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Inelastic x-ray scattering study of collective electron excitations in MgB_2

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We report an experimental inelastic x-ray scattering study of the collective electron excitations in MgB_2. Single-crystal and polycrystalline samples were used to study the free-electron-like (~20 eV) plasmon and the recently theoretically predicted low energy (~3 eV) plasmon mode. We present the energy-loss spectra for several momentum transfer values and find that the excitations exhibit a strong directional dependence. We discuss the dispersion of collective excitations and find a good agreement between the experimental results and the published theoretical calculations. Some discrepancies between the experimental data and the calculations were observed, namely slightly differing excitation energies and momentum-transfer dependence. However, these discrepancies are the same order of magnitude as the uncertainties within the various computational methods.

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Following the discovery of superconductivity in MgB_2 at $T_c = 39$ K,[1] numerous studies have been published concerning the origin of its superconductivity.[2–10] Isotope substitution experiments[2,11] suggest that the electron-phonon interaction plays a major part in the superconduction electron pairing of MgB_2. Due to the surprisingly high superconduction transition temperature, alternative mechanisms causing electron pairing has been proposed. Acoustic plasmons (AP) have been suggested as a possible source of superconductivity[12] in layered structures, but the issue remains controversial as there seems to be no consensus in more recently published theoretical studies.[13–15] Also the theory of hole superconductivity used to describe the high T_c cuprate superconductors was proposed to explain the superconductivity in MgB_2.[16] Nevertheless, as MgB_2 is built up from light elements only and having a relatively simple crystal structure, the electronic structure of MgB_2 has been given substantial attention both theoretically[4,5,17] and experimentally.[18–20]

The macroscopic physical quantity that can be used for characterizing the electronic structure of MgB_2 is the dielectric function, $\epsilon(\mathbf{q},\omega)$. It describes the response of an electron system to an electromagnetic perturbation that transfers momentum $\mathbf{q}$ and energy ω to the system. The dielectric function is a macroscopic manifestation of the electron dynamics at the microscopic level, and provides means for studying phenomena such as screening, single- and many-particle excitations.

Plasmons are excitations associated with the collective oscillations of the electrons. Comparison with the experimental data offers means to evaluate the accuracy of the theoretical models[21] for this fundamentally interesting many-body phenomenon. Experimental methods for probing the dielectric response of the system rely on introducing a suitably weak probe into the system. In this paper, inelastic x-ray scattering (IXS) has been used, being a well-established tool for studying the electronic excitations in matter.[22–26] The cross section of the scattered photons is proportional to the energy-loss function $\mathrm{Im}[-1/\epsilon(\mathbf{q},\omega)]$, from where the dielectric function can be extracted via the Kramers-Kronig transformation.[27]

Recently, two theoretical studies[28,29] on the dielectric response of MgB_2 as a function of momentum transfer were published. To address the results of these studies, we have performed inelastic x-ray scattering experiments using both single-crystal and sintered polycrystalline samples of MgB_2. The measured dispersion of the theoretically predicted plasmon modes are presented and compared with the theoretical calculations[28,29] in detail.

The experiments were carried out at the beamline ID16 at the European Synchrotron Radiation Facility. The x rays produced by three consecutive undulators were monochromatized using a double-crystal monochromator employing the Si(111) reflection. The energy of the scattered photons was analyzed using a spherically bent silicon crystal positioned on the Rowland circle ($R = 0.5$ m), utilizing the Si(444) reflection. The energy-loss spectra were measured via the so-called inverse scan technique.[30] The momentum-transfer resolution dominated by the finite size of the analyzer crystal was 0.21 a.u. (atomic units) and could lead to smearing as a function of q. The total energy resolution of 1 eV was determined from the width of the quasielastic line. The energy of the elastic line was 7.9 keV and was stable within 0.1 eV during the measurements.

MgB_2 crystallizes in a hexagonal-layered structure formed by alternating graphitelike honeycomb boron layers and hexagonal Mg planes.[1] In this paper, the axis perpendicular to the boron layers will be addressed as the c axis while the a axis lies in the hexagonal plane. The single-crystal sample of MgB_2 was a platelet with an area of approximately 0.5×0.3 mm^2 and thickness of about 100 μm, thus both transmission and reflection geometries could be utilized in the measurements. The sample with $T_c = 38.7$ K was manufactured using a high-pressure anvil technique.[31] The sintered polycrystalline MgB_2 sample had dimensions of $2 \times 2 \times 4$ mm^3. A more detailed description of the polycrystalline sample preparation can be found in Ref. 32. The single-crystal sample was oriented using the Laue technique, after which the sample was glued onto the tip of a copper pin sample holder. All experiments were carried out at room

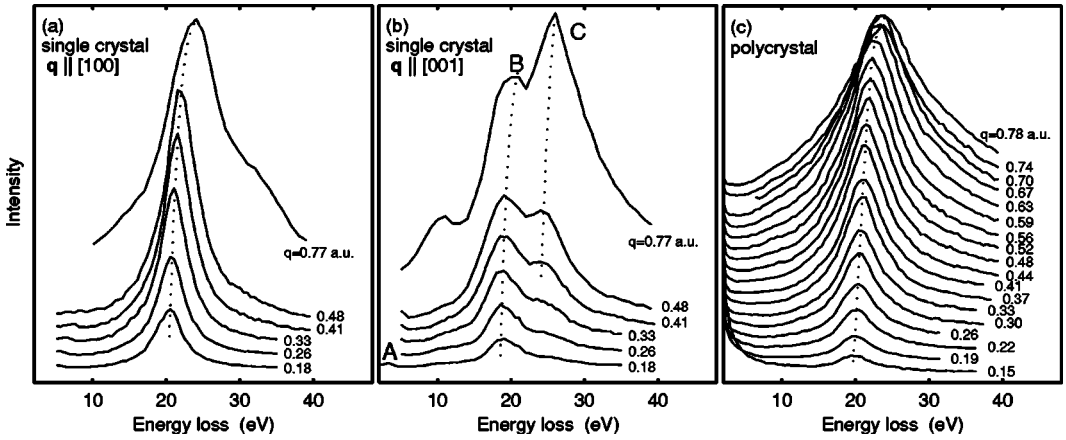

FIG. 1. The experimental energy loss functions for single-crystal and polycrystalline MgB_2 samples using several momentum transfer **q** values. Error bars due to counting statistics are the order of the linewidth. The dotted lines indicate the position of various peaks and are intended as guides for the eye. The peak values of the energy-loss spectra measured at the largest momentum transfer values correspond to about 10^4 counts/5 s. The spectra are displaced along the vertical axis for clarity.

temperature under a He atmosphere and in vacuum for the single-crystal sample and the polycrystalline sample, respectively. No visible degradation of the samples were found upon visual inspection using a microscope before and after the experiments.

In Fig. 1 we present the experimental energy-loss spectra along two directions for the single-crystal sample together with the results using the polycrystalline sample. We observe a strong directional dependence of the loss function. For the low momentum-transfer values with $\mathbf{q}\|[100]$ [Fig. 1(a)], the plasmon has a Lorentzian shape resembling the plasmon in a free-electron-like system. As the momentum transfer q is increased, the plasmon disperses to higher energies and at high momentum-transfers the plasmon severely distorts. On the other hand, when **q** is parallel to the c axis [Fig. 1(b)], the plasmon exhibits a double-peaked shape, even at low-momentum transfer values. The peak at ~19 eV (peak B) shows almost negligible dispersion as a function on q, while the high-energy shoulder at ~25 eV (peak C) moves to slightly higher energies as q is increased. The small peak at around 3 eV in Fig. 1(b) will be addressed later in this paper.

In Fig. 1(c), the energy-loss spectra measured using the polycrystalline sample are shown. At low q values, the plasmon has an almost symmetric Lorentzian lineshape, but a slight high-energy shoulder develops at larger q. Assuming no texture, the orientations of the crystallites in a polycrystalline sample are random and the measurement effectively averages over the directions of **q**. The contribution of the hexagonal plane is emphasized due to its high symmetry, thus causing a close resemblance between the polycrystalline spectra and the spectra in Fig. 1(a).

Recent theoretical calculations of Zhukov *et al.*[28] and Ku *et al.*[29] both predict the free-electron-like plasmon just below 20 eV at low q. For $\mathbf{q}\|[001]$, the calculated plasmon in Ref. 29 exhibits a smooth Lorentzian shape, while the first study[28] predicts a double-peaked structure corresponding to peaks B and C. Also in Ref. 28 the energy-loss spectra for $\mathbf{q}\|[100]$ are presented, showing a single peaked plasmon, again reproducing the experimental spectra well.

In Fig. 2 the dispersion of the plasmon-peak position for different directions of **q** is displayed. The position of the peak maxima in the experimental energy-loss spectra were found by inspecting the zero crossings of the derivatives. The theoretical result was taken from Fig. 2(a) in Ref. 28. Both in our experiment and in the calculation the dispersion of peak B (with $\mathbf{q}\|[001]$) is small, but the energy of peak C depends on q, and in the hexagonal plane the dispersion is almost linear. However, the plasmon energy seems to be consistently underestimated by about 0.3 eV in the theoretical calculations.[28] The plasmon energy of the polycrystalline sample resides between the values of the single-crystal measurements. The experimental plasmon dispersion obtained from the polycrystalline sample is similar to that of the plasmon in the hexagonal plane. The only difference is that the plasmon energy in the polycrystalline sample is about 0.3 eV lower. In the other theoretical study[29] the plasmon with $\mathbf{q}\|[001]$ is found to disperse almost linearly from 18.5 to 19.7 eV as the momentum transfer is increased from 0 to 0.25 a.u. This is in a clear contrast with our experimental result where we find practically no dispersion for the high

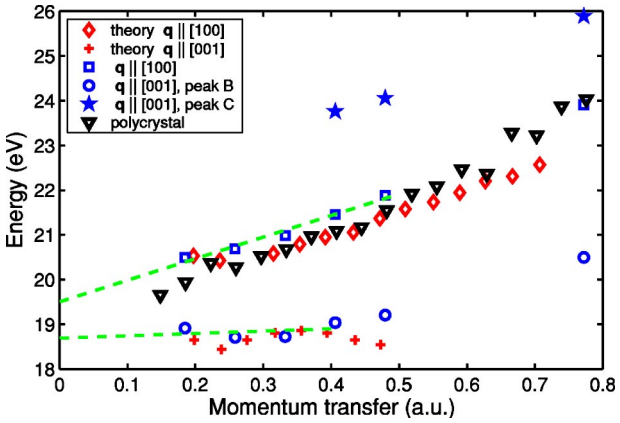

FIG. 2. (Color online) Experimental and theoretical dispersion of the free-electron-like plasmon in MgB_2 for various momentum transfer values and directions. Peaks B and C are defined in Fig. 1(b). The theoretical data was taken from Ref. 28. Dashed lines represent the linear fit to the experimental data. Error bars are smaller or equal to the size of the markers.

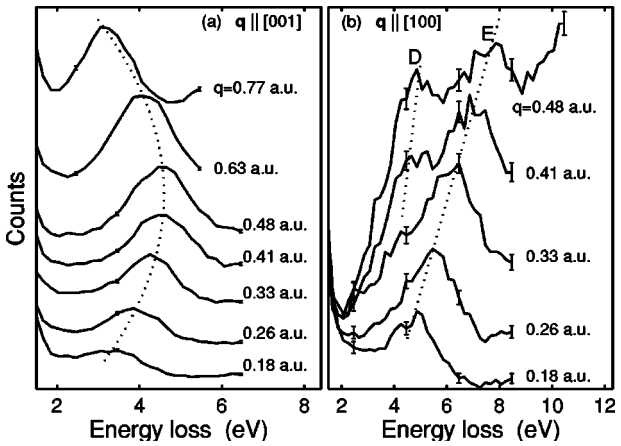

FIG. 3. Experimental energy-loss spectra of MgB_2 using small-energy transfer values with **q** both perpendicular to and in the hexagonal boron plane. Dotted lines showing the position of various peak maxima are intended as guides for the eye. The peak values at $q=0.48$ a.u. correspond to about (a) 3×10^3 counts and (b) 10^3 counts in 15 s. Error bars due to counting statistics for selected data points are shown. The spectra are displaced vertically for clarity.

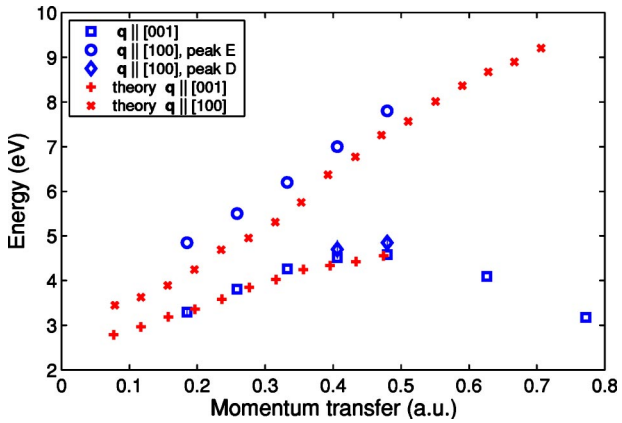

FIG. 4. (Color online) Experimental and theoretical dispersion of the low-energy collective modes in MgB_2. Peaks *D* and *E* are defined in Fig. 3(b). The theoretical results were taken from Ref. 28. Error bars are shown, where the uncertainty due to counting statistics is larger than the size of the marker.

energy plasmon with **q** along this direction. Linear extrapolations of the experimental dispersion data points give plasmon energies at zero momentum transfer as (19.5 ± 0.2) eV for $\mathbf{q}\|[100]$ and (18.8 ± 0.2) eV for $\mathbf{q}\|[001]$. The error estimates were obtained by observing the sensitivity of the extrapolation to the datapoints included in the linear fitting. These values are in an excellent accord with the theoretical results of 19.4 eV (Ref. 28) for $\mathbf{q}\|[100]$ and 18.8 eV (Ref. 28) and 18.5 eV (Ref. 29) for $\mathbf{q}\|[001]$.

Now we turn our attention to the small feature [peak *A* in Fig. 1(b)] residing around 3 eV from the elastic line. For low momentum-transfer values with $\mathbf{q}\|[001]$, both theoretical calculations predict a very sharp plasmon mode, which is interpreted as a coherent charge fluctuation between the boron and the magnesium sheets.[28,29] We present an experimental verification of this mode in Fig. 3(a), where the energy-loss spectra closer to the elastic line are shown for several momentum transfer values. The experimental energy resolution is high enough to clearly separate this feature from the elastic line. For small *q* values the plasmon exhibits a positive dispersion, which turns negative for large values of *q*. There have been indications that this plasmon mode was observed in an earlier report.[18] However, in that study, fitting procedures had to be used in order to separate this feature from an overlap of several peaks.

The energy-loss spectra with $\mathbf{q}\|[100]$ is depicted in Fig. 3(b). For low *q* there is a clear peak in the spectra also for this direction of **q**. Upon comparison with Fig. 3(a) it is evident that this feature resides at a higher energy, is considerably wider [note the different energy scale in Figs. 3(a) and 3(b)], and has lower intensity, which is visible as a higher statistical noise in the spectra. At higher *q* values, the feature transforms into a double-peaked structure. In Ref. 28 the corresponding energy-loss spectra shows a small feature roughly at the correct energy.

The dispersion of the low-energy modes were found again by inspecting the zero crossing of the derivative of the experimental data. However, due to the low experimental resolution, the plasmon partly overlaps with the tail of the elastic peak. In order to estimate the accuracy of the determined plasmon energy, the spectra in Fig. 3(a) were fitted using Gaussian functions. From this we estimate that the plasmon energies could be determined from the experimental data within 0.2 eV. The resulting dispersion of these low-energy modes are depicted in Fig. 4 along with the results of the theoretical calculation in Ref. 28. The results for $\mathbf{q}\|[001]$ presented in Ref. 29 are identical to the results of Ref. 28 within visual accuracy. There is a very good agreement between the experiment and the theory along the [001] direction up to the boundary of the first Brillouin zone at around 0.48 a.u. By further increasing the momentum transfer the plasmon starts dispersing negatively. Along the [100] direction, the correspondence is not as good. While the dispersion of peak *E* in Fig 3(b) is similar to that of the calculated one, the calculation underestimates the energy of this peak by about 0.5 eV.

Generally speaking the agreement between the current experimental results and the theoretical calculations[28,29] is good. The calculation presented in Ref. 28 reproduces the features in the experimental spectra well and gives an accurate prediction about the related dispersion. The biggest difference is in the absolute position of these features and this difference is only few tenths of an eV. Such a small discrepancy can be attributed to uncertainties in both the calculation or the determination of the peak positions in the experiment. Zhukov *et al.*[28] use random phase approximation (RPA) for the response function. On using either the tight-binding version of the linear muffin-tin orbital (LMTO) method or plane-wave pseudopotential method in the solution of the single-particle states they obtain a 0.4 eV difference in the extrapolated $q=0$ energy position of the $\mathbf{q}\|[001]$ low-energy collective mode.[28] They estimate the numerical accuracy of these results to be better than 0.2 eV, i.e., smaller than the reported difference. Also in Ref. 29 the loss function was calculated within RPA but with the single-particle states solved using a full-potential linearized augmented plane-wave method (Ref. 17 in Ref. 29). The $q=0$, $\mathbf{q}\|[001]$ plas-

mon energy presented in Ref. 29 is about 0.3 eV lower than that of Ref. 28. Overall, this seems to indicate that the differences between experiment and theory for the absolute position of the spectral features is of the same magnitude as the differences due to different choices for calculating the single-particle states. Differences between theory and experiment could also be due to effects beyond RPA.[33]

According to the current experimental result in Fig. 4, the dispersion of the low-energy collective excitation turns negative as q is increased beyond the boundary of the first Brillouin zone at around 0.48 a.u. Zhukov *et al.*[28] give no information on the low-energy excitation in this momentum transfer region. On the other hand, according to Ref. 29, this excitation decays into electron-hole pairs at momentum transfers $q \geqslant 0.6$ Å^{-1}, corresponding to $q \geqslant 0.32$ a.u. This should result in an increase in the width of this mode. Within the experimental energy resolution we do not observe any increment in the width of the low-energy collective excitation. In fact, the excitation remains well defined and gains intensity all the way to $q=0.77$ a.u., the largest momentum transfer used in probing this collective mode.

In this paper, the experimental verification of the theoretically predicted low-energy collective mode is presented. While the correspondence between the theory and the experiment is good, we feel that further studies should be carried out to address the above-mentioned discrepancies. Precise theoretical calculations are needed to cast light on the negative dispersion of the low-energy plasmon in the second Brillouin zone and experiments with a considerably better energy resolution should be carried out to evaluate the q dependence of the width of the low-energy plasmon mode.

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