Observation of Leggett's Collective Mode in a Multiband MgB_2 Superconductor

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(Received 30 March 2007; published 29 November 2007)

We report observation of Leggett's collective mode in a multiband MgB_2 superconductor with $T_c = 39$ K arising from the fluctuations in the relative phase between two superconducting condensates. The novel mode is observed by Raman spectroscopy at 9.4 meV in the fully symmetric scattering channel. The observed mode frequency is consistent with theoretical considerations based on first-principles computations.

DOI: 10.1103/PhysRevLett.99.227002 PACS numbers: 74.70.Ad, 74.25.Gz, 74.25.Ha, 78.30.Er

The problem of collective modes in superconductors is almost as old as the microscopic theory of superconductivity. Bogolyubov [1] and Anderson [2] first discovered that density oscillations can couple to oscillations of the phase of the superconducting (SC) order parameter (OP) *via* the pairing interaction. In a neutral system these are the Goldstone soundlike oscillations which accompany the spontaneous gauge-symmetry breaking; however, for a charged system the frequency of these modes is pushed up to the plasma frequency by the Anderson-Higgs mechanism [3] and the Goldstone mode does not exist. The collective oscillations of the amplitude of the SC OP have a gap, which was first observed by Raman spectroscopy in $NbSe_2$ [4,5], and which plays a role equivalent to the Higgs particle in the electroweak theory [6]. Several other collective excitations have been proposed, including an unusual one that corresponds to fluctuations of the relative phase of coupled SC condensates first predicted by Leggett [7]. The Leggett mode is a longitudinal excitation resulting from equal and opposite displacements of the two superfluids along the direction of the mode's wave vector q. In the ideal case considered by Leggett, the mode is "massive" and its energy (mass) at $q = 0$ is below twice the smaller of the two gap energies. In this Letter we report the observation of Leggett's collective mode in the multiband superconductor MgB_2 with $T_c = 39$ K [8]. The novel mode is observed in Raman response at 9.4 meV, consistent with the theoretical evaluations.

The multigap nature of superconductivity in MgB_2 was first theoretically predicted [9] and has been experimentally established by a number of spectroscopies. A double-gap structure in the quasiparticle energy spectra was determined from tunneling spectroscopy [10,11]. The two gaps have been assigned by means of ARPES [12,13] to distinct Fermi surface (FS) sheets belonging to distinct quasi-2D σ-bonding states of the boron $p_{x,y}$ orbitals and 3D π-states of the boron p_z orbitals: $\Delta_\sigma = 5.5$–6.5 and $\Delta_\pi = 1.5$–2.2 meV. Scanning tunneling microscopy (STM) has provided a reliable fit for the smaller gap, $\Delta_\pi = 2.2$ meV [14]. This value manifests in the absorption threshold energy at 3.8 meV obtained from magneto-optical far-IR studies [15]. The larger $2\Delta_\sigma$ gap has been demonstrated by Raman experiments as a SC coherence peak at about 13 meV [16].

Polarized Raman scattering measurements from the *ab* surface of MgB_2 single crystals grown as described in [17] were performed in back scattering geometry using less than 2 mW of incident power focused to a $100 \times 200\ \mu$m spot. The data in a magnetic field were acquired with a continuous flow cryostat inserted into the horizontal bore of a SC magnet. The sample temperatures quoted have been corrected for laser heating. We used the excitation lines of a Kr^+ laser and a triple-grating spectrometer for analysis of the scattered light. The data were corrected for the spectral response of the spectrometer and the CCD detector and for the optical properties of the material at different wavelengths as described in Ref. [18].

The factor group associated with MgB_2 is D_{6h}. We denote by $(\mathbf{e}_{\rm in}\mathbf{e}_{\rm out})$ a configuration in which the incoming (outgoing) photons are polarized along the $\mathbf{e}_{\rm in}$ ($\mathbf{e}_{\rm out}$) directions. The vertical (V) or horizontal (H) directions were chosen perpendicular or parallel to the crystallographic a axis. The "right-right" (RR) and "right-left" (RL) notations refer to circular polarizations: $\mathbf{e}_{\rm in} = (H - iV)/\sqrt{2}$, with $\mathbf{e}_{\rm out} = \mathbf{e}_{\rm in}$ for the RR and $\mathbf{e}_{\rm out} = \mathbf{e}_{\rm in}^*$ for the RL geometry. For the D_{6h} factor group the RR polarization scattering geometry selects the A_{1g} symmetry while both RL and VH select the E_{2g} representation.

Light can couple to electronic and phononic excitations *via* resonant or nonresonant Raman processes [19]. The Raman scattering cross-section can be substantially enhanced when the incident photon energy is tuned into resonance with optical interband transitions. For MgB_2 the interband contribution to the in-plane optical conductivity $\sigma_{ab}(\omega)$ contains strong IR peaks with a tail extending to the red part of the visible range and a pronounced resonance around 2.6 eV [20] (Fig. 2). The IR peaks are associated with transitions between two σ-bands while the peak in the visible range is associated with a transition from the σ band to the π band [20,21].

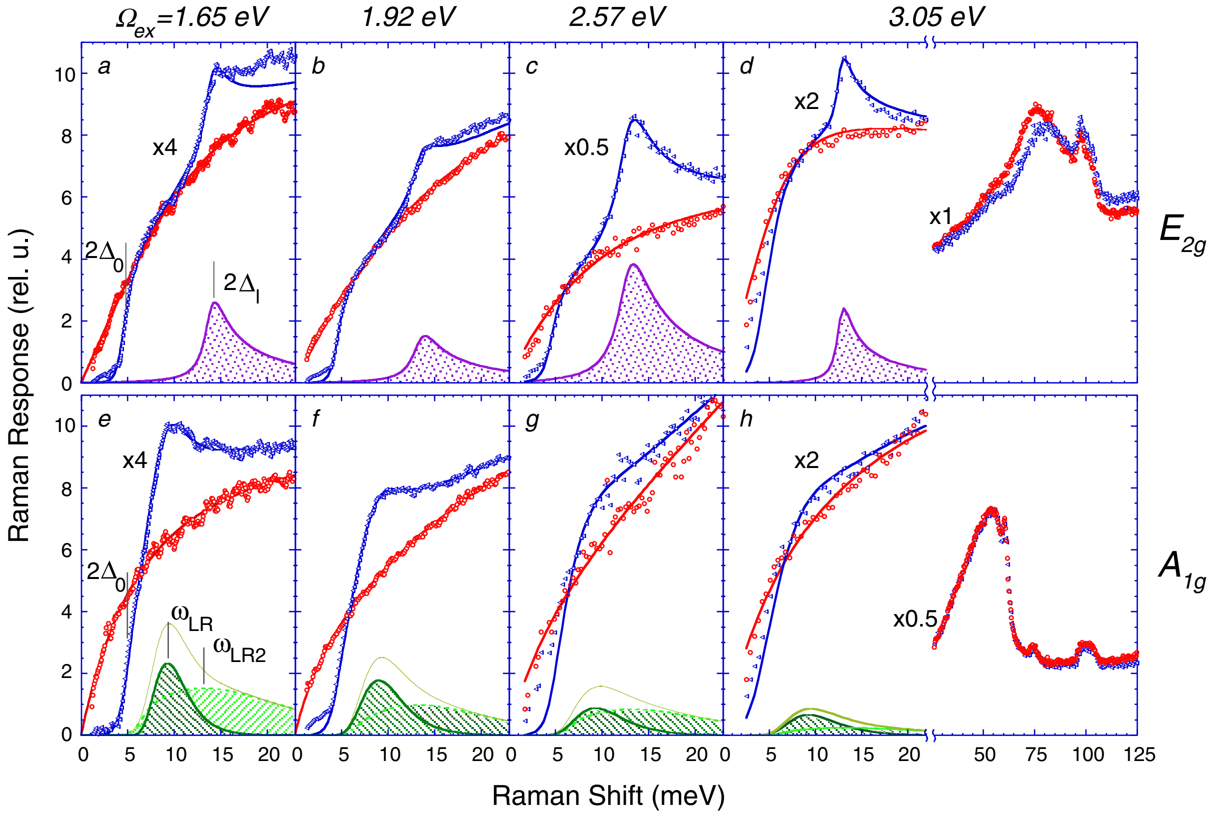

FIG. 1 (color online). The Raman response spectra of an MgB_2 crystal in the normal (red) and SC (blue) states for the E_{2g} (top row) and A_{1g} (bottom row) scattering channels. The E_{2g} channel is accessed by RL (a)–(c) or VH (d) polarization and the A_{1g} channel by RR (e)–(h) polarization. The low temperature data are acquired at 5–8 K. The normal state has been achieved either by increasing the crystal temperature to 40 K (d) or by applying a 5 T magnetic field parallel to the c-axis [(a)–(c), (e)–(h)] [32]. The columns are arranged in the order of increasing excitation energy Ω_{ex}. Solid lines are fits to the data points. The normal state continuum is fitted with $\omega/\sqrt{a + b\omega^2}$ function. The data in the SC state is decomposed into a sum of a gapped normal state continuum with temperature broadened $2\Delta_0 = 4.6$ meV gap cutoff, the SC coherence peak at $2\Delta_l = 13.5$ meV (shaded in violet), and the collective modes at $\omega_{LR} = 9.4$ meV and $\omega_{LR2} = 13.2$ meV (shaded in dark and light green). The solid hairline is the sum of both modes. To fit the observed shapes the theoretical BCS coherence peak singularity $\chi'' \sim 4\Delta_l^2/(\omega\sqrt{\omega^2 - 4\Delta_l^2})$ is broadened by convolution with a Lorentzian with HWHM = 5%–12% of $2\Delta_l$ [22]. The collective mode ω_{LR} is fitted with the response function shown in Fig. 3. Panels (d) and (h) also show the high energy part of spectra for respective symmetries. The broad E_{2g} band at 79 meV is the boron stretching mode, the only phonon that exhibits renormalization below T_C [25]. For the A_{1g} channel the spectra are dominated by two-phonon scattering.

In Fig. 1 we show the Raman response from an MgB_2 single crystal for the E_{2g} and A_{1g} scattering channels for four excitation photon energies in the normal and SC states. Besides the phononic scattering at high Raman shifts all spectra show a moderately strong featureless electronic Raman continuum. The origin of this continuum is likely due to finite wave-vector effects [19,22,23]. For isotropic single band metals the Raman response in the fully symmetric channel is expected to be screened [19,22,24]. However, for MgB_2 the electronic scattering intensity in the A_{1g} and E_{2g} channels is almost equally strong.

The low-frequency part of the electronic Raman continuum changes in the SC state (Fig. 1), reflecting renormalization of electronic excitations resulting in four new features in the spectra: (i) a threshold of Raman intensity at $2\Delta_0 = 4.6$ meV, (ii) a SC coherence peak at $2\Delta_l = 13.5$ meV in the E_{2g} channel, and two new modes in the A_{1g} channel, (iii) at 9.4 meV, which is in-between the $2\Delta_0$ and $2\Delta_l$ energies, and (iv) a much broader mode just below $2\Delta_l$. The observed energy scales of the fundamental gap Δ_0 and the large gap Δ_l are consistent with Δ_π and Δ_σ as assigned by one-electron spectroscopies [12–14].

(i) At the fundamental gap value $2\Delta_0$ both symmetry channels display a threshold without a coherence peak. This threshold is cleanest for the spectra with lower photon energy excitations Ω_{ex} for which the low-frequency contribution of multiphonon scattering from acoustic branches is suppressed [25]. Lack of the coherence peak above the threshold is consistent with the expected behavior for a superconductor with SC coherence length larger than the optical penetration depth [22].

(ii) The $2\Delta_l$ coherence peak appears in the E_{2g} channel as a sharp singularity with continuum renormalization extending to high energies, which agrees with expected behavior for clean superconductors [19,22,23]. The Raman coupling to this mode is provided by densitylike fluctuations in the σ-band hence the peak intensity is enhanced by about an order of magnitude when the excitation photon energy Ω_{ex} is in resonance with the 2.6 eV $\sigma \rightarrow \pi$ interband transitions (Fig. 2).

(iii) The novel peak at 9.4 meV is observed only in the A_{1g} scattering channel. This mode is more pronounced for off-resonance excitation for which the electronic continuum above the fundamental threshold $2\Delta_0$ is weaker. We assign this feature to the collective mode proposed by Leggett [7]: If a system contains two coupled superfluid liquids a simultaneous cross tunneling of a pair of electrons becomes possible (Fig. 3, inset). Leggett's collective mode is caused by counterflow of the two superfluids leading to small fluctuations of the relative phase of the two condensates while the total electron density is locally conserved. In a crystalline superconductor, its symmetry is that of the fully symmetric irreducible representation of the group of the wave vector q. If the energy of this mode is below the smaller pair-breaking gap energy, dissipation is suppressed and the excitation should be long-lived. In the case of MgB_2 the two coupled SC condensates reside at the σ- and π-bands. The oscillation between the condensates involves the scattering of a pair of σ-band electrons with momentum $(k, -k)$ into a pair of π-band electrons with momentum $(k', -k')$ due to the interaction between the electrons. The Leggett mode is gapped (massive). Its dispersion for small momentum q obeys relation [7,26]

$$\Omega_L(q)^2 = \omega_L^2 + v^2 q^2, \tag{1}$$

where the excitation gap ω_L is given by solution of [27]

$$L(\omega)^2 = \omega^2, \tag{2}$$

with

$$L(\omega)^2 = \frac{4\Delta_\sigma \Delta_\pi V_{\sigma\pi}}{\det V} \frac{N_\sigma f_\sigma(\omega) + N_\pi f_\pi(\omega)}{N_\sigma f_\sigma(\omega) N_\pi f_\pi(\omega)}. \tag{3}$$

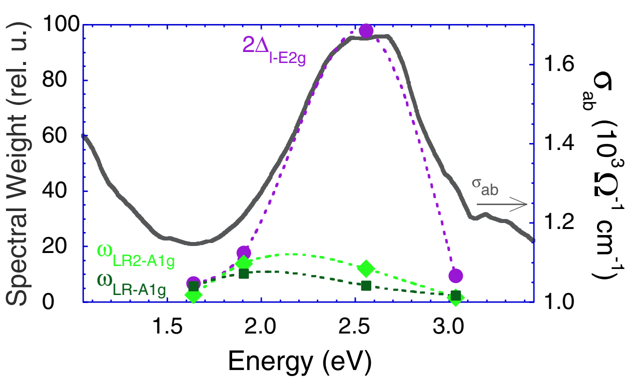

FIG. 2 (color online). The comparisons of the ab-plane optical conductivity σ_{ab} (solid line) [20] to the integrated spectral weight under SC coherence peaks as a function of excitation energy: $2\Delta_l$ in the E_{2g} (circles) and Leggett's collective modes ω_{LR} (squares) and ω_{LR2} (diamonds) in the A_{1g} channel. All dashed lines are guides for the eye.

Here V is the matrix of intra- and interband interaction with pairing potentials $V_{\sigma\sigma}$, $V_{\pi\pi}$ and $V_{\sigma\pi}$; N_σ and N_π are the density of states in corresponding bands, and we define a complex function $f_{\sigma,\pi}(\tilde{\omega}) = \frac{\arcsin\tilde{\omega}}{\tilde{\omega}\sqrt{1-\tilde{\omega}^2}}$, with $\tilde{\omega} = \omega/2\Delta_{\sigma,\pi}$. The solution for Leggett's mode Eq. (2) exists if

$$\det V > 0. \tag{4}$$

If $\omega_L \ll \min(\Delta_\sigma, \Delta_\pi)$ it reduces to the original Leggett expression [7,26]

$$\omega_L^2 = \frac{N_\sigma + N_\pi}{N_\sigma N_\pi} \frac{4V_{\sigma\pi}\Delta_\sigma\Delta_\pi}{\det V}. \tag{5}$$

This mode is fully symmetric with respect to operations that leave the wave vector q invariant and therefore it contributes only to the A_{1g} Raman response. Because of its neutrality, the mode remains unscreened by Coulomb interactions. Generalization of Eqs. (10a)–(10c) and (18) from Ref. [22] to the two-band case [27] leads to Raman response

$$\chi_{A_{1g}}(\omega) = -\frac{8\Delta_\sigma\Delta_\pi V_{\sigma\pi}}{\det V} \frac{(\gamma_\sigma - \gamma_\pi)^2}{L(\omega)^2 + \omega_V^2 - \omega^2}. \tag{6}$$

Here $\gamma_{\sigma,\pi}$ are the bare light coupling vertices for corresponding bands and $\omega_V^2 = 4\Delta_\sigma\Delta_\pi V_{\sigma\pi}(V_{\sigma\sigma} + V_{\pi\pi} - 2V_{\sigma\pi})/\det V$ is due to the vertex correction. For light to couple to Leggett's excitation γ_σ and γ_π should not be equal, the coupling is further enhanced if $\gamma_\sigma\gamma_\pi < 0$. The latter condition is satisfied for MgB_2 since the σ-bands are holelike while the π-bands are predominantly electronlike. The integrated intensity of the Leggett's mode as a function

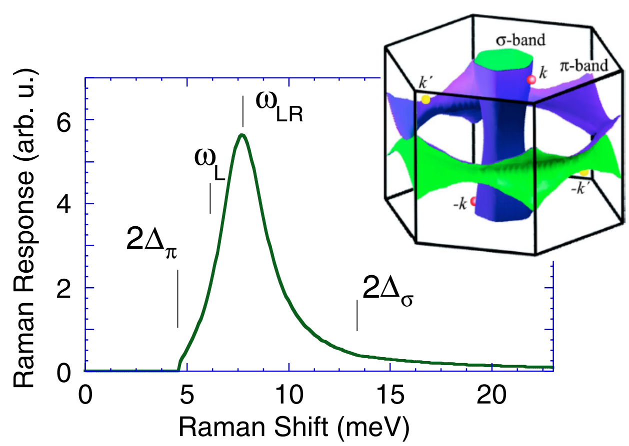

FIG. 3 (color online). Im$\chi_{A_{1g}}(\omega)$ given by Eq. (6) using the interaction matrix by Liu *et al.* [9]. Inset: An illustration of the MgB_2 FS in the first Brillouin zone adapted from Ref. [33]. A nearly cylindrical sheet of the FS around the $\Gamma - A$ line results from the σ-band. The π-band forms a FS of planar honeycomb tubular networks. For clarity only a single FS for each σ- and π-band pair is shown [9]. In the SC state the σ-band Cooper pairs are bound stronger than the π-band pairs, at the binding energies $2\Delta_\sigma$ and $2\Delta_\pi$, correspondingly. Leggett's collective mode originates from dynamic scattering of the σ-band pairs of electrons (illustrated in red) with momentum $(k, -k)$ into the π-band electron pairs (yellow) with momentum $(k', -k')$.

TABLE I. Estimates of Leggett's mode frequency ω_L, the vertex correction ω_V and the Raman resonance frequency ω_{LR} based on values of intra- and interband pairing potentials V_{ij} ($i, j = \sigma, \pi$) deduced from first principal calculations (two-band model) [9,28–30]. The effective density of states $N_\sigma = 2.04$ and $N_\pi = 2.78$ Ry^{-1} spin^{-1} cell^{-1} [9] and the experimental values for the SC gaps $\Delta_\sigma = 6.75$ and $\Delta_\pi = 2.3$ meV are used.

References	$V_{\sigma\sigma}$ (Ry)	$V_{\pi\pi}$ (Ry)	$V_{\sigma\pi}$ (Ry)	ω_L (meV)	ω_V (meV)	ω_{LR} (meV)
Liu *et al.* [9]	0.47	0.1	0.08	6.2	7.1	7.9
Choi *et al.* [29]	0.38	0.076	0.054	6.2	6.7	7.8
Golubov *et al.* [30]	0.5	0.16	0.077	5.1	5.7	6.9

of excitation energy does not follow the optical conductivity and is about 5 times weaker than the resonantly enhanced coherence peak in the E_{2g} channel (Fig. 2).

The estimates of the two-band interaction matrices by first principle computations [9,28,29] which are collected in Table I show that for MgB_2 the condition (4) is satisfied. In Fig. 3 we show the calculated Raman response function (6) for the first set of parameters from Table I in the $q \to 0$ limit. Finite wave-vector contribution from the π-band will stretch the π-band Raman continuum in agreement with the data. Model calculations suggest that interference with the σ-band coherence peak might produce a structure at about $2\Delta_l$. We note that the estimates for bare Leggett's mode frequency ω_L are close to the ~6.2 meV value observed by tunneling spectroscopy [31] and the estimates for the peak in Raman response (6), ω_{LR}, are consistent with the observed mode at 9.4 meV. Because the collective mode energy is between the two-particle excitation thresholds for π- and σ-band, $2\Delta_\pi < \omega_L < \omega_{LR} < 2\Delta_\sigma$, Leggett's excitation relaxes into the π-band continuum. Indeed, the measured Q factor for this mode is about two: the mode energy relaxes into the π-band quasiparticle continuum within a couple of oscillations.

(iv) Finally, we note that MgB_2 has four FSs, two nearly cylindrical sheets due to the σ-bands split and two tubular network structures originate from π-bands. Solution to the Leggett problem extended to 4-bands [27] with 4×4 interaction matrix given by Liu *et al.* [9] leads to two Raman resonances: $\omega_{LR} = 8.4$ meV and second ω_{LR2} just 0.05 meV below the $2\Delta_l$ gap. We interpret the superconductivity induced intensity in the A_{1g} channel just below the $2\Delta_l$ energy as evidence either for a second Leggett resonance or for interference between SC contributions from the π-band with large-qv_{Fc} and the σ-band with small qv_{Fc}. A sum of two modes peaking at 9.4 and 13.2 meV with very similar excitation profiles provides a good fit to the experimental data.

We conclude that despite being short lived, Leggett excitations in MgB_2 are observed in A_{1g} Raman response.

The authors thank D. van der Marel, I. Mazin, and W. E. Pickett for valuable discussions. A. M. was supported by the Lucent-Rutgers program and N. D. Z. by the Swiss National Science Foundation through NCCR pool MaNEP.

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