

ПО ИТОГАМ ПРОЕКТОВ  
РОССИЙСКОГО ФОНДА ФУНДАМЕНТАЛЬНЫХ ИССЛЕДОВАНИЙ  
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## THz phonon spectroscopy of doped superconducting cuprates

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Facts are presented evidencing a strong electron-phonon interaction in doped BSCCO superconductors. A pronounced fine structure in  $dI/dV$ -characteristics of Josephson junctions has been observed which is caused by interaction of AC Josephson current with Raman-active optical phonon modes. “Quantization” of the “gap” voltage for natural nanosteps on the cryogenically cleaved surfaces of BSCCO proves the existence of the intrinsic Josephson effect. A sharp extra structure in the current-voltage characteristics of nanosteps is attributed to the presence of the extended van Hove singularity.

**Introduction.** According to Abrikosov [1] a high transition temperature  $T_c$  in layered cuprates is caused by the presence of an extended van Hove singularity (EVHS) near the Fermi level. In Abrikosov’s model, optical phonons with small wave vectors play a dominant role in pairing. The electron-phonon coupling in high-temperature superconductors (HTSC) was confirmed experimentally via the pump-probe optical spectroscopy [2], the effect of renormalization of the quasiparticle density of states [3–8], the effect of generation of optical phonons by AC Josephson current [9–12], the photoemission spectroscopy [13, 14], and the isotope effect [15].

It is well known that the transition temperature  $T_c$  for cuprates varies with the hole concentration,  $p$ , according to a parabolic law:  $T_c = T_{c,max}[1 - 82.6(p - 0.16)^2]$  (the doping level  $p$  is defined as the hole density per Cu site normalized to one  $\text{CuO}_2$  plane) [16, 17]. At the same time there is a contradictory information about a doping dependence of a superconducting gap  $\Delta(p)$ .

In the present investigation a transition from overdoped (OD) to underdoped (UD) samples was achieved by substituting Sr with La [18]. The intrinsic Josephson effect in nanosteps on cryogenically cleaved surfaces of doped Bi-2212(La) single crystals, Bi-2212 whiskers and Bi-2223 polycrystals has been studied. A discreet character of the “gap” voltage  $V_{gn} = n(2\Delta/e)$  for natural nanosteps ( $j||c$ ) was observed ( $n$  is the number of contacts in a nanostep). The obtained results support a previously observed scaling of the superconducting gap  $\Delta$  with the critical temperature  $T_c$  on doping [19]. In addition, we have registered a sharp extra structure

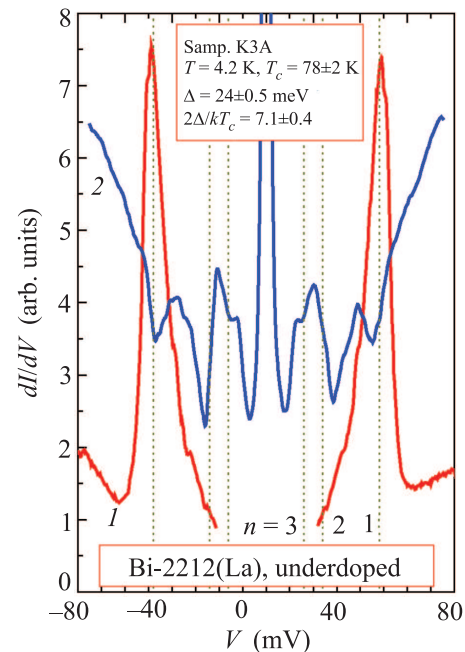


Fig. 1.  $dI/dV$ -characteristics of a single tunneling SIS-contact (1) and a single Andreev SnS-contact (2) in underdoped Bi-2212(La) at  $T = 4.2$  K ( $T_c = 78 \pm 2$  K,  $\Delta = 24 \pm 0.5$  meV,  $2\Delta/kT_c = 7.1 \pm 0.4$ )

in the current-voltage characteristics (CVC’s) of perfect Bi-2212 nanosteps which could be caused by the presence of the EVHS [20–23] close to the Fermi level in both slightly overdoped and slightly underdoped samples. An interaction between AC Josephson current and Raman-active optical phonon modes in the entire range of phonon frequencies (up to 25 THz) was observed in

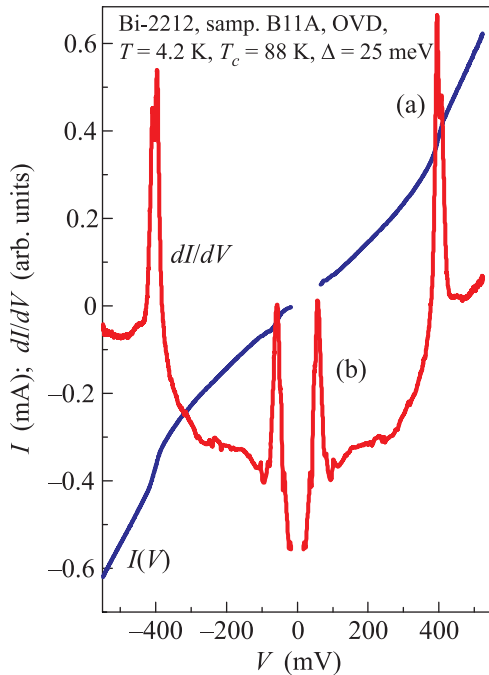


Fig. 2.  $dI/dV$ -characteristics of a Bi-2212(La) nanostep (8 contacts) at  $T = 4.2$  K (a) shunted by a single SIS contact (b) (slightly overdoped sample,  $T_c = 88$  K,  $\Delta = 25.0 \pm 0.5$  meV)

doped Bi-2212 and Bi-2223 samples, pointing to a strong electron-phonon coupling in HTSC [24–26]. A giant instability in  $I(V)$  – characteristics of Bi-2223 nanosteps is explained by a resonant emission of  $2\Delta$  – optical phonons in a process of recombination of nonequilibrium quasiparticles (Krasnov–Schnyder model [27, 28]).

**Experimental.** A break-junction technique [29] has been used to generate contacts of SIS-type (tunnelling spectroscopy) and SnS-type (Andreev spectroscopy) in Bi-2212(La) single crystals, Bi-2212 whiskers, and Bi-2223 polycrystals. To protect Bi-2212 whiskers from damaging at room temperature additional transitive substrates of thin tissue paper were used. Four strips of liquid indium-gallium solder were painted on substrates, and whiskers were located across these strips. At cooling of a sample holder an indium-gallium solder froze and fixed whiskers. Calibration of measuring channels of multifunctional I/O board AT-MIO-16X (National Instruments) was performed by a high-precision digital voltmeter.

For temperature measurements a calibrated germanium thermometer was used. A typical error of measurements of a dynamic conductance of junctions didn't exceed one percent.

The magnitude of the gap measured by tunnelling and Andreev spectroscopies on the same sample usually coincided within experimental errors (Fig. 1). In addition,

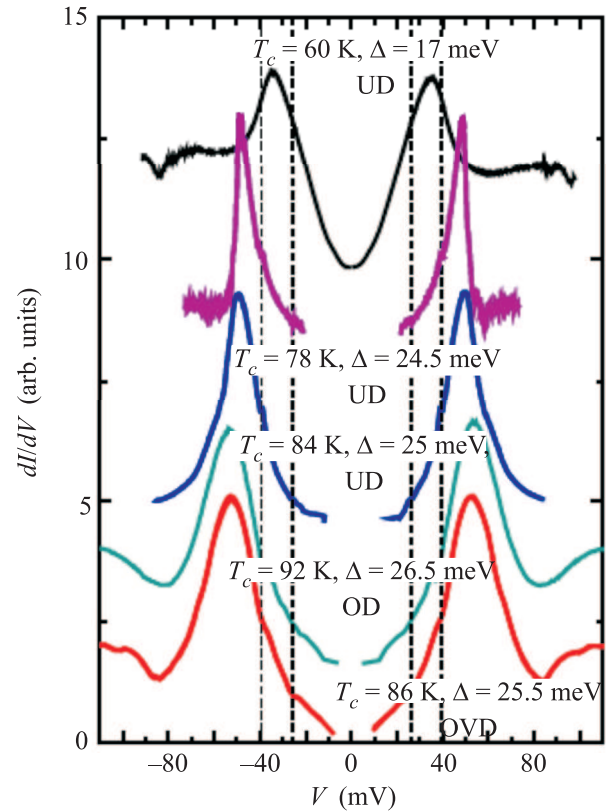


Fig. 3.  $dI/dV$ -curves for SIS contacts in underdoped Bi-2212

tion, using the same technique we have studied the current – voltage characteristics (CVC's) of natural nanosteps with a height from 1.5 to 30 nm which are always present on cryogenically cleaved surfaces of bismuth cuprates. In most cases these nanosteps were shunted by a single SIS contact, which allowed to estimate the number of contacts  $n$  in a stack (Fig. 2,  $dI/dV$ -characteristic of a Bi-2212(La) nanostep (8 contacts) at  $T = 4.2$  K (a) shunted by a single SIS contact (b)).

We have used the data of tunnelling, intrinsic tunnelling and Andreev spectroscopies to derive the dependence of a superconducting gap  $\Delta$  on the impurity hole concentration  $p$  (Figs.1–4). It should be noted, that for underdoped samples of bismuth cuprates it becomes progressively difficult to prepare true single SIS contacts with the current in  $c$ -direction. The layered structure of the material and weakening of bonding between superconducting blocks causes the formation of complicated network of contacts in the vicinity of the surface. In the present investigation the electron-phonon resonances were used as reliable calibration marks, which helped to judge a single SIS contact from a stack. Dotted lines in Fig. 3 indicate the position of electron-phonon resonances  $V_{res}$ , corresponding to a nonlinear interac-

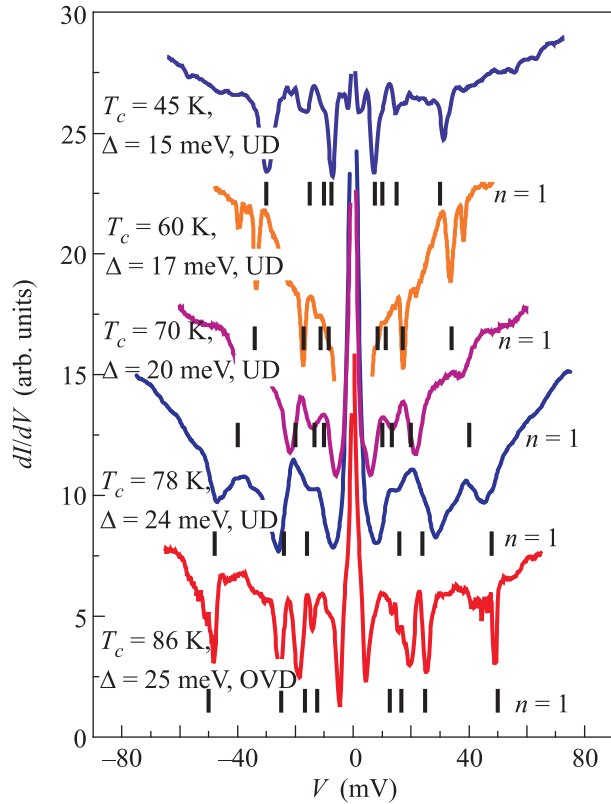


Fig. 4. Resistive transitions  $R(T)$  and gaps  $\Delta(T)$  in underdoped Bi-2212 samples

tion of AC Josephson current with Raman-active optical phonon modes [30]. For an apical oxygen phonon mode  $O_{Sr}$ :  $E_{\text{phon}} = 2eV_{\text{res}} \approx 80$  meV [9].

In all cases the superconducting gap  $\Delta(T = 4.2$  K) was found to scale with the transition temperature  $T_c$  (Figs. 5 and 6) in the entire doping range (the ratio  $2/\Delta kT_c$  is close to 7). The flattening of the “gap” parabola in the vicinity of optimal doping (Fig. 6) is probably an indication of pinning of the Fermi level to the EVHS [31].

We have found, that La substitution (red solid circles in Fig. 6) does not affect the character of scaling of  $\Delta$  and  $T_c$  (empty squares correspond to as grown crystals without La). A similar dependence was reported in [19], though a conflicting experimental information can also be found [32]. Recently scaling of superconducting gap  $\Delta$  and  $T_c$  was also observed in [33].

The results obtained in the present investigation and in [19, 33] support the conclusion that the frequency range of HTSC Josephson contacts (important for THz applications) is maximal for optimal doping.

Direct measurements done by the scanning tunneling microscopy (STM) method showed that the height of nanosteps on cryogenically cleaved surfaces is pro-

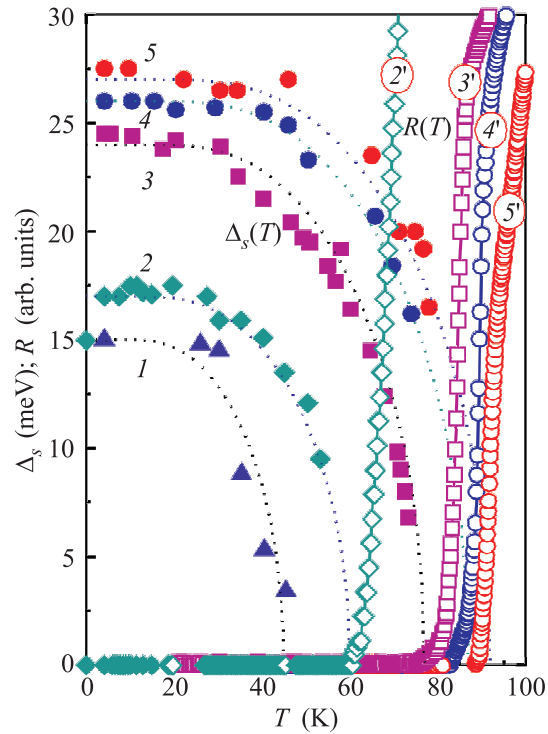


Fig. 5. Resistive transitions  $R(T)$  and gaps  $\Delta(T)$  in underdoped Bi-2212 samples

portional to half the height of the unit cell: 1.5 nm (the cleavage surface is located between two neighbouring BiO planes) [18, 19]. Note that half a unit cell in the  $c$ -direction corresponds to a single Josephson junction. According to Kaneko et al. [34] and Mitchell et al. [35], the nanostep width does not exceed  $1 \mu\text{m}$ . This result coincides with the estimates made in Ref. [19]. By tuning the junction with a micrometric screw in a single experiment it was possible to move from one nanostep to another and record their CVC’s individually.

The gap voltage for nanosteps with different number of SIS contacts  $n$  is “quantized”:  $V_{gn} = n(2\Delta/e)$  (Figs. 7 and 8), which proves the applicability of the “intrinsic Josephson effect” scenario for cuprates [36]. The sharpness of the gap structure is typical for Bi-2212(La) and Bi-2223 nanosteps and allows to estimate  $V_{gn}$  with sufficient accuracy. No signs of overheating at bias voltages  $V \approx V_{gn}$  were observed. For slightly underdoped Bi-2212(La) single crystal in Fig. 7 an elementary gap voltage  $2\Delta/e$  equals 50 mV at  $T = 4.2$  K.

The gap feature in the CVC’s has a shape typical for an “s-symmetry” (isotropic) gap parameter. At the first glance it is difficult to match this result with the photoemission spectroscopy data, according to which the gap parameter in the  $ab$  plane is highly anisotropic [37]. However, the situation changes when there is a van Hove

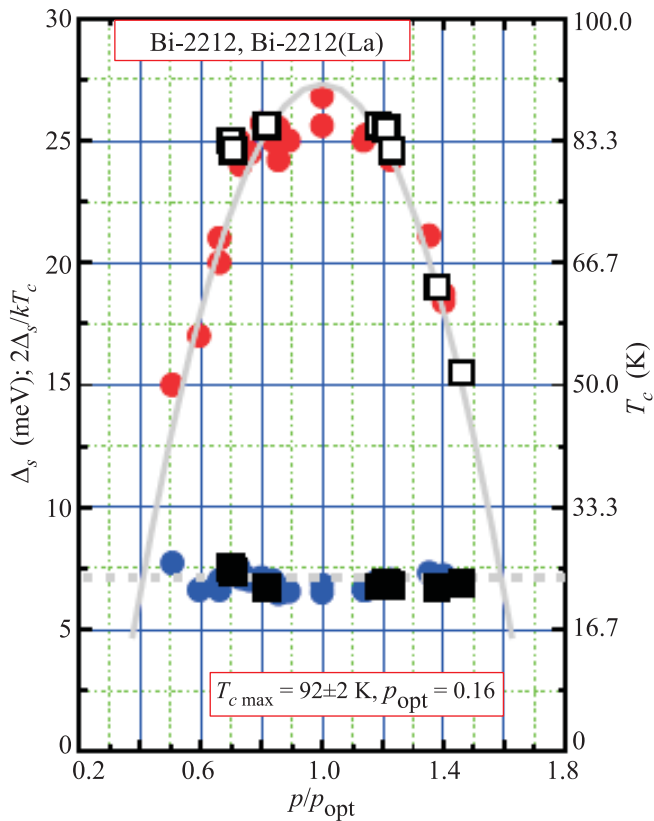


Fig. 6. Doping dependence of  $\Delta$  and  $T_c$  for Bi-2212

singularity at the Fermi level. Wei et al. [38] had found that a van Hove singularity enhances the gap structure in the CVC's of junctions even when the gap parameter in the ab plane is highly anisotropic. For slightly overdoped and slightly underdoped samples a sharp extra structure in the CVC's of Bi-2212 nanosteps was observed (Figs. 9 and 10), which we attribute to the presence of the extended van Hove singularity (EVHS) close to the Fermi level [1, 20, 21, 23, 39]. This extra structure is absent in the CVCs of optimally doped samples (Fig. 2) where it falls into a  $2\Delta$ -region. For strongly underdoped and strongly overdoped samples the extra structure is also not detectable. The latter effect could be the result of a pronounced drop of a quasiparticle lifetime above the superconducting gap [40].

The evolution of CVC's with temperature in Figs. 9 and 10 agrees qualitatively with theoretical calculations of Bok and Bouvier [21] (van Hove scenario). The inner singularity in Figs. 9 and 10 (and in [21]) closes at  $T_c$  and obviously corresponds to the gap structure, the outer singularity does not disappear at  $T_c$  and may be caused by EVHS (see also a recent publication: A. Piriou et al., First direct observation of the Van Hove singularity in

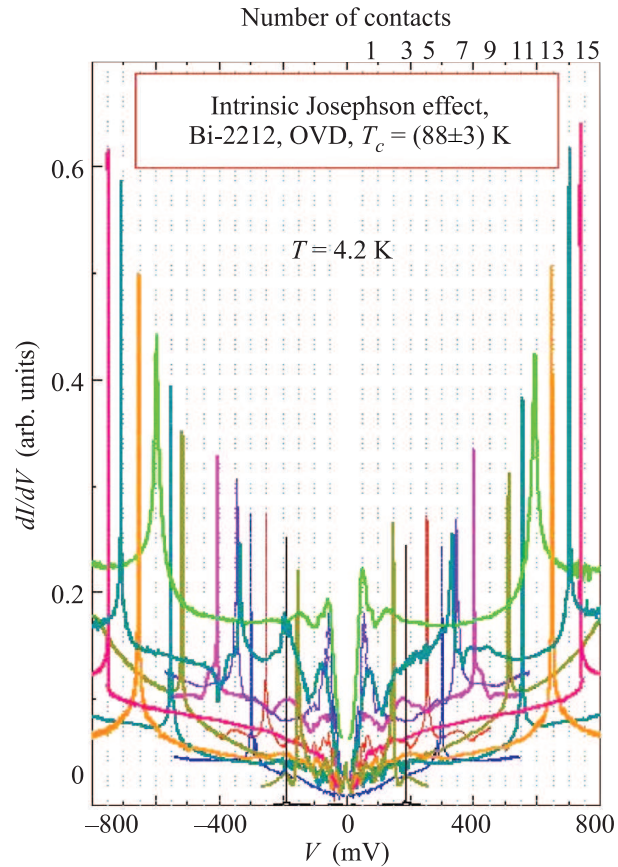


Fig. 7.  $dI/dV$ -curves for nanosteps with different number of contacts  $n$  at  $T = 4.2$  K (Bi-2212, overdoped,  $T_c = 88 \pm 3$  K,  $\Delta = 25$  meV). The discreteness of the gap voltage  $V_{gn} = n(2\Delta/e)$  is clearly seen

the tunneling spectra of cuprates, Nature Communications 2, 221, 01 March 2011 [23]).

Fig. 11 presents a dynamic conductance  $dI/dV$  of a break-junction with a partially suppressed background as a function of energy  $E = 2eV$  (optimally doped Bi-2212 single crystal,  $T = 4.2$  K). A pronounced structure in the  $dI/dV$ -characteristic (Fig. 11) is caused by an interaction of AC Josephson current with Raman-active optical phonon modes [30] in the range of phonon frequencies up to 20 THz, including the apex oxygen mode with the energy close to 80 meV. Vertical dashed lines in Fig. 11 correspond to the energies of Raman-active optical phonon modes (from Ref. [9]).

It is essential that the optical phonon spectra in Bi-2223 and Bi-2212 have a two-dimensional character. Structures of SrO–BiO–BiO–SrO spacers in these phases – are identical, and superconducting blocks differ by one  $\text{CuO}_2$ -plane. From Raman spectroscopy data and according to the present investigation the optical phonon spectra in these phases practically coincide.

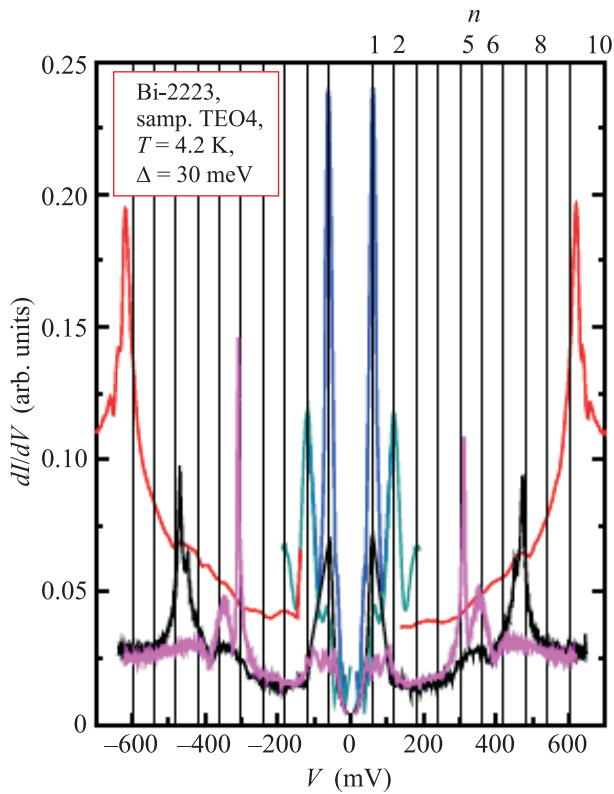


Fig. 8.  $dI/dV$ -curves for nanosteps with different number of contacts  $n$  at  $T = 4.2$  K (Bi-2223, overdoped,  $T_c = 104$  K,  $\Delta = 30$  meV). The discreteness of the gap voltage  $V_{gn} = n(2\Delta/e)$  is clearly seen

It has been found that the structure in  $dI/dV$ -characteristics of Bi-2212 Josephson junctions related to generation of optical phonon modes  $\omega_i$  at bias voltages  $V_i = \hbar\omega_i/2e$  can be observed for both underdoped and overdoped Bi-2212 and Bi-2223 single crystals (Figs. 11 and 12), with the doping level having only a negligible effect on the frequency of the main phonon modes (Fig. 13). This means that the electron-phonon coupling in BSCCO does not change significantly with doping over the entire region where superconductivity exists. Our experimental data support a model of a strong electron-phonon interaction [1, 24–26] in HTSC. At the same time we have not observed any structure which could be related to the “magnetic resonance” mode whose energy is expected to change significantly on doping [41, 42] (green rectangles in Fig. 13 mark expected positions of a “magnetic resonance” [42] for every sample). Thus the role of magnon modes in pairing is questionable. As for a dip-hump structure [32], which is often associated with magnetic pairing, it is caused, from our point of view, by a specific complex state of the crystal surface and has nothing to do with renormalization of the electron spectrum. We have found out, that

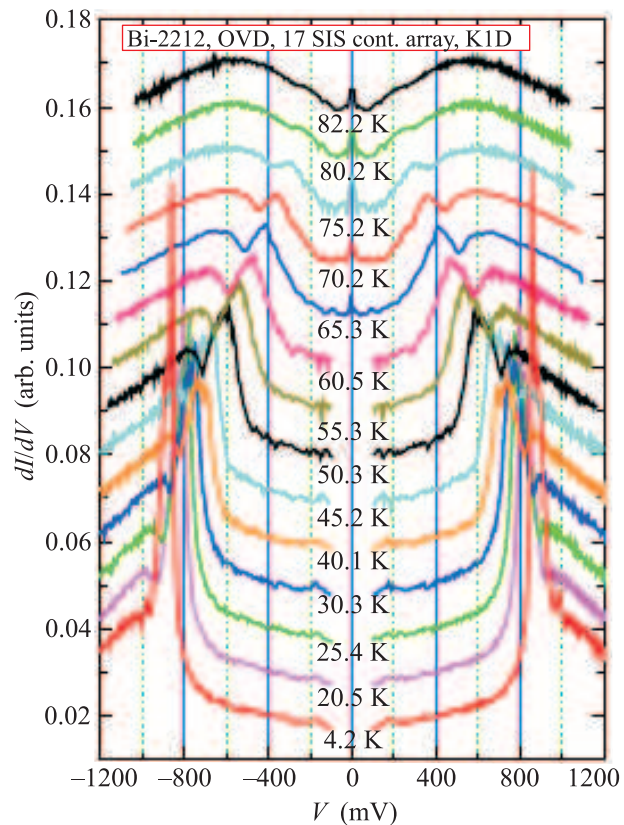


Fig. 9.  $dI/dV$ -characteristics of an overdoped Bi-2212 nanostep with 17 contacts at different temperatures

a dip-hump structure is absent in the CVCs of perfect nanosteps on the cryogenically cleaved whisker surfaces.

A giant instability in  $I(V)$ -characteristics of Bi-2223 nanosteps has been observed at helium temperatures (Fig. 14). A periodic switching between 7th and 9th branches in a multibranch characteristic presented in Fig. 14 could be caused by a resonant emission of  $2\Delta$ -optical phonons with the energy  $\approx 60$  meV ( $O_{Bi}$ -mode in Figs. 11 and 12) in a process of recombination of non-equilibrium quasiparticles in a stack of SIS junctions (Krasnov–Schnyder model [27, 28]). Two main factors were found to influence the amplitude of the instability of this kind. The instability amplitude reaches its maximum when: 1) EVHS crosses the Fermi level, 2) the value  $2\Delta$  coincides with the energy of one of the optical phonon modes. The instability amplitude is very sensitive to temperature and quickly drops in a “step-like” way when equality  $2\Delta(T) = \hbar\omega_{opt. phon}$  is not valid any more. For Bi-2223 phase the  $2\Delta$ -value at helium temperature does not exceed 70 meV (optimal doping) and the “apical oxygen” mode ( $\sim 80$  meV) remains beyond reach. At the same time, using chemical doping we can tune the  $2\Delta$ -value at least to two optical phonon modes with energies  $E_{phon} \cong 60$  meV ( $O_{Bi}$  mode in BiO-planes,



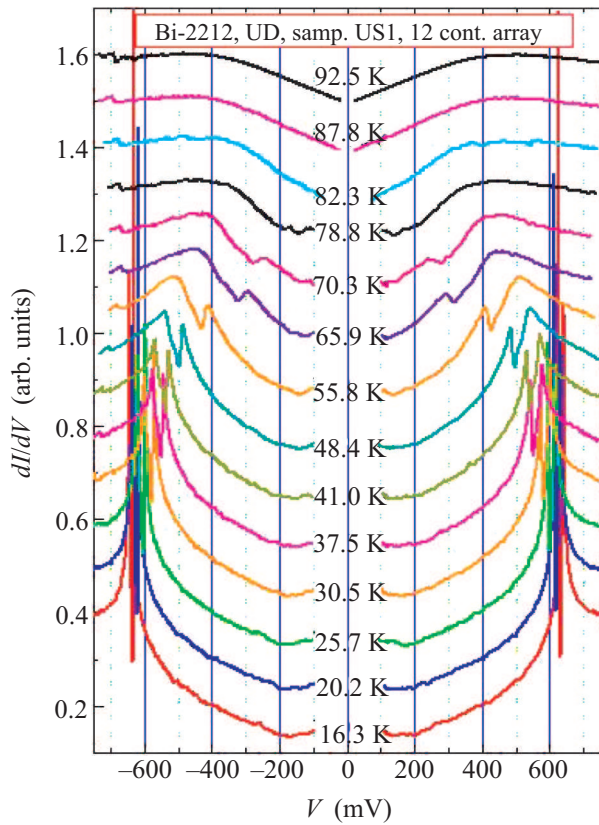


Fig. 10.  $dI/dV$ -characteristics of an underdoped Bi-2212 nanostep with 12 contacts at different temperatures

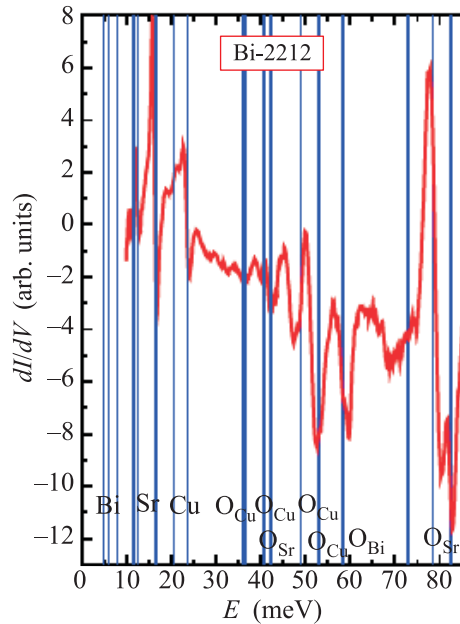


Fig. 11. (Color online) Phonon resonances on a  $dI/dV$ -characteristic of a break junction in optimally doped Bi-2212 at  $T = 4.2$  K ( $E = 2eV$ ). Vertical blue lines correspond to the energies of Raman-active phonon modes [9]

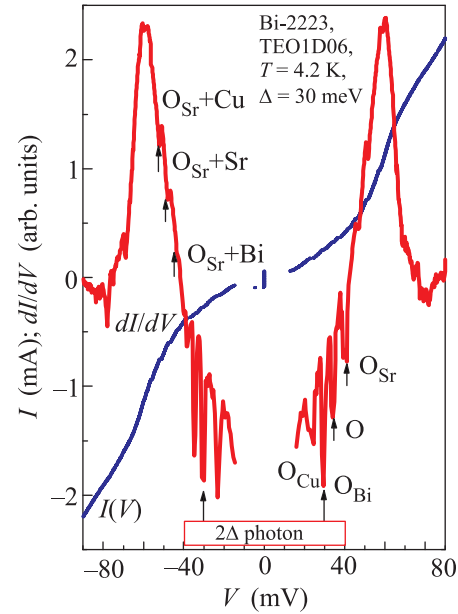


Fig. 12.  $I(V)$ - and  $dI/dV$ -characteristics of a break junction in Bi-2223 ( $T = 4.2$  K,  $\Delta = 30$  meV). Single-phonon and two-phonon resonances are marked by arrows

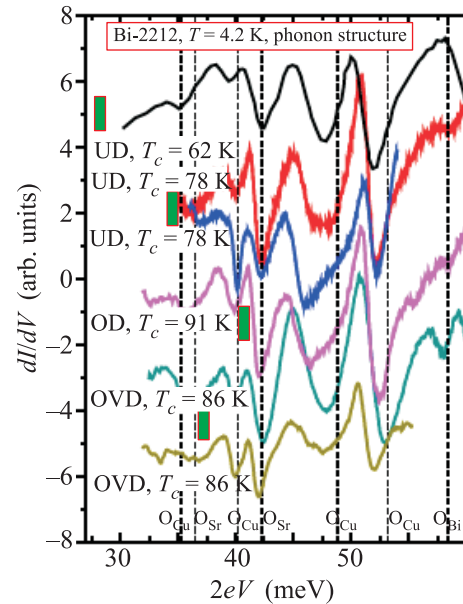


Fig. 13. Phonon resonances on  $dI/dV$ -characteristics of break junctions in doped Bi-2212 at  $T = 4.2$  K

Figs. 11 and 12) and  $E_{\text{phon}} \cong 50$  meV ( $O_{\text{Cu}}$  mode in  $\text{CuO}_2$ -planes). We succeeded to observe instabilities in CVCs of B-2223 nanosteps for both cases. For Bi-2212 phase the  $2\Delta$ -value does not exceed 52–54 meV (optimal doping) and instability easily develops in Bi-2212 nanosteps close to optimal doping.

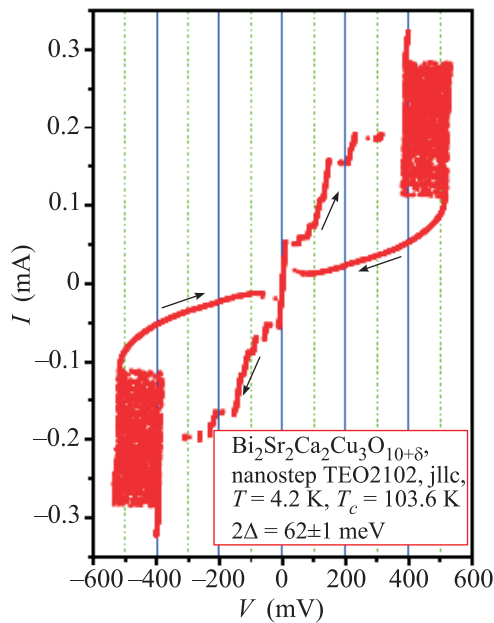


Fig. 14.  $I(V)$ -characteristic of a Bi-2223 nanostep with a giant instability at  $T = 4.2$  K

**3. Conclusions.** Tunneling, intrinsic tunnelling and Andreev spectroscopy studies of doped Bi-2212 and Bi-2223 samples are overviewed. Facts are presented evidencing the importance of the electron-phonon interaction in HTSC. A sharp extra structure in the CVCs of Bi-2212 contacts is attributed to the presence of the extended van Hove singularity close to the Fermi level in slightly overdoped and slightly underdoped samples. A giant instability in  $I(V)$ -characteristics of Bi-2223 and Bi-2212 nanosteps could be probably an indication of phonon pairing in HTSC.

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