Evidence for Two Superconducting Gaps in MgB$_2$

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We have measured the Raman spectra of polycrystalline MgB$_2$ from 25 to 1200 cm^{-1}. A superconductivity-induced redistribution in the electronic Raman continuum was observed. Two pair-breaking peaks appear in the spectra, suggesting the presence of two superconducting gaps. The measured spectra were analyzed using a quasi-two-dimensional model in which two s-wave superconducting gaps open on two sheets of Fermi surface. For the gap values we have obtained $\Delta_1 = 22$ cm^{-1} (2.7 meV) and $\Delta_2 = 50$ cm^{-1} (6.2 meV). Our results suggest that a conventional phonon-mediated pairing mechanism occurs in the planar boron σ bands and is responsible for the superconductivity of MgB$_2$.

The recent discovery [1] of superconductivity in MgB$_2$ at temperatures below 39 K has generated a great deal of interest [2]. The electronic band structure of MgB$_2$ has been calculated by a number of groups who have arrived at a consistent picture for the Fermi surface [3–5]. It appears that the carriers involved in superconductivity are associated with the planar boron σ orbitals that give rise to a Fermi surface consisting of two approximately cylindrical sheets. Carriers in the σ bands are predicted to be strongly coupled to phonons that involve an appropriate motion of the boron atoms. Conventional superconductivity with an s-wave gap, or multiple gaps [6], has been predicted, and the unusually high $T_c = 40$ K is obtained with intermediate coupling strength [5]. On the other hand, the experimental results are quite inconsistent, have yielded conflicting evidence in some cases, and have not provided confirmation for the theoretical predictions. In particular, the magnitude of the superconducting gap (Δ) has been measured with techniques including NMR, tunneling, high-resolution photoemission spectroscopy, scanning tunneling spectroscopy, IR reflectivity, and specific heat measurements, and the results vary from 2 to 8 meV [7–13]. The discrepancies between these results and the lack of knowledge about the k dependence of the superconducting gap have become a major difficulty in understanding the nature of the superconducting mechanism of MgB$_2$.

Raman spectroscopy is an effective technique for studying the superconducting gap in superconductors [14–16]. Typically, at temperatures below T_c, a superconductivity-induced renormalization in the Raman spectrum occurs as a result of the opening of the superconducting gap. In particular, the intensity of the electronic Raman continuum is depleted at low frequencies because of the lack of available electronic states below the gap. Moreover, scattering from electronic excitations across the gap usually results in the appearance of a pair-breaking peak, and the peak frequency is a measure of the size of the gap (2Δ). When the gap is anisotropic, its k dependence can be determined by investigating the polarization dependence of the Raman spectra below T_c, as different scattering geometries essentially probe different portions of the Fermi surface [16]. In fact, Raman spectroscopy has been successfully used in the studies of the superconducting gap in both conventional [14] and high-T_c superconductors [15,16].

In order to determine the magnitude and k dependence of the superconducting gap in MgB$_2$, we have carried out an experimental investigation of MgB$_2$ using Raman spectroscopy. We observed two pair-breaking peaks in the low-temperature spectra, which indicates the existence of two superconducting gaps. Moreover, to determine the gap energies and gain insight into the superconducting mechanism, we have analyzed the experimental data using a quasi-two-dimensional model. The results are consistent with expectations based on the calculated band structure. In this Letter, we report the results of our investigation and discuss their physical significance.

Polycrystalline MgB$_2$ samples used in this study were prepared by the rapid reaction of stoichiometric quantities of powdered amorphous boron (B) and magnesium (Mg). The samples show very clean powder x-ray diffraction patterns with all major MgB$_2$ peaks the same as those observed by Nagamatsu *et al.* [1]. The critical temperature as determined by resistivity and susceptibility measurements is $T_c = 38.75$ K and the resistive transition width is $\Delta T_c = 0.23$ K (10%–90%). The fine structure of the samples was examined with a scanning electron microscope and the size of the crystal grains was found to range from 0.15 to 0.3 μm.

The Raman spectra were obtained in a quasibackscattering geometry using the 514.5 nm line of an Ar-ion laser, which was focused onto the sample with a cylindrical lens to provide an incident intensity of about 1 W/cm^2. In particular, the incident laser power was 0.2 mW and the size of the sampling spot was about 40 μm × 600 μm. By

examining the temperature and laser power dependence of the spectra, the laser heating effect was estimated to be 5 ± 3 K. The temperatures reported in this paper are the ambient temperatures without any correction. Two polarization configurations were used in the Raman measurements, VV and HV, where VV (HV) represents the scattering geometry in which the polarization direction of the incident light is vertical (horizontal), and the polarization direction of the scattered light is always vertical.

Figure 1 shows the VV and HV Raman spectra of MgB_2 measured at 15 and 45 K. All the spectra presented in this paper have been divided by the Bose factor (considering the laser heating effect, a 5 K correction has been added to the temperature in the Bose factor). The intensity levels of the spectra have been normalized using their integrated intensity in the frequency region of interest. Clearly, there are no well-defined phonon lines in either the VV or HV spectra. Instead, a broad maximum centered at about 620 cm^{-1} appears in both scattering geometries, and changes slightly when the temperature is cooled below T_c. This broad feature can be interpreted as due to phonon contributions throughout the Brillouin zone. The frequency range of this feature is consistent with theoretical calculations of the phonon energies [5,17] as well as the result of neutron scattering measurements of the density of states of phonons [18]. As we know, in disordered materials phonons away from the Brillouin zone center can become Raman active [19]. In this case the phonon density of states is reflected in the Raman spectra. In fact, the broadness of this feature and the similarity between the shapes of the polarized (VV) and depolarized (HV) spectra, as well as the intensity ratio of the VV and HV spectra, are very similar to what has been observed in amorphous materials [20]. However, since the x-ray diffraction patterns clearly show typical sharp lines of powdered crystals, our samples are unlikely amorphous. Moreover, considering the possibility of heterogeneity, we examined spectra from different sampling areas but did not find any significant difference.
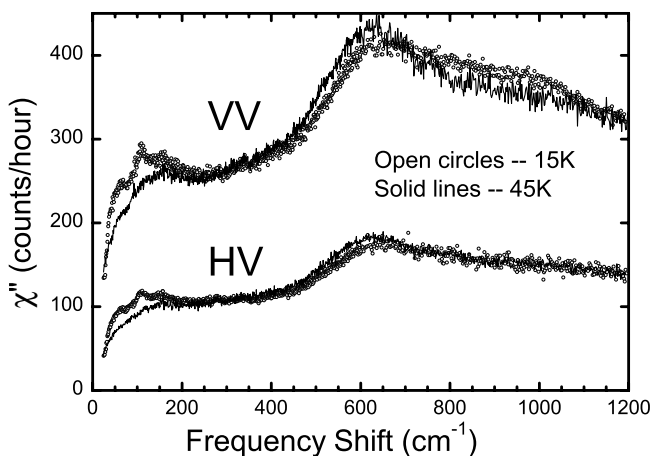
Therefore, we believe that the samples are reasonably homogenous but strongly disordered.

As shown in Fig. 1, when the temperature is decreased below T_c, a superconductivity-induced redistribution occurs in the low-frequency region ($\omega < 280$ cm^{-1}) of the spectra. To investigate this redistribution more closely, we have subtracted the 45 K spectra from the 15 K spectra and plotted the results in Fig. 2. Clearly two peaks appear at frequencies of about 50 and 105 cm^{-1}. These peaks are identified as pair-breaking peaks [14] which originate from electronic excitations across the superconducting gap. The frequency of a pair-breaking peak is a measure of the binding energy of the Cooper pairs, which is two times the gap value (2Δ). The presence of two pair-breaking peaks in the spectra suggests two superconducting gaps in MgB_2.

A careful comparison between the VV and HV spectra in Fig. 2 reveals that the shape of the spectrum is independent of polarization configuration. Such polarization independence can be interpreted as the consequence of several possible reasons, such as the disorder of the material and the isotropy of the superconducting gap. In the following data analysis, we will focus on the VV spectrum and ignore the polarization dependence of the Raman tensor.

According to Klein and Dierker [14], in the small wave vector limit ($q \rightarrow 0$), the photon cross section for Raman scattering from pairs of superconducting quasiparticles at zero temperature is given by

$$\frac{d^2R}{d\omega d\Omega} = \frac{4Nr_0^2}{\omega} \left\langle \frac{|\gamma(\mathbf{k})|^2 |\Delta(\mathbf{k})|^2}{\sqrt{\omega^2 - 4|\Delta(\mathbf{k})|^2}} \right\rangle \quad (1)$$

where N is the density of states for one spin, r_0 is the Thomson radius, $\gamma(\mathbf{k})$ is the polarization-dependent

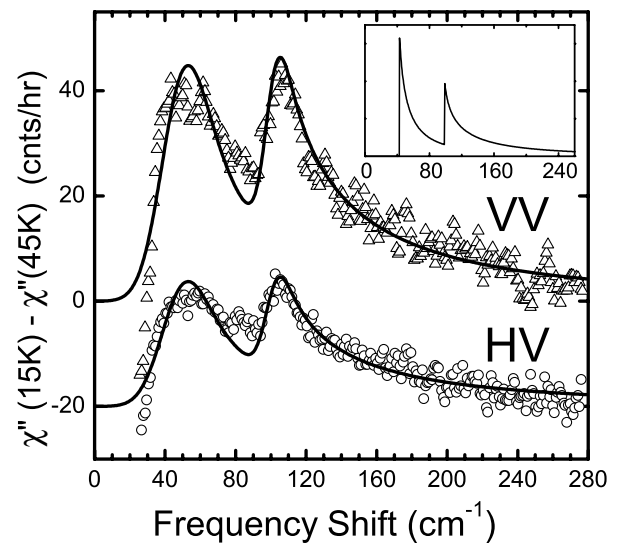FIG. 1. Raman spectra of polycrystalline MgB_2 (after dividing by the Bose factor).

FIG. 2. Low-temperature electronic Raman continua obtained by subtracting the 45 K spectra from the 15 K spectra. The thick solid lines are theoretical fits. The HV spectra have been shifted downward by 20 units. The inset is a calculated spectrum without convoluting with a Gaussian function.

Raman vertex, and the brackets denote an average over the Fermi surface (FS) with the restriction $\omega^2 > 4|\Delta(\mathbf{k})|^2$. Kortus *et al.* [3] have calculated the electronic band structure and mapped out the FS of MgB_2. We are particularly interested in the two sheets of cylindrical FS from the planar boron σ bands near the Γ point. For a given k_z, since these surfaces are isotropic in the $k_x - k_y$ plane, we simply assume that two isotropic s-wave gaps (Δ_1 and Δ_2) open on these two sheets of FS. Then, Eq. (1) becomes

$$\frac{d^2R}{d\omega d\Omega} = \begin{cases} 0, & \omega < 2\Delta_1, \\ \dfrac{S_1^2\Delta_1^2}{\omega\sqrt{\omega^2-4\Delta_1^2}}, & 2\Delta_2 > \omega > 2\Delta_1, \\ \dfrac{S_1^2\Delta_1^2}{\omega\sqrt{\omega^2-4\Delta_1^2}} + \dfrac{S_2^2\Delta_2^2}{\omega\sqrt{\omega^2-4\Delta_2^2}}, & \omega > 2\Delta_2, \end{cases} \tag{2}$$

where S_1 (S_2) is proportional to the area of the first (second) sheet of the FS. As shown in the inset of Fig. 2, the calculated spectrum using Eq. (2) qualitatively agrees with the measured spectra, i.e., two peaks at $2\Delta_1$ and $2\Delta_2$ and a vertical slope at $2\Delta_1$. To achieve a more detailed agreement, we would need to take into account the slight dispersion along the k_z direction [3–5] and the coupling effect between the two σ bands [6]. As an approximation, we simply convolute the calculated spectrum with a Gaussian function whose HWHM is 7 cm^{-1} for contributions from S_1 and 3.5 cm^{-1} for those from S_2. As shown in Fig. 2, this yields a reasonably good fit with the experimental data. The parameters obtained from the best fit to the *VV* spectrum are $S_1 = 125$, $S_2 = 42$, $\Delta_1 = 22$ cm^{-1}, and $\Delta_2 = 50$ cm^{-1}. After multiplying by an intensity scaling factor of 0.52, the same parameters also yield a good fit to the *HV* experimental data (see Fig. 2).

Ideally, for isotropic s-wave gaps, there should be a complete depletion [14] in the low-temperature Raman spectra at frequencies below the smaller gap because of the lack of available electronic states. As shown in the inset of Fig. 2, the Raman scattering intensity at frequencies below ($2\Delta_1$) should be zero and the spectrum has a vertical slope at $2\Delta_1$. However, such a depletion cannot be seen in the spectra shown in Fig. 1. In fact, the scattering intensity at low frequencies is not zero in any of the spectra. Apparently the low-frequency spectra include significant contributions of scattering from excitations other than the superconducting quasiparticles. Such excitations could arise from normal electrons in the π bands, or could be due to the presence of normal state material in the samples. To remove these unwanted contributions from the spectra, we subtracted the 45 K spectra from the 15 K spectra. The results, more accurately representing the scattering spectra from superconducting quasiparticles, are shown in Fig. 2. A nearly vertical slope appears slightly below $2\Delta_1$, which is a feature expected for isotropic s-wave gaps [14,16].

Figure 3 shows the temperature dependence of the electronic Raman spectrum measured in *HV* scattering geometry. When the temperature is decreased below T_c, the spectra gradually gain weight in the low-frequency region and the two pair-breaking peaks are well developed at 15 K. Recently Bouquet *et al.* [21] reported specific heat data which can be fit to a two-gap model.

In summary, we have measured the Raman spectra of polycrystalline MgB_2. A broad maximum centered at 620 cm^{-1} arises from phonon scattering throughout the Brillouin zone and suggests that the samples are strongly disordered. When the temperature is decreased below T_c, a superconductivity-induced redistribution in the electronic Raman spectrum occurs as a result of the opening of the superconducting gaps. The appearance of two pair-breaking peaks indicates the existence of two superconducting gaps in MgB_2. Furthermore, we have analyzed the experimental data using a quasi-two-dimensional model based on the theoretical calculations of Kortus *et al.* [3]. The results suggest that two s-wave gaps open on two sheets of the Fermi surface from the planar boron σ bands near the Γ point with gap values of $\Delta_1 = 22$ cm^{-1} (2.7 meV) and $\Delta_2 = 50$ cm^{-1} (6.2 meV), respectively, i.e., $2\Delta_1/k_BT_c = 1.6$ and $2\Delta_2/k_BT_c = 3.7$. Note that the values of the two gaps embrace a range covering most of the results of the reported gap measurements [7–13]. The result of our data analysis suggests that both gaps are conventional s-wave gaps and a BCS phonon-mediated pairing mechanism occurring in the planar boron σ bands is responsible for the superconductivity of MgB_2.
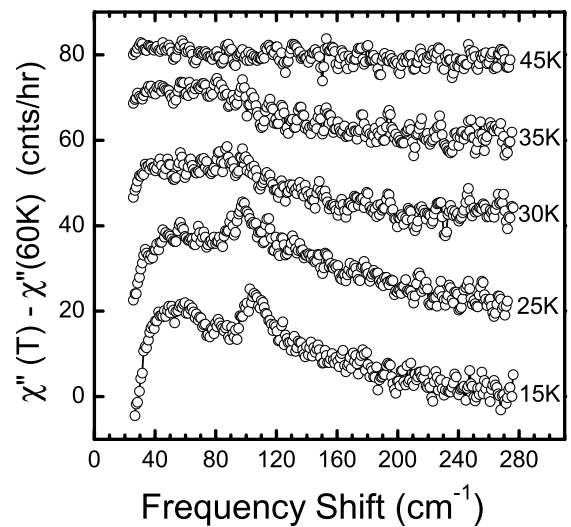

FIG. 3. *HV* electronic Raman continua obtained by subtracting the 60 K spectrum. The 15, 25, 30, 35, and 45 K spectra have been shifted upward by 20, 40, 60, and 80 units, respectively.

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Note added.—After the submission of this paper, Giubileo *et al.* [22] (scanning tunneling microscopy) and Szabo *et al.* [23] (point-contact spectroscopy) reported experimental data showing two superconducting gaps with approximately the same gap values as we have obtained. These data indicate that the two gaps open simultaneously at T_c and their temperature dependence agrees with BCS theory, which is consistent with our results.

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