Quantum size effects and temperature dependence of low-energy electronic excitations in thin Bi crystals

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The quantum size effect (QSE) and temperature dependence of the low-energy electronic properties of thin bismuth crystals are studied by means of the high-resolution electron-energy-loss spectroscopy (HREELS) technique. Electronic interband transitions, taking place at the points L and T of the bismuth Brillouin zone (BZ), are distinctly brought into evidence at 47 and $\sim$200 meV, and the corresponding complex dielectric function in this energy region is determined. This provides direct experimental determination of the electronic transition from the Fermi level (E_F) to the point T_6^+. The quantum size effect in thin Bi crystals is studied following the evolution of these electronic excitations as a function of the crystal thickness (110–2500 Å). A downshift (upshift) of the transition at the point L (T) of the BZ is measured by HREELS, and shown to be related to the Fermi-level modification as a function of thickness. This experimental finding is consistent with the theoretical predictions for the QSE-induced Fermi-level shift. In addition, the same experiment is performed as a function of temperature for crystals 750 Å thick, for which QSE's are not expected, and for crystals 200 Å thick which exhibit QSE's. A redshift by $\sim$12 meV of the lower-lying electronic excitation is measured on decreasing the temperature from 298 to 155 K. The energy shift is mainly due to the temperature dependence of the gap energy (E_g) in L. However, the temperature evolution of the occupancy of the filled and empty levels involved in the transition (through the width of the Fermi-Dirac distribution function around E_F) cannot be neglected in fully determining the observed temperature dependence. These two causes are still determinant when the crystal is in a QSE regime.

I. INTRODUCTION

The size quantization of the electronic energy spectrum in a metal thin film is pronounced when the film thickness is comparable with the De Broglie wavelength of the electrons. In ultrathin films of semimetallic crystals, the restriction of the carrier motion (electrons and holes) in the direction normal to the surface leads to the quantization of the energy of both types of carriers, and the Fermi-level position depends on the charge neutrality condition. The weight of such a quantum size effect (QSE) can vary depending on the boundary conditions to be used at the film edge. Bismuth is a unique good candidate for studying such a QSE because the electrons and the holes can be easily driven into the extreme quantum limit, on changing the crystal thickness with relatively large dimensions. Moreover, the values of the Bi band parameters (of the order of kT at room temperature) also render this element a good choice for investigating the temperature dependence of the electronic properties in and out of the QSE regime.

Before specifically introducing the effects of size quantization and of temperature on the low-energy electronic structure of bismuth, we shall briefly describe its properties in the bulk limit.

A. Thick crystalline bismuth

Bismuth presents unique electronic properties, which place this group-V element—in its crystalline form—between ordinary metals and semiconductors.[1] From the structural point of view, Bi crystallizes in a rhombohedral ($A7$) lattice with two atoms *per* unit cell, which can be considered as derived by a face-centered-cubic lattice slightly stretched along a body diagonal, with a relative shift of the neighbors along the same diagonal (as in the "deformation theory").[2] It presents a rather complicated electronic band structure,[3–11] as the formerly degenerate levels (in a cubic lattice) running close to the Fermi energy are split and reduced in symmetry by the crystal field and by the "deformation" from a cubic to a rhombohedral structure. Consequently three equivalent electron bands are formed at point L of the rhombohedral Brillouin zone (BZ) and one overlapping hole band at point T. Semimetallicity is ensured by the Fermi-level crossing the electron band above the bottom of the point L_s, and the hole band below the point $T_{4,5}^-$, as shown in the scheme of Fig. 1. The spin orbit must be taken into account,[9,11] owing to its large value with respect to the band parameters, thus determining a small overlap between E_F and the electron and hole bands, and giving rise to low gap energies, of the order of kT at room temperature (RT). Owing to the charge neutrality condition, the density of carriers in the electron and hole pockets must be equal ($3n_e = n_h \sim 3\times 10^{17}$ cm^{-3}),[1] while it is noticeable that the free-carrier density is indeed very low, two and three orders of magnitude lower, respectively, than in the other group-V semimetals antimony and arsenic.[12] These low free-carrier density, E_F and E_g values, determined by the large relativistic effect on the bands crossed by E_F, render bismuth particularly different from arsenic and antimony with respect to the influence of size

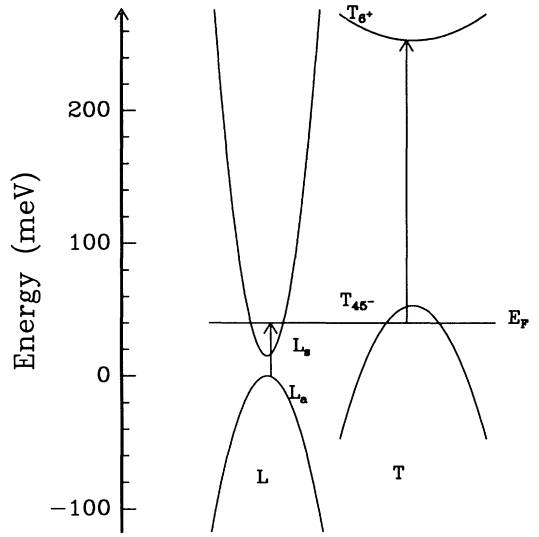

FIG. 1. A schematic representation of the electronic energy bands of Bi near points L and T of the Brillouin zone. The vertical axis is in the correct energy scale and the zero is positioned at the point L_a. The horizontal line represents the Fermi level, while the vertical arrows schematically indicate the observed electronic transitions in L and T.

quantization and temperature.

According to the band scheme of Fig. 1, electronic interband excitations can be expected at the points L and T of the Bi-BZ. The main interband transition for the electrons in L (between L_a and E_F) was already determined at about 60 meV in the late 1950s.[13,14] However, there are only indirect and contrasting estimations of the energy gap in T ($T_{4,5}^- - T_6^+$), ranging between 200 and 570 meV,[7,9,15–18] while a direct measurement of the corresponding electronic transition between the Fermi level and T_6^+ is still lacking.

B. Quantum size effect (QSE) in thin bismuth crystals

The very low Fermi energy (of the order of a few tens of meV) and the low and anisotropic effective masses (of the order of 10^{-2} of the free-electron mass, m_e) in bismuth lead to a De Broglie wavelength of the order of hundreds of Å. Therefore, these band parameters provoke interesting *quantum size effects* at *crystal thickness of the order of hundreds of* Å.[1] These peculiar characteristics give us the opportunity to study a physical system in the extreme quantum limit with relatively large dimensions. Let us review what are the consequences of a QSE on the low-energy electronic properties of Bi.

If one considers the carriers as confined in a three-dimensional infinite potential well, their motion will be confined and quantized along the direction normal to the film plane. As a consequence, both the electron and hole densities, as well as the density of states of the system, will be quantized as a function of the film thickness.[19,20] The hole effective mass in T is larger than the electron effective mass in L, thus the discrete energetic levels will be closer to each other for the holes than for the electrons. On decreasing the film thickness, the level separation increases while the density of states decreases, and this effect is larger for the electrons than for the holes. Since the Fermi-level position in a semimetal is determined by the charge neutrality condition, E_F also depends on the film thickness, and in particular it can be verified that *the Fermi energy increases as the film thickness decreases*[19,21,22] for maintaining the charge neutrality condition.

The presence of a QSE in the energy spectrum of thin Bi crystals and the consequences on its electronic properties have not yet been fully studied, although resistivity and Hall effect measurements,[20,21,23,24] infrared magneto-optical spectroscopy experiments,[24–26] and theoretical investigations[19,22,27] were performed. In particular, an optical study performed on bismuth crystallites showed a redshift of an infrared band on growing the specimen thickness.[25] This band was erroneously interpreted in terms of a Bi plasmon, although a plasmon had already been measured,[13,28] and we also estimate,[29] at much lower energy. Its energy shift was attributed to changes in the electron effective masses rather than to a real modification of the Fermi-level position. There is not yet any experimental investigation of the QSE on the low-energy electronic transitions of Bi in good-quality ultrahigh-vacuum (UHV) -grown Bi crystals.

C. Temperature dependence

The presence of a very low-energy gap associated with the electron pockets in L, and the low Fermi energy (both of the order of kT at room temperature), along with a low density of electrons, and very low and anisotropic electron effective masses,[1] lead us to expect a strong temperature dependence of the Bi band parameters.[30] In particular, a temperature-dependent electronic interband transition in L can be foreseen. In general, the temperature influences both the shape and the energy position of the valence and conduction bands through two main mechanisms: the variation of the lattice parameter of the crystal, and the thermal motion of the ion cores with a mean-squared ion displacement different from zero (through the Debye-Waller factor). It is hard to determine *a priori* the net effect of the temperature on the gap value, as it can be obtained only by introducing both factors (lattice parameter and dynamics dependence) in a band-structure calculation. As an example of reversed temperature effect, Tsang and Cohen[31] calculated the direct-band-gap dependence on temperature for two narrow-gap semiconductors, namely PbTe and SnTe. Using a modified pseudopotential method, they derived a positive temperature coefficient for PbTe, while a negative coefficient was found for SnTe. On the other hand, there are model relations describing the temperature dependence of the fundamental gap of semiconductors, treating the thermal dilatation of the lattice and the temperature-dependent electron-phonon interaction in a semiempirical way.[32–34] However, such semiempirical models can deliver an increase of the energy gap with the temperature, but only taking as negative some parame-

ters related to the Debye temperature, which is an unphysical assumption. In the case of bismuth, there is no band-structure calculation, including the temperature dependence, while there was an experimental estimation of the temperature dependence of the energy gap in L by magneto-optical measurements.[30] However, to our knowledge, an experimental study of the temperature dependence of the electronic excitations across E_g and involving E_F, for Bi in and out of QSE conditions, is still lacking.

D. Questions and method

From the previous discussion, a few open questions stand out for elucidation.

(i) A precise determination of the interband electronic transition between the Fermi level and the T_6^+ band, at point T of the Bi-BZ.

(ii) An evaluation of the Bi complex dielectric function in the ~20–400-meV energy range, recalling that an approximate determination of the bismuth optical constants is available only up to ~120 meV,[25] and above 200 meV only in large 0.2-eV energy steps.[35]

(iii) An experimental study of the QSE on the low-lying interband electronic transitions at points L and T of the Bi-BZ, on varying the crystal thickness.

(iv) An investigation of the temperature dependence of the electronic excitation in L, for Bi crystals in and out of QSE conditions.

In order to answer these and related questions, as well as to address new problematics, we performed a detailed experimental investigation of the electronic properties of thin Bi crystals at room and low temperatures, mainly by using high-resolution electron-energy-loss spectroscopy (HREELS). This technique has been revealed to be a superb probe for investigating the electronic structure of semiconducting narrow-gap systems, such as the clean Si(111)-(2×1) surface[36] and several semimetal/III-V interfaces.[37–43] Moreover, owing to the high-energy resolution achievable by HREELS, it is also a particularly suitable technique for investigating the evolution of low-energy electronic properties influenced by QSE and by temperature. The experiments were performed on wide-area UHV-grown Bi crystals, obtained by bismuth deposition at room temperature on cleaved GaAs(110) surfaces, as will be discussed later.

The paper is organized as follows. After an experimental section (II), the results and discussion (Sec. III) will be collected in three subsections: the first dealing with the low-energy electronic interband excitations in thick Bi and with the experimental determination of the complex dielectric function in that energy range (Sec. III A); the second devoted to the experimental observation of quantum size effects for these electronic transitions, related to the Fermi-level position, on varying the Bi crystal thickness (Sec. III B); the last dealing with the experimental determination of the temperature dependence of the lower-lying electronic transition in and out of QSE conditions (Sec. III C). The conclusions and perspectives will be outlined in Sec. IV.

II. EXPERIMENT

Experiments were carried out at the surface physics laboratory Spettroscopia Elettronica Superfici Adsorbati Modena (SESAMO), at the Dipartimento di Fisica, Università di Modena. The HREELS spectrometer (Leybold-Heraeus ELS-22) is contained in an ultrahigh-vacuum (UHV) chamber, also equipped with low-energy electron-diffraction (LEED) and photoemission spectroscopies. This system is UHV-connected to a preparation chamber containing all ancillary facilities (cleaver, evaporators, thickness monitor, etc.) for sample preparation and characterization. Base pressure in both chambers was in the 10^{-11}-mbar range, ensuring excellent conditions for clean crystal growth and investigation. Thin Bi crystals of different thickness (ranging from 110 to 2500 Å) were prepared by subsequent evaporations of the semimetal from a resistively heated quartz crucible, determining the thickness with a calibrated quartz microbalance. Evaporation rates ranged between 10 and 50 Å *per minute*, depending on the desired thickness. Pressure rose in the low- to mid-10^{-10} mbar during the evaporations. Depositions were performed at room temperature (RT) on freshly UHV-cleaved GaAs(110) surfaces as the substrate. Bismuth started to grow along an axis very close to the trigonal axis C_3 for a thickness of ~90 Å, in a *quasisingle* crystalline fashion, as stated by the hexagonal-like LEED pattern of rhombohedral Bi.[44,45] Measurements at low temperature (LT) were done after having prepared the Bi crystal at RT. The sample could be cooled down to ~110 K by using a liquid-nitrogen *reservoir* connected to the crystal holder through an oxygen-free copper ribbon. A Chromel-Alumel thermocouple, fastened to the GaAs bar, was used for determining the sample temperature. Cleanness was checked by photoemission and by the HREELS spectrum itself; however, this system showed itself to be extremely unreactive in UHV conditions. HREELS measurements were taken in the specular direction, with primary beam energies (E_p) ranging between 5 and 20 eV, and with incident and collecting angles between 63° and 65°. The energy resolution, defined as the full width at half maximum (FWHM) of the elastically scattered peak, was better than 10 meV, ensuring a precision of the order of a couple of meV in the energy-shift measurements.

III. RESULTS AND DISCUSSION

A. Low-energy electronic properties of thick Bi

The HREELS data relative to a 700-Å-thick Bi crystalline film (much larger than the QSE critical thickness), taken at RT in the 0–400-meV energy-loss range, are shown in the lower part of Fig. 2(a). Besides the quasielastic peak, a clear structure peaks at 47 meV, while a less intense and broader feature appears approximately centered at 200 meV. To better bring into evidence the latter loss structure, we fit the quasielastic peak with a Lorentzian-Gaussian curve [shown as a dashed line in Fig. 2(a)], and subtracted it from the spectrum. The resulting curve presents a broad but distinct structure

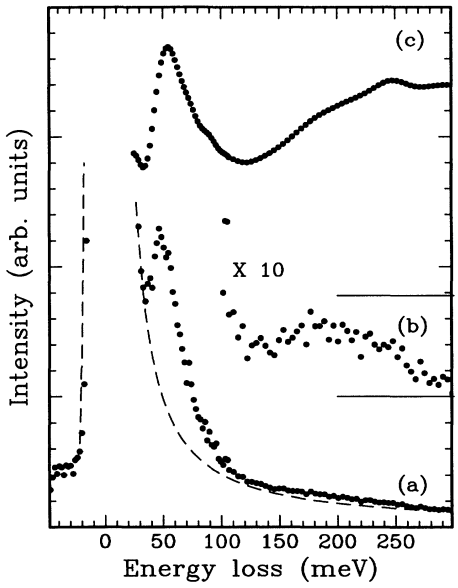

FIG. 2. (a) HREELS (scattering efficiency) data relative to a 700-Å-thick Bi crystal, in the −50–300-meV energy range, taken with $E_p = 20$ eV and an angle of incidence of 65°. The dashed line represents a Gaussian-Lorentzian fit to the elastic peak. (b) The energy-loss spectrum in the 100–300 energy range, after subtraction of the fit elastic peak, and enlarged by a factor 10, for bringing into evidence the loss structure at ~200 meV. (c) The loss function derived from the HREELS data relative to the 700-Å-thick Bi crystal.

roughly centered at 200 meV, as shown in Fig. 2(b). The first loss peak is 20 meV wide and very feeble (~0.2% of the elastic-peak intensity); the second structure is even wider (~100 meV) and much less intense than the previous one. The experimental resolution in this spectrum (assumed to be at maximum the FWHM of the quasielastic peak) is about 8 meV, much narrower than the actual energy width of both the loss peaks. The energy width and intensity of both peaks lead us to attribute them to electronic transitions. In fact, vibrational structures are extremely narrow (they have very low intrinsic linewidths) and present a much higher scattering efficiency than the two structures shown here. Moreover, the lattice dynamics of bismuth is characterized by optical phonons at 8.7 and 12.4 meV,[46,47] even in its nanocrystalline form at very low thickness.[48] A loss structure, analogous to the 47-meV peak in Bi, was measured at ~125 meV in a HREELS experiment performed on antimony.[37] In that case, comparing the experimental data with relativistic band-structure calculations and previous experiments, we could attribute the loss structure to an electronic excitation across the ~0.1-eV narrow gap at point L of the Sb-BZ. Similarly, the loss peak at 47 meV in Bi can be identified as being due to direct interband electronic excitations from the point L_a of the Bi-BZ to the Fermi level, which runs a few tens of meV above L_a (see scheme in Fig. 1). Moreover, the wide loss structure roughly centered at ~200 meV can safely be recognized as the direct interband electronic excitation taking place between the Fermi level and T_6^+, at the point T of the Bi-BZ.

These attributions can be supported by relativistic band-structure calculations,[9–11] and by a few experimental works.[13,14,16,25,30] In particular, in early magneto-optical experiments on crystalline Bi performed at a temperature (T) of 4 K, Boyle and Rodgers[13] measured the zero-magnetic-field cutoff of the pass band in the higher-energy infrared (IR) region of their data to ~20 μm (~62 meV), attributing it to a transition from lower-lying states up to the Fermi level, as did Brown, Mavroides, and Lax[14] for a structure at ~65 meV in an experiment performed at $T = 2$ K. Later on, Harris and Piper[25] measured a maximum absorption signal in the IR data relative to Bi crystallites (at RT) at ~31 μm (~40 meV), but they used this value within the free-electron theory for determining the carrier mobility, thus erroneously considering this structure as due to a plasmon excitation. From the theoretical point of view, and taking into account only relativistic band-structure calculations (owing to the great importance of spin orbit in bismuth), E_g of the order of 15 meV and $E_F \sim 27$ meV were estimated,[7] leading to an E_F-L_s energy difference of about 42 meV, roughly in agreement with our experimental data.

As we already mentioned in Sec. I, there are only indirect and contrasting estimations of the gap in T, ranging between 200 and 570 meV,[7,9,15–18] while no measurement of the direct interband transition in T is available. Thus, to our knowledge, our data are the first direct measurement of the direct interband electronic excitation $E_F \rightarrow T_6^+$ at the point T of the Bi-BZ (see the band scheme drawn in Fig. 1).

So far we have identified and attributed the two main electronic excitations of Bi at low energy, but data reduction through appropriate methods is necessary for giving a more accurate transition energy determination. We briefly recall that the scattering efficiency (S_E) of a HREELS spectrum can be factorized—in a first approximation—as $S_E = (\mathrm{KF} \times \mathrm{LF})/(R \times I_0)$;[49] where KF is the kinematic prefactor (depending on E_p, angles of incidence and collection, and loss energy, thus on the parallel component of the momentum transferred to the excitation), R is the reflectivity of the system at the probed energy (it can be assumed to be constant in this energy-loss range), and I_0 is the intensity of the impinging electrons. The physical information on the system is contained in the loss function (LF), which can be correlated to the optical-absorption coefficient through the imaginary part of the dielectric function.[49] Thus we normalized the spectrum of Fig. 2(a) to the elastic peak intensity ($R \times I_0$), divided it by the appropriate kinematic factor (given the actual scattering conditions), and obtained the loss function, shown in the upper part of Fig. 2(c). The higher-energy structure stands out more clearly in the LF than in the original S_E data, presenting two broad maxima at ~175 and ~245 meV, while the low-energy peak lies at 54 meV. These energies correspond to the maxima of the Bi absorption, produced by the transitions in the points T and L of the Bi-BZ.

The knowledge of the LF is necessary for deriving the

complex dielectric function of Bi in this energy range (25–400 meV). For doing this, the behavior of the LF in a very wide energy range and its absolute value are also required. Thus, other data are necessary for appropriately complementing our measurements. There are optical data extending down to the far infrared ($\sim$8 meV),[25] but they are limited up to $\sim$120 meV, and are taken on a bismuth film constituted by crystallites. On the other hand, the LF derived by absorption measurements on good quality Bi is known starting from 200 meV up to very high energy (containing the whole "oscillator strength" of the electron response), although it is available only at 0.2-eV steps in the low-energy range.[35] Hence we connected our LF to the latter data, having a few overlapping data points which also gave us the opportune proportionality factor for getting the absolute LF value. We then introduced a linear and a cubic extrapolation of the LF to low and high energies, respectively,[50] obtaining the complete LF relative to Bi. Afterwards, the Kramers-Kronig (KK) procedure[50] was applied, eventually obtaining the real $[\epsilon_1(\omega)]$ and imaginary $[\epsilon_2(\omega)]$ parts of the Bi complex dielectric function in the $\sim$0–0.4-eV energy range, as shown in Fig. 3. The high value of $[\epsilon_1(\omega)]$ and $[\epsilon_2(\omega)]$ in this energy range is consistent with the estimation of the infinite-frequency dielectric constant in the infrared, which is of the order of 10^2.[1] $\epsilon_2(\omega)$ is characterized by two main structures, the first with a maximum at 36 meV, the second with two broad maxima at $\sim$165 and $\sim$235 meV, corresponding to the interband electronic transitions observed at the L and T points of the Bi-BZ, respectively. The latter value (165 meV), corresponding to a LF maximum at 175 meV, definitely states a lower limit to the absorption at the point T of the Bi-BZ. The nature of interband transitions is confirmed by the line shape of both the real and imaginary part of the dielectric function.

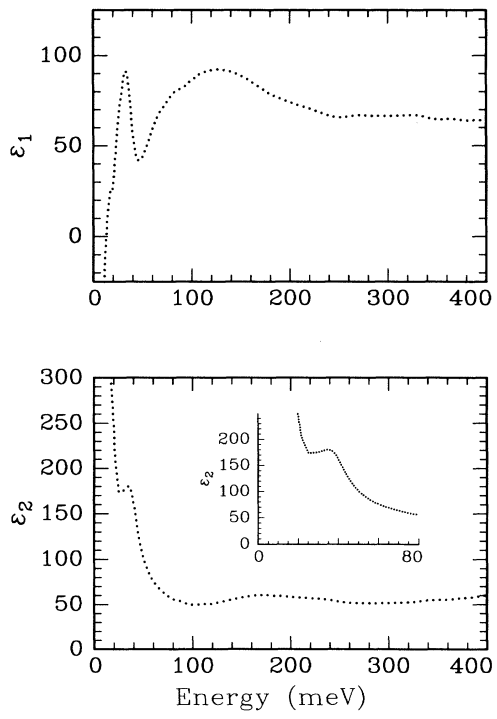

FIG. 3. Real $[\epsilon_1(\omega)]$ and imaginary $[\epsilon_2(\omega)]$ parts of the complex dielectric function of Bi in the 20–400-meV energy range, as derived from the HREELS data. The inset shows an enlargement of $\epsilon_2(\omega)$ in the 0–80-meV energy range.

The zero crossing by $\epsilon_1(\omega)$—marking the free-electron plasma of Bi—lies below 20 meV. This determination is affected by a rather large error (about $\pm$5 meV), owing to the uncertainties of our procedure at such low energies, influenced by the choice of the extrapolation curve to low energy. However, our determination is in agreement with a Bi plasmon previously determined at $\sim$23 meV with optical measurements,[13,28] and also calculated in the energy range 9–19 meV,[29] depending on the excitation direction. Moreover, a free-carrier plasmon at such low energies, induced by the density of electrons and holes in their respective band pockets, only contributes to the elastic-peak width in our HREELS data, while it actually does not produce a definite loss structure, owing to the huge damping experienced by the plasmon, provoked by the temperature broadening at RT and by the rather strong "oscillator strength" associated with the hole-electron excitation at 36 meV, in which the free-carrier mode decays.

B. Quantum size effect in thin Bi crystals

We presented and discussed the low-energy electronic properties of thick Bi. What about the thinner Bi crystals? HREELS data taken on Bi crystalline films of thickness ranging from 110 to 2500 Å are shown in Fig. 4. The thinnest Bi layer presented here is already thick enough to completely screen all the excitations present at the interface with the GaAs substrate.[29,51] At first sight, an evident shift to lower energy of the loss structure associated with the interband transition in L is clearly detectable as the film thickness increases. The structure also broadens and loses intensity in the thinner films. For getting more quantitative values, we fit the data with Gaussian curves, obtaining a shift of the maximum from 80 meV (110-Å Bi) to a saturation value of 47 meV (2500-Å Bi). An analogous energy shift, but with reverse sign, comes out from the data relative to the loss structure representative of the electronic transition in T. To better show this latter feature, the loss function was extracted from the raw scattering efficiency data, thus enhancing the high-energy structures. The LF's corresponding to Bi crystals 700 and 120 Å thick, are shown in Fig. 5: a clear blueshift (17 meV) for the electronic transition in L, as well as an energy shift of the same amount toward lower values for the electronic transition in T, are visible as the film thickness is decreased. In a HREELS study on antimony grown on GaAs(110), the interband electronic transition taking place at point L of the Sb-BZ was determined at $\sim$0.16 eV for thick semimetallic Sb.[38] This structure undergoes a redshift on lowering the film thickness from $\sim$200 to $\sim$40 Å, thus with an opposite sign and in a different thickness range with respect to Bi. In the case of Sb, the shift could be interpreted rather well

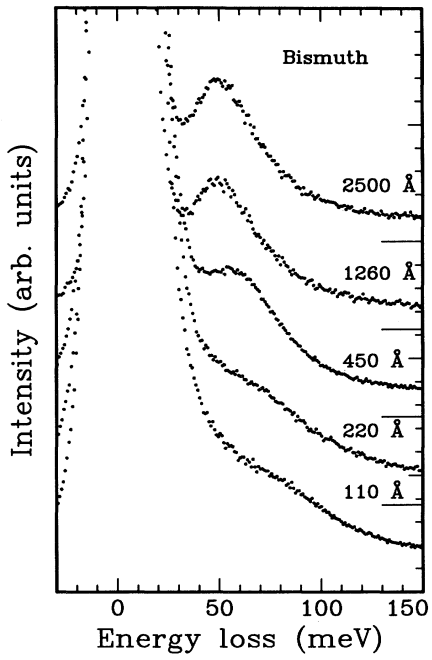

FIG. 4. HREELS (scattering efficiency) data relative to thin Bi crystals, with thickness $d = 2500$, 1260, 450, 220, and 110 Å (from the top to the bottom), taken with $E_p = 15.9$ eV and angle of incidence of 63°. Data are enlarged by a factor 2000 with respect to the elastic peak intensity. The various spectra are displaced along the vertical axis for convenience.

as being due to the varying boundary conditions experienced by the effective dielectric function of the antimony layer embedded between GaAs and the vacuum.[38] That result was achieved by performing a dielectric model calculation (using a semiclassical approach)[49] for the antimony layer in that thickness range. We applied the same model calculation with the parameters of the Bi layer, but we could not reveal any substantial modification of the model spectra in the actual bismuth thickness range.[29] Hence the origin for the opposite direction shift encountered by the electronic transitions in L and T must be found in a real modification of the energetic levels of bismuth, as the crystal thickness is changed. In particular, we notice that a critical value for the incoming of the QSE in the Bi bands across the Fermi energy is of the order of 10^2 Å.[1] We can thus attribute the measured energy shifts to a different position of the Bi Fermi level at different crystal thickness.

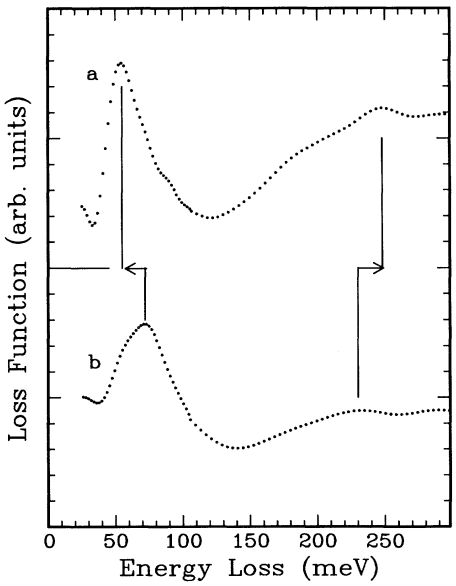

FIG. 5. The loss function relative to Bi at two different thicknesses: (a) 700 Å (bulk limit) and (b) 120 Å (in the QSE condition).

We recall that a shift toward higher energies of the Fermi level was calculated as the film thickness decreases:[19,21,22] in fact, as the thickness becomes lower than a critical value determined by the Bi band parameters, the electron and hole levels become confined in a bidimensional potential well, giving rise to discrete levels along the direction normal to the surface. Calculating the electron and hole densities in their respective bands, it comes out that they strongly depend on the thickness d.[19,21] Since in a semimetal the position of the Fermi energy is determined by the charge neutrality condition, the Fermi energy position also depends on d. Moreover, the effective mass of the holes at point T of the BZ is one order of magnitude higher than the effective mass of the electrons at point L (along the growth direction, parallel to the trigonal axis of Bi), thus the discrete energetic levels for the electrons are more separated from each other than the corresponding states for the holes. On decreasing d, the discrete level separation increases, while the carrier densities become lower. Since the latter effect is larger for the electrons than for the holes (given the Bi band structure in points L and T), *the Fermi level shifts to higher energies on decreasing the thickness* in order to preserve the charge neutrality condition. This situation is schematically pictured in Fig. 6, and is fairly well consistent with our experimental HREELS data.

The energy shift of the transition in L as a function of the crystal thickness, along with theoretical estimations of the Fermi energy change (appropriately shifted to account for the gap value), are shown in Fig. 7. Zaluzny and Lukasik[19] calculated an energy shift (ΔE) of E_F by 6 meV on decreasing d from large values to 500 Å, as did Gol'dfarb and Tavger,[22] while Garcia, Kao, and Strongin[21] calculated $\Delta E = 12$ meV as d decreases to 200 Å. We measure $\Delta E = 7$ meV (for d lowering to 450 Å) and $\Delta E = 16$ meV (for d decreasing to 200 Å), in very good agreement with theoretical estimations. As a consequence, the measured energy increase (decrease) of the transition at the point L (T) of the BZ, on decreasing the film thickness, is a clear *determination of the Fermi-level modification induced by quantum size effects* (as schematically pictured in Fig. 6).

Coming back to the HREELS data (Fig. 4), apart from the energy shift, a broadening and an intensity lowering of the loss structure associated with the transition in L are visible as the crystal thickness is decreased. Although the main influence of a QSE lies in the position of E_F, in-

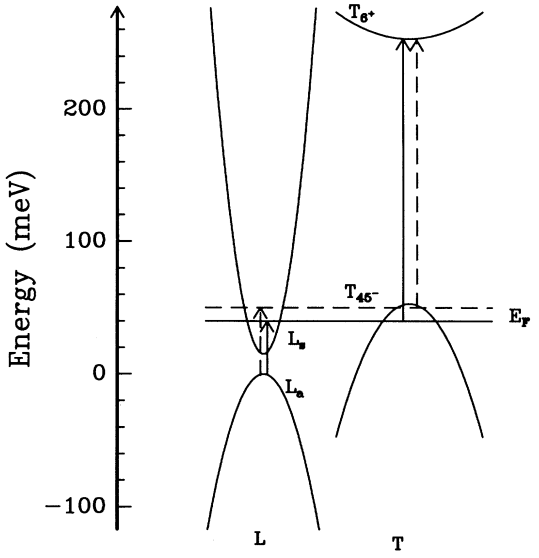

FIG. 6. A schematic representation of the electronic energy bands of Bi near points L and T of the Brillouin zone. The vertical axis is in the correct energy scale and the zero is positioned at point L_a. The continuous horizontal line represents the Fermi level for bulk Bi, while the dashed horizontal line qualitatively indicates its position in QSE conditions. Similarly, continuous vertical arrows indicate the observed electronic transitions in the bulk limit, while the dashed vertical arrows schematically represent the electronic transitions under the QSE regime.

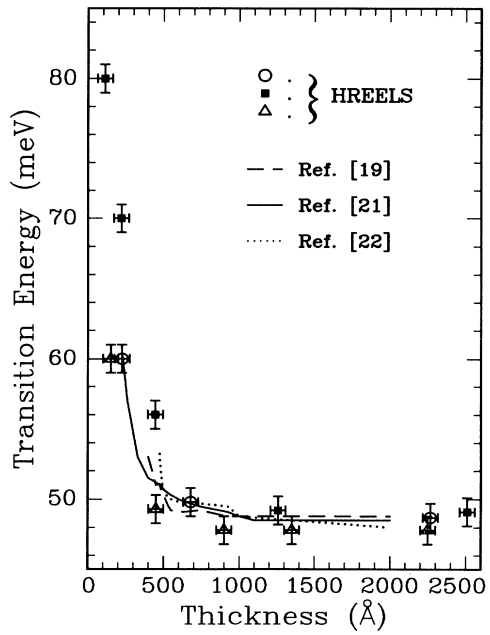

FIG. 7. The energy of the electronic transition in L as a function of Bi thickness (data points). The dashed, continuous, and dotted lines represent the Fermi-level position as calculated by Zaluzny and Łukasik (Ref. 19), Garcia, Kao, and Strongin (Ref. 21) and by Gol'dfarb and Tavger (Ref. 22), and opportunely shifted by 21, 23, and 27 meV, respectively, for taking into account the energy-gap value.

volved in the measured electronic transitions, which is well reflected by the energy shift of the loss structures, there nevertheless is a change in the "distribution" of the quantized states contained in the potential well, which can qualitatively account for the different intensity and width of the measured electronic transition. As a matter of fact, only a detailed and accurate band-structure calculation leading to an estimation of the joint density of states (JDOS) in QSE conditions could quantitatively account for the observed line shape. This is, however, beyond the aim of this experimental work.

C. Temperature dependence

The temperature dependence of the previously analyzed electronic transition located at point L of the BZ was studied by means of HREELS both in and out the QSE regime. HREELS measurements relative to a 750-Å-thick Bi film were performed at different temperatures ranging from 155 to 298 K (RT), with an uncertainty on temperature of ±5 K, due to a possible thermal shift during an experimental run (Fig. 8). Focusing our attention to the loss structure relative to the electronic transition at point L of the BZ, we observe a clear shift of this excitation toward lower loss energies, as the temperature decreases from 298 to 155 K. Energy values of the transition maximum versus temperature are reported in Fig. 9, along with a best fit of the experimental trend, which is expressed by the quadratic function

$$E(T)(\text{meV}) = a + bT(K) + cT(K)^2 ,$$

where $a = 29.8$, $b = 4.4 \times 10^{-3}$, and $c = 2.5 \times 10^{-4}$. The energy shift of the loss structure is related to the dependence of all the band parameters, in particular the energy

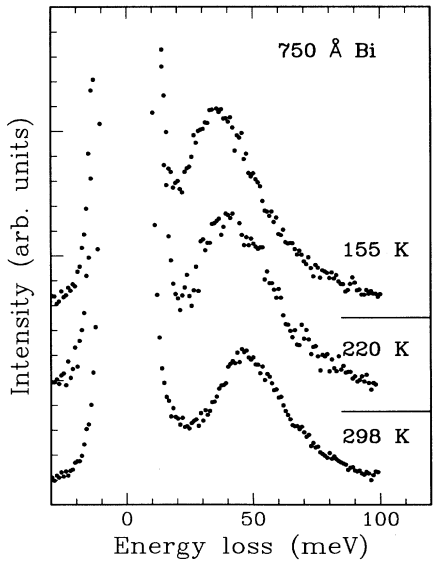

FIG. 8. HREELS data relative to 750-Å-thick crystalline Bi as a function of temperature, in the temperature range 155–298 K, taken with $E_p = 5$ eV and angle of incidence of 65°. Data are displaced along the vertical axis for the sake of clarity.

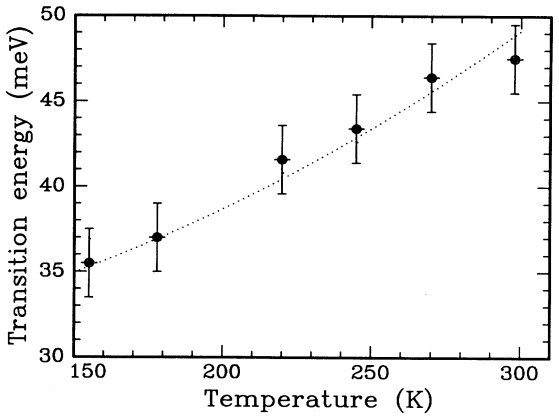

FIG. 9. The loss energy of the low-energy electronic transition of Bi as a function of temperature. The dotted line represents a second-order polynomial least-squares fit to the data.

gap, on the temperature. A first determination of this dependence was obtained by Vecchi and Dresselhaus[30] from magnetoreflection measurements on single-crystal Bi in the temperature range 4–280 K. The interpretation of these data was carried out in terms of the magnetic energy-level structure, derived from a two-band nonparabolic model of the electron pockets at the L point. They obtained an E_g dependence on T reproducible by a quadratic best fit with parameters $a=13.6$, $b=2.1\times10^{-3}$, and $c=2.5\times10^{-4}$, which is in substantial agreement with our result (bearing in mind that we refer to the transition maximum and not directly to E_g). In particular, they determined an E_g change from 35 meV at 280 K, to 20 meV at 155 K, i.e., a 15-meV reduction against our 10-meV shift in the same temperature range.

The determination of E_g from energy-loss data is not a trivial problem in this case. In fact, with Bi being a semimetal, the electronic transition in L takes place from the valence band to the conduction states at the Fermi level: therefore, its energy position is not simply determined by the E_g value, but also by the Fermi energy and (since the transitions is direct) by the ratio between the valence and the conduction effective masses (m_v and m_c, respectively). This means that, supposing $m_v=m_c$ and at $T\simeq0$ K, the so-called direct edge would be at an energy $E=E_g+2E_F$. Moreover, at RT, or even at $T\sim100$ K, the Fermi-edge broadening (derived by the Fermi-Dirac distribution function) is ~10–25 meV, thus of the same order of magnitude as the energies involved in the transition. Because of this, electronic excitations become possible between a valence-band level and a conduction state lower than E_F. Therefore, at temperatures significantly different from absolute zero (as in our case), we cannot either associate the transition edge with the E_g+2E_F value, nor extrapolate in a simple way a precise value for E_g and E_F separately. Moreover, the shift of the transition to lower energy on decreasing the temperature, is built up by several contributions.

(i) The E_g dependence upon temperature.

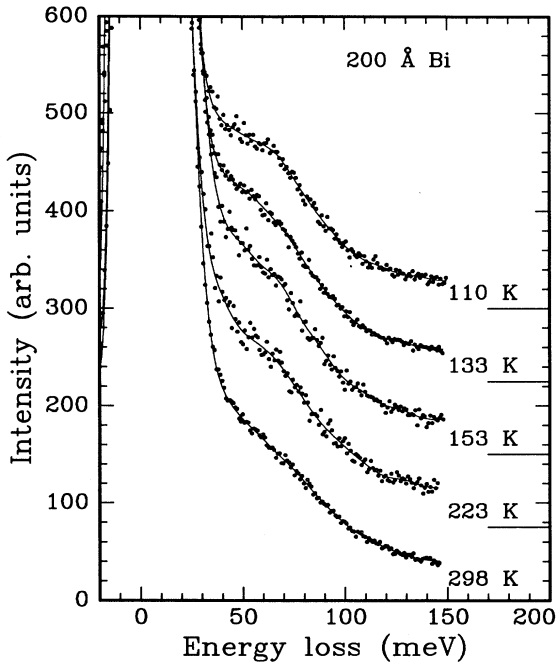

FIG. 10. HREELS data relative to 200-Å-thick (under the QSE regime) crystalline Bi as a function of temperature, in the temperature range 110–298 K, taken with $E_p=5$ eV and an angle of incidence of 65°. Data are displaced along the vertical axis for the sake of clarity.

(ii) The temperature dependence of the other band parameters such as E_F, m_v, and m_c.

(iii) The effect that the Fermi-edge sharpening on decreasing temperature has on the energy of the allowed excitation (for a transition to be permitted, it is necessary for the final state to be empty).

Even if a preliminary modelization of the transition has been made through a simple calculation of the temperature-dependent dielectric function,[29] its extremely crude degree of approximation (in particular that of considering parabolic bands) makes it unreliable for what concerns a quantitative separated evaluation of the different contributions above outlined. Nevertheless, it seems to indicate the importance of taking into account all of them, in particular the Fermi-edge broadening, to achieve the correct dependence of the energy gap upon temperature. We are dealing with the possibility of improving this first modelization—treating the bands in the nonparabolic approximation—so to make it a reliable means of distinguishing the different temperature-dependent contributions to the measured energy shift of the transition.

Finally, for what concerns the temperature dependence of the electronic transition in the quantum-size-effect regime, we show in Fig. 10 the HREELS data relative to a 200-Å-thick Bi film, in the region 0–150 meV, for T ranging from 110 K to RT. Also, in the QSE regime, a shift of the electronic transition loss structure toward lower energies is evident as the temperature decreases.

The intrinsic width of this loss feature makes the quantitative estimation of the shift somewhat uncertain; however, it could be evaluated (through a Gaussian fit) as 15±5 meV. We can therefore estimate a substantially equivalent temperature dependence of the energy gap in L of a Bi film, both in and out of the quantum-size-effect regime. Moreover, on lowering the temperature, both series of measurements show a sensible increase of the loss structure intensity and a light decrease of its width. The sharpening of the Fermi edge is probably the principal reason responsible for these effects. In fact, only the electron energy levels which are $\sim kT$ lower then E_F could be empty and therefore could become final states for the transition. As the temperature lowers, the energies of the possible final states become closer to E_F, though reducing the transition structure width and probably enhancing its intensity as its oscillator strength redistributes on fewer states.

IV. CONCLUSIONS AND PERSPECTIVES

We performed HREELS measurements on ultrathin crystalline Bi films for different thickness d and as a function of temperature. When $d \geq 500$ Å, the Bi film is almost equivalent to bulk crystalline bismuth. We have singled out two loss structures at 47 and about 200 meV, which, due to their width and low intensity, could be identified as electronic transitions. In particular, they could be associated with the electronic excitations from the valence band to conduction states at the L and T points of the BZ, respectively. This is a direct experimental determination of the electronic transition from the Fermi level to point T_6^+ of the Bi-BZ. Moreover, from the HREEL spectrum of bulk Bi, we have calculated the complex dielectric function of Bi in the low-energy range 20–400 meV.

Since Bi is a semimetal whose free carriers have very small Fermi energy (25 meV) and effective masses ($\sim 10^{-2} m_e$), it is possible to bring Bi thin films into the extreme quantum limit by allowing its dimension d to be of the order of the De Broglie wavelength of its carriers, i.e., of the order of few hundred Å's. In the quantum limit, the Fermi energy level becomes dependent on the Bi thickness, and in particular increases as d decreases. The analysis of the HREELS data as a function of the film thickness showed a shift by 33 meV toward lower energies for the transition in L, while the transition in T shifts by the same amount, but toward higher energies. This is a strong evidence for the E_F dependence upon film thickness (since the Fermi level is the final state for the transition in L, while it is the initial state for that in T), in substantial agreement with the theoretical prediction on this effect.

Finally, we have studied the Bi electronic excitations, both in and out of the QSE regime, as a function of temperature. The HREELS data show in both cases a redshift of the transition energies in L by 15±5 and 12±2 meV, respectively, as temperature decreases, which can mainly be related to the temperature dependence of the energy gap in L. Since the other band parameters also depend on the temperature, they very probably contribute to this energy shift, while a quantitative evaluation of the energy-gap variation from the transition energy shift is not straightforward. A simple model of the contribution of the transition to the imaginary part of the dielectric function, taking into account the influence of the Fermi-edge broadening on the transition energy, is the object of future work. Another possible subject of further investigation is the study of the Bi free-carrier plasmon as a function of thickness and temperature.

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