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Research Report

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Abstract

We report on tunneling spectra measured on sintered and melted Hg–1223 (T_c onset = 133 K) and on single crystals of lead-doped Hg–1234 (T_c onset = 127 K) using a low-temperature scanning tunneling microscope. The conductance curves dI/dV with well-defined gaplike features are usually obtained in the point contact mode, but for the single crystals true noncontact tunneling has also been achieved. From their temperature dependence a scaling between the superconducting gap Δ measured at 4.2 K and an effective transition temperature T_c^* of the surface is derived.

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1 Introduction

Ever since the record for the highest superconducting transition temperature of $T_c = 133$ K was set [1] by one member ($n = 3$) of the layered $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ series, much effort has been made to increase the number of family members and to improve the quality of the samples. The mercury-cuprate compounds, usually multiphased, with $n = 1$ to 7 are synthetized [2-4] with a parabolic dependence of T_c on the number of CuO_2 layers [5, 6] peaking at $n = 3$. The structure containing stacks of n CuO_2 layers sandwiched between BaO–Hg–BaO insulating blocks along the c-axis is similar to that of the Tl- and Bi-based homologous series, with one main difference: in the Hg layer only a small fraction δ (10–40%) of oxygen sites is occupied compared to the full occupancy of the Tl_2O_2 or Bi_2O_2 layers. Electronic structure calculations have shown that the oxygen nonstoichiomety δ plays the crucial role by being the only source of hole doping [7, 8]. The occurrence of superconductivity above 150 K [9, 10] in Hg–1223 under pressure has raised the hope that suitable chemical substitution could also increase T_c in this range by proper doping. In fact it was concluded from the strong increase in T_c under pressure that the CuO_2 planes are rather underdoped.
A report on point contact tunneling by Chen et al. [11] on polycrystalline Hg–1201 (T_c onset = 97 K) claims for unusually symmetrical BCS-like conductance curves $G(V) = dI/dV$, with well-defined peaks and lower and flatter subgap values than observed in other high-temperature superconductors (HTS). More recently, similar point contact spectroscopy on the sintered Hg–1223 ($T_c = 132$ K) has been reported by Jeong et al. [12] showing mainly v-shape-like tunneling conductance with strong asymmetry and with the occasional appearance of two energy gaps at 48 meV and 22 meV. The linear conductance observed for $|eV| < \Delta$ was assumed to originate from the coverage of the surface by a normal layer of distributed thickness. We present here data on sintered and melted samples of Hg–1223 [13] as well as on high-quality single crystals of HgPb–1234 [14, 15]. In general our results for Hg–1223 agree well with the measurements of Jeong et al. [12] in terms of shape, asymmetry and with the observation of an energy gap of 24 meV at 4.2 K. Whereas point contact tunneling is usually necessary for the observation of adequate $I - V$ curves in polycrystalline samples, the better surface topography of single crystals allowed us to obtain reliable conductance curves with the scanning tunneling microscope (STM) tip in a true noncontacting mode. We observe that the gap values derived by fitting the data with a smeared BCS density of states vary from sample to sample between 9 and 34 meV. These variations of Δ found on cleaved and uncleaved surfaces emphasize the influence of the stucture and chemistry of the top layer on the tunneling properties. Indeed we demonstrate a linear correlation between the gap amplitude at 4.2 K and an effective superconducting transition temperature of the surface, T_c^*, derived from the temperature dependence of the zero-bias conductance $G(V = 0)$. The value of T_c^* is usually much lower than the bulk transition temperature T_c.

2 Experimental

2.1 Sample preparation

The *sintered* samples were synthesized with a standard precursor-based technique from $Ba_2Ca_2Cu_3O_x$ powder mixed with HgO, sealed in quartz tubes containing 1 bar O_2, and heated in several steps up to 800 °C; further details are given in [4]. In order to optimize their oxygen content and therefore their critical temperature T_c (onset) around 133 K, a post-annealing treatment at 300 °C in O_2 was performed. The specimens, characterized by x-ray techniques, show large amounts (up to 70%) of Hg–1223. Before mounting the sample on the STM, the surface of the pellets was carefully flattened and cleaned with a small abrasive jet of fine glass beads, and annealed again for a few hours at 300 °C in flowing O_2. Some of the samples were also *melted* under 10 kbar Ar at 1060 °C in order to encourage the growth of larger crystallites still imbedded in the material, as these crystallites are better suited for STM investigation. In order to synthesize *single crystals* of the mercury phase, mixtures of the stoichiometric Hg–1223 compound with either PbO, or $BaCuO_2$ + CuO or HgO were melted under 10 kbar Ar gas pressure at $T \sim 1040$–1070 °C [14, 15]. An additional annealing step for 2 h at 860 °C was usually necessary to better oxygenate the crystals, which predominantly have the Hg–1234 composition instead of the expected 1223. The best crystals were obtained with the PbO flux, but with a partial substitution of Pb for Hg leading to the composition $Hg_{0.8}Pb_{0.2}Ba_2Ca_3Cu_4O_{10+x}$ as determined by energy-dispersion x-ray (EDX) measurements. The addition of Pb reduces the melting temperature, stabilizes the phase, and allows T_c to be tuned by letting more oxygen enter the structure [16, 17]. The structure was refined using a four-circle crystal diffractometer as reported elsewhere [18]. Small amounts ($< 6\%$) of intergrowth with the 3- and 5-layer materials have been observed. The presence of stacking faults seems to be an intrinsic property of the members of the Hg–12(n-1)n series, where $n \geq 2$. The crystals have tetragonal symmetry with lattice parameters $a = 3.85$ Å and $c =$ 19 Å. Their size is rather small, typically less than 0.5×0.5 mm^2. Susceptibility measurements were done with a dc SQUID (BTI) magnetometer in magnetic fields < 30 Oe applied along the c-axis. Data from samples of the same batch show rather sharp superconducting transitions ($\Delta T_c \leq 15$ K) with T_c onsets between 120 and 127 K.

2.2 Experiment

The tunneling measurements were performed with a low-temperature STM inserted in a conventional cryostat and operated in a He gas atmosphere, as shown in Fig. 1. The STM is of the beetle type [19], appropriately damped against vibrations by a cushion of graphite fibers, and thermally isolated by two copper shields. The temperature of the STM unit can be controlled and stabilized by means of an integrated Si diode sensor and a heater. An extensive description of our low-temperature, ultra-high vacuum (UHV) version of the beetle STM is provided in [20]. The tips are made either of etched Au or Pt–Ir wire. The spectroscopy data are usually taken as a 2D array of current–voltage ($I - V$) curves over a given scan area (max 0.25 μm at 4.2 K), at a constant tip–sample distance by briefly opening the feedback loop during the bias voltage sweep. By changing the tip–sample distance, the tunneling resistance can be adjusted and, if necessary, reduced until the point contact mode is reached. The conductance curves $G(V) = dI/dV$ are derived numerically. For positive bias voltage, the electrons flow from the sample to the tip. Reasons for using an STM operating under ambient pressure instead of the UHV setup described in [20] are that the first available samples with appropriate purity were sintered pellets, that the single crystals are still too small to be manipulated and cleaved under UHV conditions, and finally our experience that, except for BiSrCaCuO crystals, oxygen is readily lost from the top layers when cleavage is performed in UHV and at room temperature. The surface quality of the samples have been checked with a scanning electron microscope (SEM, Hitachi S4000), and, in the case of single crystals, with the additional use of an atomic force microscope (AFM, Nanoscope III) controlled by an home-built data acquisition unit.

3 Results

Data for sintered and melted Hg–1223 [13] are presented along with data for newly obtained single crystals of doped HgPb–1234. The complicated nature of the sample surface in the presence of possibly underdoped insulating top layers as well as various impurities and defects inherent to the cuprates makes true vacuum tunneling more difficult than ordinary point contact tunneling. In fact, most of the $I-V$ characteristics must be determined in the contact mode with rather large feedback currents in order to observe gaplike structures. The background conductance is mainly parabolic at low bias voltage and then increases linearly at higher bias, as often reported for HTS S–I–N (superconducting–insulating–normal) junctions [21]. In several optimal cases it was nevertheless possible to find an ohmic dependence of the conductance and nice gaplike structures. The first set of experiments was performed on *sintered pellets* using the STM in the point contact mode between 4.2 K and T_c. Two examples of the conductance curves measured at 4.2 K and 77 K are shown in Fig. 2. The tunnel resistance of this junction is $R_t = 3.6$ MΩ, a typical value for our point contact junctions (1–100 MΩ). In order to estimate a value for the superconducting gap Δ, the normalized conductance curves have been fitted by the following equation:

$$G_s/G_n = \int_{-\infty}^{\infty} N_s(E)[-\delta f(E+eV)/\delta(eV)]dE \quad (1)$$

using the proposed smeared BCS density of states of Dynes et al. [22]. This yields

$$N_s(E) = \mathrm{Re}\left\{ \frac{|E-i\Gamma|}{[(E-i\Gamma)^2-\Delta^2]^{1/2}} \right\} \quad , \quad (2)$$

where Γ is a smearing parameter accounting for lifetime broadening effects such as inelastic scattering. The Fermi function f in Eq. (1) accounts for thermal smearing.

The derived gap values are $\Delta = 24$ meV at 4.2 K and 21 meV at 77 K with the corresponding Γ values of 6.9 and 7.1 meV, respectively. Using the onset value of 133 K for T_c, the ratio $2\Delta/kT_c$ becomes 4.2 and 3.7 at the two temperatures. In fact we observe almost no variation of Δ in this sample, until about 80 K (Fig. 3), whereas at higher temperatures the gaplike features vanish so quickly that no proper evaluation of Δ is possible. This fast disappearance might be related to phase inhomogeneity, reduced superconducting parameter at the surface, or large thermal fluctuations. In spite of reproducible point contact tunneling data, polycrystalline samples are still not optimal probes because of their small grain size, less than 10 μm as checked by SEM, and their random crystallographic orientation. For these reasons, attempts were made to melt the Hg–1223 powders under high Ar gas pressure in order to generate bulk samples with large-sized crystallites. By fracturing the melted specimens, flat crystallites up to a few hundred microns could be exposed to the tip for point contact tunneling. Unfortunately melting also leads to the uncontrolled growth of several phases with other n, i.e., Hg–1201, Hg–1234, Hg–1245 as shown by the corresponding transitions in the susceptibility data. On one of the samples, we measured two onsets in the susceptibility curve $\chi(T)$ at 125 K and around 70 K [Fig. 4(a)]. A typical $I-V$ curve measured at 5 K and its corresponding conductance $G(V)$ are plotted in Fig. 4(b). In general, the curves appear more symmetrical and smoother than for the sintered materials, with a lower zero-bias conductance G_0 (<10%). After normalizing the conductance $G_s(V)$ by its normal state value $G_n(V)$ approximated by a second-order polynomial fit to the data, a fit with Dynes' equation leads to the parameter values $\Delta = 15$ meV and $\Gamma = 6.8$ meV. This observation of a smaller gap can be attributed to the lower T_c phase, possibly Hg–1201, found in the susceptibility data. This gap value of

15 meV is in agreement with the results reported by Chen et al. [11] on polycristalline Hg–1201 and yields $2\Delta/kT_c = 5.0$.
Thanks to the recent success in growing *single crystals* of reasonably high quality [14, 15], a further step can be taken in the investigation of the superconducting properties of the top layers and their influence on the tunneling spectroscopy data. Whereas single crystals are certainly appropriate for STS investigations, care must still be taken to generate clean surfaces with small amounts of impurities, defects, and residues of other phases such as flux droplets. For this purpose we succeeded, in some cases, in cleaving the single crystals in air and quickly measuring them. This process is unfortunately not always reproducible and encumbered by the small size and the hardness of the crystals. A typical AFM image of the surface of a HgPb–1234 crystal before and after cleavage is displayed in Fig. 5. The as-grown surface gives evidence of many small PbO flux droplets or possibly outgrowths of mercury separated by larger flat areas. The height of these droplets ranges between 1 and 5 nm. The cleaved surface is rather clean with the presence of fracture steps having a height of one single unit cell ($c = 1.9$ nm) or multiples thereof. Lack of atomic resolution with the AFM does not allow us to determine its nature, but from the crystal structure we expect the cleavage to occur at the HgO plane. This plane is indeed oxygen-deficient and the Hg sites can be partially substituted by Pb^{4+} ions, Cu and/or CO_3 groups [18]. This leads to some local distortions and a reduction of the electron density.
In several areas, small imbedded precipitates appearing either as plain or broken spheres are visible, demonstrating their presence even in the bulk of the crystals. Spectroscopy on uncleaved crystals can be successful and lead to conductance curves in an almost "true vacuum" tunneling mode, i.e. $R_t > 100$ MΩ. In such a case, the exponential dependence of the tunnel current on the tip–sample distance was verified, with no significant change in the shape of the normalized conductance. An example of good reproducibility is shown in Fig. 6, the untreated $G(V)$ data having been taken along a line on the sample surface at liquid helium temperature at a tunneling control current of 1.5 nA. Well-defined peaks at about ± 45 meV and a clear subgap feature at ± 16 meV are observed. In this case, the tunneling resistance is 160 MΩ. By normalizing the curves with a second-order polynomial fit to the data (assumed to represent the normal-state dependence at that temperature) a fit with Dynes' relation can be attempted. A fit at the peak positions leaves too much discrepancy at low bias voltage, whereas a fit within the voltage range corresponding to a maximum d^2I/dV^2 value appears more adequate (Fig. 7). The latter fitting procedure yields $\Delta = 34$ meV and $\Gamma = 9.5$ meV. Note that Δ values determined in this manner are usually comparable to (or slightly larger) than those derived from the intersection points with an interpolated baseline, which in the present case yields $\Delta = 29$ meV. We have used the fitting procedure with a smeared BCS density of states merely for convenience and for the purpose of comparing samples. It is clear that the details of the conductance features often reported for the HTS cannot be explained with such a simple model. For example, the origin of the subgap shoulder at 16 meV is unclear, although it is reminiscent of the gap energy measured on the melted nominal Hg–1223 sample characterized by a double transition and a lower onset at 70 K in the susceptibility data (see Fig. 4a). Other characteristics of our conductance curves are their asymmetry and the presence of a dip above the peaks as often reported for the HTS layered cuprates [21, 23].
Additional information on the superconducting properties of the surface can be found in the temperature dependence of the conductance curves. Our investigation on most of the samples suggests the following trend: The value of the zero-bias conductance increases with temperature faster than expected, i.e., the gaplike features vanish at a temperature T_c^* far below T_c, whereas the amplitude of the gap barely changes up to T_c^*. Such a behavior is displayed in Fig. 8 for the HgPb–1234 single crystal (H27/19) cleaved shortly before measurement. A

surprisingly small gap value of 9 meV, constant up to 20–25 K, is derived from the curves fitted by the smeared BCS density of states given in Eq. (2). The corresponding broadening parameter Γ remains almost constant with values close to 4 meV. Above 25 K, the gaplike features vanish into the parabolic background. By plotting the normalized zero-bias conductance $G(V = 0)/G(V_0)$, where V_0 is a fixed bias voltage, as a function of temperature, a transition is observed with an onset temperature of $T_c^* \cong 25$ K, which is characteristic for the surface. Before cleavage, this same crystal had the values $T_c^* = 48$ K and $\Delta(4.2\text{ K}) = 25$ meV. The generality of this observation is illustrated in Fig. 9 with the example of transitions measured on another crystal (H27/6) of the same batch before and after cleavage. The bulk transition measured by zero-field cooled magnetization $M(T)$ exhibits a T_c onset at 127 K with ΔT_c (10%–90%) = 14 K, whereas at the uncleaved surface, the sharp transition given by $G(0)/G(V_0)$ versus T is shifted down by over 50 K with an onset at $T_c^* = 63$ K. After cleavage, T_c^* is reduced to approximately 40–45 K. Similarly the gap value $\Delta(4.2\text{ K})$ derived from the fit of the tunneling conductance decreases from 34 meV (see Fig. 7) to 15 meV after cleavage. This behavior appears to be general and shows that a linear scaling exists between $\Delta(4.2\text{ K})$ and T_c^* as demonstrated in Fig. 10. From the slope of the line fitted to the data, an average ratio $2\Delta/kT_c^* \cong 11.5$ is derived. No scaling is apparent with T_c measured by inductive methods, which leads us to emphasize that this tunneling data must be interpreted with caution, especially when discussing the ratio with regard to strong or weak coupling. In effect, if one considers the experimental gap range of 9–34 meV and a typical T_c value for the bulk of 120 K, one calculates a ratio of $2\Delta/kT_c$ between 1.75 and 6.6, which is inconsistent. The absence of scaling between Δ and bulk T_c has been previously reported with high-resolution electron energy loss spectroscopy measurements on BSCCO crystals [24] and attributed to pair-breaking effects (inelastic scattering) that suppress T_c but do not change $\Delta(0)$ significantly.

4 Discussion and Conclusion

The present results raise several questions about the origin of the subgap feature seen for example in Fig. 7, and about the reasons for the quick growth of the zero-bias conductance below T_c^* while the gap value barely changes. The fact that the cleavage of the crystal deteriorates the superconducting properties of the surface is also puzzling. Besides gap-broadening effects (finite lifetime of quasiparticles, distribution of gaps, etc.), the presence of subgap filling has been widely discussed, in particular in relation to proximity effects on a normal-metal surface layer [25], localized states in the barrier, gapless superconductivity reflecting an anisotropic gap function with nodes (d-wave pairing) [26] or interlayer pairing [27-29]. In the point-contact mode, other effects such as the presence of leakage currents flowing parallel to the tunnel current, geometrical and pressure effects and finally Andreev reflections at the normal–superconducting (N–S) boundary can become dominant. In several cases we have indeed observed a peak in the tunneling conductance at 4.2 K, which could be attributed to Andreev reflections. According to the Blonder–Tinkham–Klapwijk (BTK) theory [30] and extensions of it [31-33], which describe the crossover from a metallic to a tunnel junction in N–S microstrictions, the differential conductance dI/dV is proportional to the transmission coefficient for electrical current given by $1 + A(eV)$–$B(eV)$. The probability of an Andreev reflection $A(eV)$ and of an ordinary reflection $B(eV)$ at the N–S interface can be calculated for different barrier strengths Z (dimensionless quantity). A consequence of Andreev processes is that the conductance increases sharply with decreasing barrier strength for $eV < \Delta$. Furthermore, depending on the barrier strength ($Z \cong 1$), the zero-bias conductance vs. temperature can be found to rise to its normal state value even below T_c [30]. This model might explain the temperature dependence of our point contact tunneling data in Fig. 8. As temperature increases, the subgap conductance increases because of the increase of the Andreev reflection probability in a range in which $\Delta(T)$ still remains constant. An additional change in the barrier strength due to a modification of the tip–sample pressure through thermal expansion effects cannot be ruled out, even if the tunneling resistance is maintained at a constant value by adjusting the tip displacement.

Another explanation of the fine subgap structures and the finite value of the conductance at zero bias was proposed in a model by Tachiki et al. [27], which describes a tunnel junction between a normal metal and a layered oxide superconductor. The latter is assumed to be a stacking of strongly superconducting layers (CuO_2) and weakly proximity-induced superconducting layers (e.g., BaO, Bi_2O_2, HgO). The main result of this treatment is that small proximity-induced energy gaps combined with additional Van Hove singularities at higher energies appear in the conductance curves. Owing to thermal fluctuations, these features are predicted to vanish around $T/T_c \leq 0.5$. Simultaneously, the zero-bias conductance produced by gapless excitations increases sharply, whereas the peak voltage remains almost constant. A similar picture was also proposed by Frick and Schneider [28], who considered the oxides as superconductor–normal–metal (S–N–M) superlattices in which adjacent layers are coupled via single-particle hopping. The induced superconductivity in the normal units leads to states below the BCS gap and to the development of a peak with increasing interlayer hopping. The formation of these low-energy structures is accompanied by a depletion of states around the Fermi level, resulting in a linear behavior of the low-energy density of states $N_s(E)$ and therefore in a gapless spectrum. Again it is found in this model that the subgap peak smears out at rather low temperatures, $T/T_c \sim 0.1$, with a fast filling of the low-lying states.

The observation of decreasing gap value scaling with decreasing surface transition temperature T_c^* after cleavage in air clearly demonstrates that the surface state is disturbed. A possible reason is the presence of dangling bonds that render the cleaved surface very reactive and immediately covered by adsorbed molecules (water, carbonates, organic groups, etc.). An additional explanation is that the cleavage plane, being the (HgPb)–O layer with its low oxygen content, forms an insulating surface barrier or a normal–metal layer with proximity-induced superconductivity. In the sintered sample the random orientation of the grains enhance the chances for the tunneling current to flow along the CuO_2 planes, and therefore makes point contact tunneling less sensitive to the quality of the surface than is the case for single crystals. It is worthwhile to point out that the flatter and lower conductance curves reported by Chen et al. [11] on Hg–1201 ($n = 1$) were measured after scraping the surface until appropriate $I-V$ curves were obtained. Moreover this particular member of the homologous series, with only one CuO_2 layer per unit cell, might have better intrinsic superconducting properties because of the absence of stacking faults or intergrowth with higher n phases.

In summary, our measurements on sintered Hg–1223 pellets and Hg–1234 single crystals show the importance of the surface quality in obtaining well-characterized tunneling conductance and uniquely defined gap values. Essentially we have demonstrated on single crystals that the superconducting gap scales with an effective surface critical temperature of $T_c^* < T_c$. However the effective ratio $2\Delta/kT_c^* \cong 11.5$ derived from this scaling is surprisingly large. It could be an intrinsic effect of the mercury compounds, which have unstable or degraded surface layers possibly due to the high vapor pressure of mercury. Models of tunnel and point-contact junctions based on the proximity effect and Andreev reflections can be invoked to explain the experimental tunneling curves. It seems nevertheless that a unique interpretation of the STM tunneling data for the high-T_c oxides would require materials of high purity having well-ordered surfaces cleaved at low temperatures under UHV conditions.

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Figure 1: Schematic view of the low-temperature beetle-like STM setup.

Figure 2: Normalized conductance $G(V)/G$ (0.1 V) of a sintered Hg–1223 sample at 4.2 K and 77 K, with T_c onset at 133 K. The dashed lines are fits using a smeared BCS density of states as proposed by Dynes et al. [22]. [cf. Eq.(2)].

Figure 3: Temperature dependence of the gap parameter Δ measured on sintered Hg–1223 and compared to the expected BCS behavior.

Figure 4: (a) Field-cooled and zero-field-cooled susceptibility $\chi(T)$ of melted nominal Hg–1223 measured in a field of 25 G. (b) Normalized conductance of the same melted sample at 5 K with smeared BCS fit (dashed line).

Figure 5: (a) AFM image of the surface of an uncleaved HgPb–1234 single crystal (H27/19). The small droplets are presumably PbO flux or Hg outgrowth; Δz = 35.8 nm. (b) Surface of the same sample after cleavage, exhibiting clear fracture steps; Δz = 12.9 nm.

Figure 6: Series of conductance curves measured along a line on the surface of an uncleaved single crystal of HgPb–1234 (H27/6) at 4.2 K. $I_{\mathrm{tunnel}} = 1.5$ nA.

Figure 7: Normalized conductance $G_{\mathrm{s}}/G_{\mathrm{n}}$ of uncleaved HgPb–1234 single crystal (H27/6) at 4.2 K. The two lines calculated with Dynes' equation [Eq.(2)] show the difficulty of fitting the experimental curve over the entire voltage range with a unique set of parameters.

Figure 8: Temperature dependence of the normalized conductance curves $G(V)/G$ (–0.05 V) measured on a cleaved HgPb–1234 single crystal (H27/19). The curves have been shifted for clarity. Above 25 K the gaplike feature has already vanished, whereas the T_c onset measured by dc SQUID is 127 K. The amplitude of the gap $\Delta = 9$ meV is almost unchanged.

Figure 9: Bulk and surface superconducting transition determined from the measurement of the zero-field-cooled magnetization (dc SQUID, H=30 G) and from the zero-bias conductance amplitude $G(0)/G$ (–0.15 V) vs. temperature (STM) on HgPb–1234 single crystal (H27/6).

Figure 10: Scaling between the gap value $\Delta(4.2\ \mathrm{K})$ and the transition onset T_c^* derived from the temperature dependence of the normalized zero-bias conductance $G(0)$ on various HgPb–1234 single crystal surfaces. The dashed line is a least-squares fit to the data.