a surface layer of different chemical composition. It should be noted that we observed this mode also for samples that had been stored under inert conditions. Probably, the surface layers form already during the material synthesis.

Goncharov et al. have also studied MgB$_2$ at high pressures by Raman spectroscopy [19]. In contrast to our results they observed only a single broad spectral feature (FWHM $\sim$300 cm$^{-1}$) centered near 620 cm$^{-1}$ (at 0 GPa) showing a large pressure dependence ($\gamma = 2.9$). They assign the feature to first-order Raman scattering, but also consider other possible interpretations. Their observations may be reconciled with ours if one assumes that the two components visible in our spectra (FWHM $\sim$180 cm$^{-1}$) contribute to the very broad spectral feature observed by Goncharov et al. The change in the relative intensities of the components (1) and (2) would then lead to a large pressure dependence of the “smeared-out” peak. The weighted average (“center of gravity”) of the two peak positions exhibits an effective Gr"uneisen parameter $\gamma = 2.0$ [Fig. 2]. A direct interpolation between peak (1) at 0 GPa and peak (2) at 14 GPa results in $\gamma = 4.0$. The resulting range for the effective $\gamma$ of 2.0–4.0 thus includes the value $\gamma = 2.9$ given in Ref. [19].

D. Low-temperature Raman spectra

We investigated whether it is possible to observe a pair-breaking excitation below $T_c$ similar to what has been reported for conventional superconductors such as Nb$_3$Sn and V$_3$Si [24].

Upon cooling of a MgB$_2$ sample below 50 K we observed a buildup of additional scattering intensity in the range 50–300 cm$^{-1}$ [Fig. 3(a)] which can be modeled by two Gaussian peaks located at 128 and 226 cm$^{-1}$, respectively, in the 2-K spectrum. These peak positions are higher in energy than $2\Delta_0 \approx 90$ cm$^{-1}$ according to BCS theory, i.e. $2\Delta_0 \approx 3.5k_B T_c$ with $T_c = 38$ K. A number of experiments, however, have indicated superconductivity in MgB$_2$ to be in the medium or strong-coupling regime with $2\Delta_0/k_B T_c$ up to 5 ($2\Delta_0 \approx 130$ cm$^{-1}$) [25]. With increasing temperature these peaks vanish only at a temperature between 74 and 100 K, i.e., well above $T_c$ [Fig. 3(b)]. They were observed only for parallel polarizations of the incident and scattered light. Furthermore, the rising intensity below 30 cm$^{-1}$ is not due to residual stray light but it originates from Raman scattering by the sample. The physical origin of the reported spectral features is unclear at present.

Chen et al. also investigated the superconducting gap of MgB$_2$ by Raman spectroscopy [21]. They reported a redistribution of spectral weight at frequencies below $\sim$200 cm$^{-1}$ and the appearance of a small peak at 110 cm$^{-1}$ which they attributed to the pair-breaking excitation. Differing from our results a polarization dependence of the Raman spectra was not observed.

V. CONCLUSIONS

Using the frozen phonon approach we have calculated the harmonic frequencies of selected optical phonons of MgB$_2$ for different volumes corresponding to a pressure range of 0 to 30 GPa. Large differences are found in the absolute values of mode Gr"uneisen parameters. In particular, for the whole $E_{2g} (\Gamma)$--$E_{2u} (A)$ branch the frequencies are highly sensitive to volume changes, as indicated by large values of the corresponding mode Gr"uneisen parameters. In earlier calculations [23] the $E_{2g} (\Gamma)$--$E_{2u} (A)$ branch of the phonon dispersion was identified as the one which exhibits the strongest electron-phonon coupling. Therefore, within a medium or strong coupling scenario it is considered to govern the superconducting properties of MgB$_2$. Within this picture the present results for the mode-Gr"uneisen parameters underline the dominant role of the phonon spectrum with respect to the observed decrease of $T_c$ with pressure.

Based on our calculations and Raman scattering experiments on MgB$_2$ at high pressures we conclude that the dominant Raman peak near 600 cm$^{-1}$ in the ambient-pressure spectra reported by various authors does not originate from MgB$_2$. We rather relate it to a contaminant phase present at the sample surface. A second peak located near 750 cm$^{-1}$, visible only as a weak shoulder in spectra of as-grown samples, is tentatively attributed to a peak in the phonon density of states. A calculation of the phonon density of states under pressure, extending previous ambient-pressure work [22], is desirable to test this assignment.

Temperature-dependent Raman experiments on MgB$_2$ showed a build-up of additional scattering intensity in the region below 300 cm$^{-1}$ upon cooling below $T_c$. A broad double-peak structure appeared at 130/230 cm$^{-1}$ and vanished only upon warming the sample to temperatures
well above $T_c$. Further study of the low-temperature Raman spectra of MgB$_2$ is clearly needed to elucidate the physical origin of the various observations.

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TABLE I. Calculated structural parameters of MgB$_2$ at zero pressure: equilibrium volume ($V_0$), lattice constants ($a_0$, $c_0$), bulk modulus ($B_0$) and its pressure derivative ($B'$). Variation of the calculated $c/a$ ratio with volume is given by the quadratic polynomial $c/a = c_0/a_0 + \alpha(1 - V/V_0) + \beta(1 - V/V_0)^2$ with the coefficients $\alpha$, $\beta$ listed below.

| $V_0$ | $a_0$ | $c_0$ | $B_0$ | $B'$ | $c_0/a_0$ | $\alpha$ | $\beta$ |
|-------|-------|-------|-------|------|-----------|----------|--------|
| 28.663 | 3.065 | 3.522 | 144.7 | 3.6  | 1.1490    | -0.258   | -0.06  |
| Experiment | 28.917(1) | 3.08230(2) | 3.51461(5) | 147–155$^b$ | (4.0$^b$) | 1.14026$^a$ |         |
| Difference | $-0.9\%$ | $-0.6\%$ | +0.2% |      |           |          |        |

$^a$Ref. [18], at 37 K. $^b$Ref. [16,18,19] with the assumption $B' = 4$.

TABLE II. Calculated pressure and volume dependence of selected phonon frequencies in MgB$_2$. The zero pressure frequency $\omega_0$ and the linear and quadratic pressure coefficients were obtained by least square fits of $\omega(P) = \omega_0 + a \cdot P + b \cdot P^2$ to the calculated data, and the mode Gr"uneisen parameters $\gamma_0$ (at equilibrium volume) are derived from a similar quadratic expression for $\omega(V)$. $P$ has been obtained from $V$ through the calculated $P - V$ relation (see text).

| Mode | $\omega_0$ (cm$^{-1}$) | $a$ (cm$^{-1}$/GPa) | $b$ (cm$^{-1}$/GPa$^2$) | $\gamma_0$ |
|------|----------------------|-------------------|-------------------|----------|
| $B_{1g}(\Gamma)$ | 695 | 3.06506 | -0.018995 | 0.6 |
| $E_{2g}(\Gamma)$ | 535 | 8.9744 | -0.0780 | 2.5 |
| $B_{2u}(A)$ | 636 | 1.70378 | -0.01163 | 0.4 |
| $E_{2u}(A)$ | 480 | 8.9019 | -0.0809 | 2.8 |

TABLE III. Harmonic contributions to the phonon frequencies at the $\Gamma$-point calculated by different ab initio methods. All frequencies are given in cm$^{-1}$.

| $B_{1g}(\Gamma)$ | $E_{2g}(\Gamma)$ | $A_{2u}(\Gamma)$ | $E_{1u}(\Gamma)$ | Method | Reference |
|-----------------|-----------------|-----------------|-----------------|--------|-----------|
| 690 | 470 | 390 | 320 | Frozen Phonon | Kortus$^1$ |
| 679 | 665 | 419 | 328 | Linear Response | Satta$^2$ |
| 692 | 585 | 401 | 335 | Linear Response | Kong$^3$ |
| 696 | 536 | 394 | 322 | Linear Response | Bohnen$^2$ - I: at $V_0^{exp}$ |
| 702 | 571 | 405 | 327 | Linear Response | Bohnen$^2$ - II: at $V_0^{th}$ |
| 702 | 486$^a$ | 402 | 328 | Frozen Phonon | Yildirim$^4$ |
| 695 | 535 | 400$^b$ | 333$^b$ | Frozen Phonon | Present work |

$^a$Frequency based on the harmonic term of the quadratic expansion of $\Delta E_{tot}(u)$ (analogous to Eq. 3). The “shifted” frequency obtained by treating the anharmonicity within the Self-Consistent Harmonic Approach or based on the energy levels of an anharmonic oscillator amounts to 565 or 601 cm$^{-1}$, respectively.

$^b$Results obtained by fitting the calculated $E(u)$ with a quadratic polynomial.

TABLE IV. Observed frequencies $\omega_0$ of Raman features of MgB$_2$ and their pressure coefficients $a = d\omega/dP$. The values for the mode Gr"uneisen parameters $\gamma_0$ are based on a bulk modulus $B_0 = 145$ GPa.

| Mode | $\omega_0$ (cm$^{-1}$) | $a$ (cm$^{-1}$/GPa) | $\gamma_0$ |
|------|----------------------|-------------------|----------|
| Peak (1) | | | |
| $P$ up | 597(1) | 1.85(15) | 0.45 |
| $P$ down | 609(2) | 1.51(19) | 0.27 |
| up/down average | 603(6) | 1.68(17) | 0.40 |
| Peak (2) | | | |
| $P$ up | 734(3) | 6.3(3) | 1.2 |
| $P$ down | 770(8) | 4.4(8) | 0.8 |
| up/down average | 752(18) | 5.4(10) | 1.0 |
FIG. 1. Phonon displacement patterns of the zone-center (Γ) modes in MgB₂ (the AlB₂ structure, point group $D_{6h}$), in the order of decreasing frequencies (at zero pressure, columnwise). The labels (a), (b) denote the different patterns corresponding to the degenerate $E$-modes. For the (optic) $A_{2u}$ and $E_{1u}$ patterns to be eigenmodes, the displacements $u, v$ of the two sublattices have to be such that the unit cell’s center of mass stays in rest, i.e. $u : v = M_{Mg} : 2M_B$. The $E_{2g}$ mode is Raman active, the $A_{2u}$ and $E_{1u}$ infrared active, the $B_{1g}$ is silent.
FIG. 2. Symmetry determined displacement patterns for the zone-boundary modes at the $A$-point of the hexagonal Brillouin zone. Only one layer of MgB$_2$ is shown in the $E$-patterns, and it is understood that equivalent atoms above and below the layer displayed vibrate in the opposite direction. The patterns are arranged so as to belong to the same branch of the phonon dispersion $\omega_j(k)$ as the corresponding $\Gamma$-modes in Fig. 1; thus e.g. the three patterns in the last column are the “end-points” of the acoustic branches.
FIG. 3. Calculated total energy of MgB$_2$ at equilibrium volume as a function of boron displacements corresponding to the $E_{2g}(\Gamma)$-(a) and $E_{2g}(\Gamma)$-(b) modes of Fig. 1. Full circles and open diamonds: ab initio total energy calculations; solid and dashed lines: quartic polynomials, Eq.
FIG. 4. Calculated harmonic frequencies of the two highest modes at $\Gamma$ and $A$ in MgB$_2$ as a function of relative volume; $V_0$ refers to calculated static equilibrium (zero pressure). The lines represent quadratic relation fitted to the calculated points, and they define the mode-Grüneisen parameters $\gamma$ listed in Table I. Note that $\gamma$ itself depends on pressure, its variation with volume is shown in the inset. The hatched areas represent the estimated frequencies of the modes $E_{2g}(\Gamma)$ and $E_{2u}(A)$ when anharmonic effects are taken into account.
FIG. 5. (a) Optical reflectance spectra of MgB$_2$ at ambient temperature and pressures up to 25 GPa. $R_d$ denotes the absolute reflectance at the diamond–sample surface. (b) Calculated imaginary part of the dielectric function (interband transitions) at 0 GPa (solid lines) and 20 GPa (broken lines) for light polarized perpendicular ($\varepsilon_{xx}$) and parallel ($\varepsilon_{zz}$) to the c axis.
FIG. 6. Raman spectra of MgB$_2$ for (a) increasing and (b) decreasing pressures ($T = 300$ K). In between the pressure was increased to $\sim 20$ GPa. After pressure release the sample was in contact with air before recording the 0-GPa spectrum in (b).
FIG. 7. Energies of the Raman features (1) and (2) of MgB$_2$ as a function of pressure. Solid and open symbols refer to data measured at increasing and decreasing pressures, respectively. Lines represent linear relations fitted to the data.
FIG. 8. Raman spectra of MgB$_2$ at ambient pressure for (a) decreasing and (b) increasing temperatures. “∥ Pol.” and “⊥ Pol.” refer to parallel and crossed polarizations of the incident and scattered light, respectively.