High-pressure anomaly in the normal state of MgB_2

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The E_{2g} mode phonon frequency anomaly, observed in high-pressure Raman measurements for the high-temperature superconductor MgB_2 and conjectured to arise due to a phonon-assisted electronic topological transition (ETT), has been corroborated by us with the details of electronic structure calculations of this compound. The present studies have been carried out with a B-atom displacement of the frozen-in E_{2g}-mode phonon that mimics the effects of thermal vibrations. We found a splitting of the doubly degenerate σ band along the Γ-A direction. The splitting of the band reduces with pressure, causing an ETT at 18 GPa. This ETT is expected to cause anomaly in the E_{2g} phonon mode by influencing the ionic system. Our calculated electron-phonon coupling constant λ, for the distorted lattice with a frozen-in displacement, also depicts an anomalous variation around 18 GPa.

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I. INTRODUCTION

It has long been conjectured that metallic compounds composed of light elements would be good candidates for the occurrence of high-temperature superconductivity due to the added efficacy of the phonon-mediated pairing because of the higher phonon frequencies. The discovery of superconductivity in the borocarbides[1] some years ago led to greater efforts at searching for superconductivity in compounds made of the light elements like B and C. Recently these efforts were successful with the discovery of superconductivity in MgB_2 ($T_c \sim 39$ K) by Akimitsu.[2,3] This has led to a great deal of interest in this compound. At ambient conditions it crystallizes[3] in the layered hexagonal AlB_2-type structure. In the basal plane Mg atoms arrange themselves in a hexagonal lattice. Interpenetrating the Mg atoms are the B atoms arranged in a honeycomb lattice.

A boron isotope effect[4] has been observed in MgB_2 with an observed partial boron isotope exponent $\alpha = 0.26$. This result not only confirmed the role of phonons in the occurrence of superconductivity but also led to further investigations which showed that the modes most relevant for pairing of electrons were the in-plane B vibrations.[5] Of the known high-temperature superconductors, MgB_2 has the highest T_c among noncuprate superconductors other than the alkali-doped fullerenes. However, unlike the cuprates or even the fullerenes, the absence of strong electronic correlations in these compounds makes it possible to apply conventional methods of electronic band structure and phononic mode frequencies to the study of this material.

The motivation for our studies came from experimental Raman studies of the E_{2g}-mode frequency under high pressure. Measurements by Meletov *et al.*[6] revealed that the mode frequency increased linearly with pressure. However, the slope of its variation changed twice: once at 5 GPa and again near 18 GPa. The first change at 5 GPa was attributed to extrinsic effects due to homogenization of defects in the sample. They however attributed the second change near 18 GPa to the occurrence of an electronic topological transition (ETT). Similar studies by Goncharov and Struzhkin[7] confirmed that the distinct slope change seen earlier near 5 GPa was an extrinsic effect as it was absent in the cleaner samples used by them. These high-pressure measurements which used liquid He as the pressure transmitting medium confirm the anomaly near 18 GPa, as earlier seen by Meletov *et al.*, who used an ethanol-methanol mixture (which freezes at around 10 GPa) as the pressure transmitting medium. Further Garg *et al.*[8] also observed an anomalous fall by 30% in the electrical resistance of MgB_2 near 18 GPa which was attributed to an ETT.

For a better understanding of these issues we have carried out *ab initio* calculations of the electronic band structure under high pressure to demonstrate the occurrence of an ETT leading to the anomaly in high-pressure Raman data in MgB_2. We have also calculated the E_{2g}-mode frequency under pressure. Our electronic structure calculations show that there is nothing happening under pressure except a small broadening of the B σ bands which lie close to the Fermi level. Meletov *et al.* had earlier suggested that the in-plane B vibrations causes the splitting of the planer B σ bands near the Fermi level which in turn leads to an ETT. This, they argued, was the cause of the phonon anomaly seen in Raman measurements at 18 GPa. It is also known that the E_{2g} mode is anharmonic,[5] and since the B atoms are light, the room-temperature vibrations correspond to a shift of the root-mean-square position of the B atoms. In order to clarify these issues and to show the presence of an ETT around 18 GPa we carried out electronic band structure calculations by displacing the B atoms, accordingly, as per the E_{2g}-mode vibrations. This causes a splitting of the degenerate σ bands, with one of the split bands along the Γ-A direction cutting the Fermi level at ambient pressure. As the pressure is increased this band gradually shifts upwards in energy until at a pressure of 18 GPa or more it lies entirely above the Fermi level along the Γ-A direction. Thus we find the signatures of a phonon-assisted ETT at about 18 GPa pressure for the first time.

Our phonon frequency calculations yield a dispersion that increases linearly with pressure. However, no change of slope is seen up to 28 GPa. This is not surprising as our phonon calculations are within the harmonic approximation,

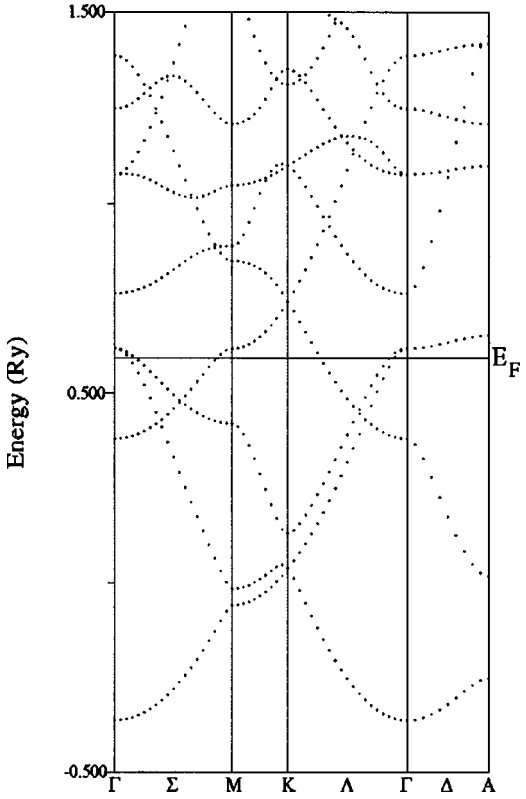

FIG. 1. Band structure of MgB_2 at 18 GPa which corresponds to 10% compression. E_F denotes the Fermi level.

and it is known that the E_{2g} mode of MgB_2 is highly anharmonic and proper consideration of anharmonic effects could be crucial for the observed phonon anomaly. To study the effect of an ETT on the phononic sector we calculated the electron-phonon coupling constant for different pressures, taking into account the σ-band splitting due to B-atom displacement, which leads to an ETT. Our calculated λ also shows the effect of a phonon-assisted ETT occurring near 18 GPa pressure. We now present the details of our investigations.

II. ELECTRONIC BAND STRUCTURE AT HIGH PRESSURE

Our *ab initio* electronic structure calculations are based on full-potential linear-augmented plane-wave (FPLAPW) method as implemented in the WIEN2K computer code.[9] As is well known, the basis functions inside the muffin-tin sphere are the radial solutions of the Kohn-Sham equation with linear expansion around a chosen energy value, and the plane-wave expansion is used in the interstitial region. The exchange-correlation terms have been treated within the generalized gradient approximation (GGA).[10] Our calculations are semirelativistic (the effects of spin-orbit coupling have been ignored as they are known to be insignificant for Mg as well as B regarding the properties discussed in the present work). The calculations are performed with the experimentally known hexagonal lattice structure of MgB_2. The muffin-tin radius for Mg ($3s^2$) is 1.8 a.u. compared to

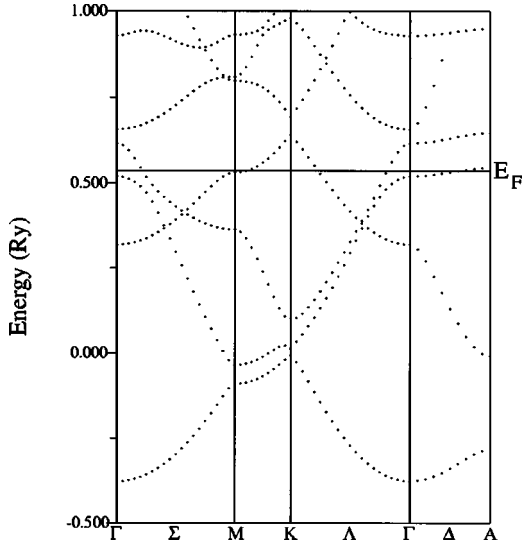

FIG. 2. Band structure of MgB_2 at ambient pressure with a frozen in E_{2g} phonon displacement.

1.45 a.u. for B ($2s^2 2p^1$). The axial ratio (c/a) of the hexagonal lattice at each volume compression is located by obtaining the minimum of the total energy at that compression. The corresponding pressure is found by fitting the calculated total energy versus volume curve to a polynomial and then evaluating the slope of the curve. We have used 296 **k** points for the Brillouin zone summation in its irreducible wedge. About 670 plane waves have been used in the interstitial region ($RK_{MAX}=9$ in WIEN2K). The tolerance used for charge convergence is 10^{-5} which gives better than 10^{-5} Ry convergence in the total energy.

The details of our calculations of the band structure at ambient pressure have been presented elsewhere,[11] and so we present here only the results of our calculated band structure at 18 GPa which corresponds to 10% compression of the ambient volume. The calculated energy bands along the symmetry directions in the Brillouin zone are plotted in Fig. 1. The eigenvalue at Γ of this band is shifted down towards the Fermi level by 4 mRy and at A is shifted up by 2 mRy, giving 6 mRy additional broadening under compression. To explore the possibility of an ETT driven by lattice displacement we have also performed the band structure in the presence of a frozen-in distortion of the boron atoms by 0.06 Å of the E_{2g}-mode symmetry which is a reasonable distortion corresponding to rms displacement at room temperature. In Fig. 2 we show the calculated band structure in this case. The degeneracy along the Γ-A direction is lifted, and the σ bands along the Γ-A direction split with the lower band intercepting the Fermi level. The results are very similar to those obtained by An and Pickett[12] who studied the band structure with similar (0.057 Å) frozen-in distortion at ambient pressure.[13] To approximately estimate the B-atom displacement at 18 GPa, we have assumed that the energy per mode is characterized by the temperature, as in harmonic vibration, and use the relation $\Omega_0^2\langle u_0^2\rangle = \Omega_p^2\langle u_p^2\rangle$ where Ω_p is the phonon frequency and u_p the B-atom displacement at pressure P.

We now turn our attention to the calculation of the E_{2g} phonon frequency at high pressure. Our calculations are

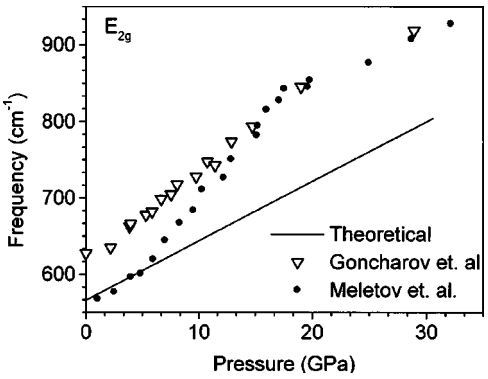

FIG. 3. Calculated E_{2g}-mode frequency at various pressures compared with experimental results.

based on density functional perturbation theory and are performed using the plane-wave self-consistent field (PWSCF) method.[14] The Hessian of the Born-Oppenheimer surface required for the phonon frequency calculations needs the ground-state electron charge density, as well as its linear response to a distortion of the nuclear position. The equilibrium geometry of the system is given by the condition that the Hellmann-Feynmann force acting on any individual nucleus vanish and hence dynamical ETT effects cannot be incorporated in this type of calculation. von Barth–Car pseudopotentials are used for both Mg and B atoms. The energy cutoff chosen for the pseudo wave functions is 70 Ry, whereas 484 **k** points were used for Brillouin zone sampling. At the harmonic level we find a linear variation of the frequency with pressure. The results for the calculated frequency as a function of pressure are given in Fig. 3. The mode frequency at ambient pressure is 570 cm^{-1} which compares well with the value of 580 cm^{-1} measured by Meletov *et al.*[6] but disagrees with the value of 630 cm^{-1} reported in Ref. 7. The rate of hardening of the mode frequency with pressure obtained by us also differs from the experimental value. From ambient pressure study[15] it is known that anharmonic effects are strong[5] and have the effect of hardening the phonon frequency. Having estimated the phonon frequency we are now in a position to arrive at the room-temperature rms value of 0.047 Å for the B-atom displacement at 18 GPa. Using this number we once again calculated the band structure. The obtained band structure is shown in Fig. 4. Along the Γ-A direction the lower split σ band almost touches the Fermi level. This result is an indication that there is a phonon-assisted ETT at high pressure, around 18 GPa (as this flat band along Γ-A, though split, does not intersect the Fermi level), which is close to the pressure at which anomalies are seen in the variations of the E_{2g}-mode phonon frequency, electrical resistance, and T_c. We would like to note that the effect of pressure on the Fermi surface in superconductors has been previously studied in the case of Hg-based cuprate superconductors where electronic structure studies[18,19] revealed that application of pressure drives the Van Hove singularity in the density of states to the Fermi level, a kind of ETT.

III. PHONON ANHARMONICITY AND λ CALCULATION

It is to be noted that the ETT obtained by us is phonon assisted. The electronic structure calculation has been carried

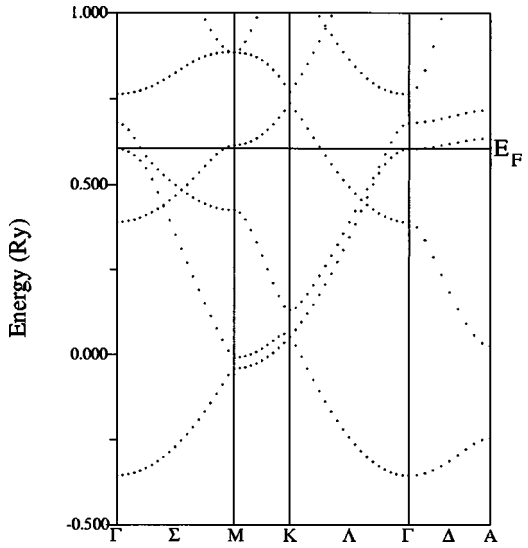

FIG. 4. Band structure of MgB_2 at 18 GPa pressure with a frozen-in E_{2g} phonon displacement.

out in the presence of a frozen-in displacement of the B atoms corresponding to the E_{2g} phonon mode. The magnitude of the displacement of the atoms corresponds to the rms amplitude of thermal vibrations of this mode, and it reduces with increasing pressure due to a hardening of the phonon frequencies. The phonon frequencies themselves have been calculated for small displacements about the original 0 K equilibrium positions of the atoms and thus do not include the effect of the thermal vibrations that cause changes in the electronic spectrum. Ideally one could think of estimating anharmonic effects by carrying out the calculations of phonon frequencies for theoretically optimized lattice constants and room-temperature experimental lattice parameters. However, it is known that theoretically optimized lattice parameters vary with the approximations made for exchange-correlation terms and hence such a comparison is not conclusive. In fact, we found a reduction of the phonon frequencies with experimental volumes as they are larger than theoretically optimized volumes under compression.[20] This is an inherent shortcoming of the perturbed density-functional method (as implemented in the code PWSCF) employed by us to calculate the phonon frequencies and calculations that include the frozen-in displacements of the B atoms cannot be performed within this method and is consistent with above calculations. Thus any feedback of the electronic band splitting on the phonons would only be through the electronic self-energy due to the electron-phonon coupling in this material. Considering the usual linear electron-phonon coupling we find that the corresponding phonon self-energy is proportional to the electronic density-density correlation function. This correlation function is given, in the lowest order in the electron-phonon coupling, by $\chi(q,\Omega)=\Sigma_k(n_{k+q}-n_k)/(\varepsilon_{k+q}-\varepsilon_k-\Omega)$. Here q and Ω are the phonon wave-vector and frequency respectively, ε_k is the electronic energy (modified due to the frozen-in displacement of B atoms), and n_k is a Fermi factor. As the experimental anomaly is a phonon anomaly seen in Raman scattering experiments we have studied the $q=0$ zone center

phonon mode. For this choice of wave vector it is easy to see that the self-energy vanishes. This result is not changed by going to higher orders in the linear electron-phonon coupling as the self-energy still is proportional to χ within the random phase approximation. Any corrections coming from vertex corrections are negligibly small because of Migdal's theorem. Thus the only way that the ETT would be seen as an anomaly in the pressure variation of the phonon frequency of the Raman-active E_{2g} mode is through the nonlinear electron-phonon coupling which has been suggested by Yildirim *et al.*[5] to be large. However, a consideration of this effect is beyond the scope of our work. It is worth pointing out that the reasoning presented here, which rules out any Raman phonon anomaly within a linear description of phonons, constitutes strong evidence for the extreme importance of nonlinear behavior involving phonons in MgB_2. Further detailed first-principle studies[5,15] point unambiguously to the importance of anharmonic and nonlinear terms both in the phonon Hamiltonian as well as the electron-phonon coupling Hamiltonian of the E_{2g} phonon mode. It is pertinent to note that the temperature dependence of the phonon frequency of the E_{2g} Raman-active phonon has been studied experimentally[17] by Martinho *et al.* and it has been found that this temperature dependence leads to inconsistencies in the Gruneissen parameter with respect to earlier experimental studies.[7] This once again points to the inadequacy of a purely harmonic description of the phonons.

Let us consider the dimensionless electron-phonon coupling constant (λ) calculations using the PWSCF method.[21] For determination of electron-phonon coupling constant one needs to evaluate the Fermi-surface-averaged deformation potential for each zone-center phonon mode. We only consider the contribution of the E_{2g} mode at the Γ point ($\mathbf{q}=0$). We then have the relation

$$\lambda = 1/\Omega^2 \sum_{n,m} \int d^3k/V_{\mathrm{BZ}} [\delta(E_{k,n} - E_F)\delta(E_{k,m} - E_F)]/[(2\pi)^2 N(E_F) M] |\langle u_{k,m}| \boldsymbol{\varepsilon} \cdot \boldsymbol{\nabla} \mathbf{V} |u_{k,n}\rangle|^2. \quad (1)$$

Here ε is the polarization vector, M is the atomic mass, n and m are the band indices, $u_{k,n}$ is the periodic part of the wave function with the eigenvalue $E_{k,n}$, $N(E_F)$ is the density of states at the Fermi level, and ∇V is the periodic part of the gradient of the self-consistent potential with respect to the atomic displacements. We calculated the electron-phonon coupling constants for various pressures both for normal, and distorted lattices which give the ETT. Here the main effect of the lattice distortion is to change the Fermi-surface topology,[8] and so to calculate λ for the distorted lattice we have carried out a Fermi-surface average of the deformation potential in the changed topology. The pressure variations of the two sets of λ's are shown in Fig. 5. From Fig. 5 it is evident that at high pressure, when both split bands are above the Fermi level, λ's corresponding to the undistorted and distorted lattices coincide because of similar Fermi-surface topology Shukla *et al.*[16] (the value of λ at ambient pressure is also shown for comparison). At lower pressure there is a large difference between the two because of differences in the Fermi-surface topology. This also qualitatively explains the observed T_c anomaly.[7]

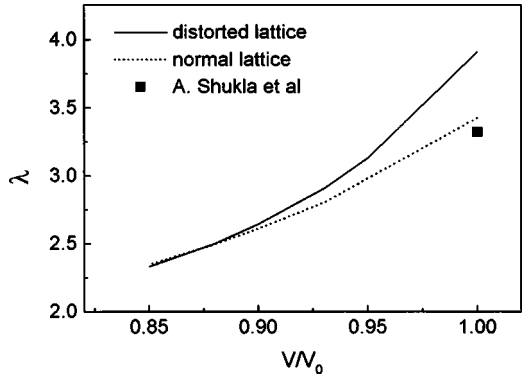

FIG. 5. Pressure variation of electron-phonon coupling constant λ. ■ represents the calculated value of λ at ambient pressure by A. Shukla *et al.* (Ref. 16).

IV. CONCLUSION

Finally we conclude by summarizing the main points of this paper. We have calculated the electronic band structure under high pressure both with and without a static distortion of the crystal lattice by displacing B atoms and find evidence for a phonon-assisted ETT near 18 GPa, whereas no ETT occurs without lattice distortion. Our calculated electron-phonon coupling constant also shows an anomaly near the same pressure region. We have also calculated the phonon frequency of the E_{2g} mode under pressure using perturbed density functional theory in the harmonic approximation. We find a linear variation of the frequency with pressure up to 28 GPa without any discontinuity in the slope of the variation, pointing to the need to include the anharmonic and/or nonlinear terms in first-principles-based estimates of the phonon frequencies, especially in simulating the effects of subtle transitions like ETT's at nonzero temperatures.

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