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Temperature-dependent changes in the structure of high-quality polycrystalline $Bi_2Sr_2CaCu_2O_{8+x}$ material

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Refinement of neutron powder diffraction patterns from high-quality polycrystalline $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) material has revealed a number of temperature-dependent structural changes coinciding with changes in the measured physical properties. Changes in the **b**-axis lattice parameter and in the period of the incommensurate structural modulation at 160 K coincide with a sharp internal friction peak measured by an acoustic composite bar technique. Further, these changes should have an effect on angle-resolved photoemission studies and may provide an alternative explanation for recent results which cite a pseudogap explanation. Below 40 K, the changes correlate with single-crystal neutron-depolarization measurements which show that flux pinning appears. These results also seem to indicate a differential expansion between the $BiSrO_3$ rocksalt sublattice and the $CaCu_2O_3$ perovskite-like sublattice over a broad temperature range. We suggest that the cause of the observed modulation in the Bi-2212 structure is not due to extra oxygen atoms binding onto the Bi atoms but is more likely simply the mismatch of the two sublattices. [S0163-1829(97)07921-6]

INTRODUCTION

After Maeda[1] discovered the bismuth-based high-temperature superconducting family of materials, a great deal of effort has been devoted to determining the exact crystallographic structure of these ceramic compounds, and, in particular, the compound $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212). Unfortunately, a great deal of the published work has been based on data from inferior quality material, leading to a number of controversies.

There are three main areas of interest in the crystallographic structure of Bi-2212: (1) the average structure, (2) the cause of the observed structural modulation, and (3) the oxygen positions and their role in (1) and (2) above. This paper is concerned directly with the second point but has implications in terms of the other two.

Using electron-diffraction, x-ray-diffraction, and neutron powder diffraction techniques, many workers[2–10] have determined that the average structure of Bi-2212 is layered Bi-O, Sr-O, and Cu-O sheets separated with Ca and that these layers are distorted by an incommensurate modulation. There is also evidence for inherent instability in the growth of this material and difficulty in obtaining single-phase material, e.g., Fung *et al.*,[11] who saw antiphase domains in the **a** and **b** directions.

Yamamoto *et al.*[12] and Gao *et al.*[13] performed a full four-dimensional analysis using both neutron powder diffraction and single-crystal x-ray diffraction to determine the presently accepted average crystal structure and amplitudes of the modulation based on a model with the four-dimensional space group $N\ Bbmb/\mathbf{111}$ or noncentrosymmetric equivalent $N\ Bb2b/\mathbf{111}$. Here, a scattering vector **Q** for a reflection is defined by

$$\mathbf{Q}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q}^*,$$

where $\mathbf{q}^*\sim 0.21\mathbf{b}^*$ is the wave vector of the modulation representing a periodic distortion over ~4.75 unit cells and m is the index of satellite reflections. Structure factor calculations include the extra information of a modulation wave expressed as a sum of harmonic components, **U** being the sum of sine and cosine terms representing the phase and amplitude of the modulation for each atom.

Zanderbergen *et al.*[14] proposed a number of models for the cause of the structural modulation and attempted to use these models to interpret their experimental x-ray-diffraction results. These models proposed that the modulation was caused by (1) extra oxygen, (2) strontium vacancies, (3) partial substitution Bi by Cu and Sr by Bi, (4) change in the orientation of the Bi lone pairs, and (5) a combination of (1) and (3). They concluded that the most likely model was (5) ruling out the possibility of a mismatch of the Bi-O layer with the perovskite Cu-O layers as this would imply that the Tl-2212 compounds should have a larger modulation due to the ionic radius of Tl being smaller than that of Bi. However, Le Page *et al.*[15] proposed that extra oxygen causes the modulation based on isostructural work with $Bi_{10}Sr_{10}Fe_{10}O_{66}$, which has a commensurate modulation of 5 times the unit

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cell compared with ~4.75 for the incommensurate Bi-2212 structure. Goodman *et al.*,[16] Zhang and Sato,[17] Levin *et al.*,[18] and Walker *et al.*[19] also concluded that extra oxygen is the cause of the modulation. Finally, Calestani *et al.*[20] analyzed their single-crystal x-ray-diffraction data using a large commensurate unit-cell approximation (5 times the **b** axis) for the modulated cell and a $Pnnn$ space group to refine the structure. Even though there were large cross correlations in the refined parameters, the r factor of 7.1% suggested a reliable model. They did not find extra oxygen and concluded that the cause of the modulation was a mismatch between the perovskite block and the stereochemical requirements of the Bi in the Bi-O layers.

One way to distinguish between these two models, for the cause of the modulation, is to look at the modulation period as a function of temperature. If the modulation is caused by oxygen substitution, the period should remain relatively constant over a wide range of temperatures as the oxygen atoms are at fixed positions in the sublattice and thus do not allow the period of modulation to change even while the lattice is expanding or contracting. Alternatively, if it is caused by a mismatch between the inherent lattice spacing of the Cu-O perovskite block and the Bi-O layers then there could be a difference in the lattice expansion characteristics of the two interpenetrating lattices. This alternative would show up as a change in the period of the modulation as a function of temperature as the period of the modulation is not fixed at sites along the lattice. This change could appear as fluctuations in the lattice parameter characteristics such as discontinuous jumps in the modulation period which would occur as the differential lattice expansion causes atoms in the lattice to move from energetically unfavorable positions.

Takenaka *et al.*[21] were one of the first groups to look for a correlation between the lattice structure and T_c using a single-crystal x-ray-diffraction data. They found no significant anomalous features over the temperature range 10–300 K and concluded that the superstructure or modulation is not directly associated with superconductivity. Yang *et al.*[22] also using single-crystal x-ray-diffraction data saw a small kink at T_c in the length of the **c** axis but not in the **a** and **b** axes. They also observed a negative thermal expansion coefficient below 50 K for all the axis parameters and an aging effect on recycling to low temperatures. However, their results were not interpreted in terms of superconducting properties. Johnson *et al.*[23] undertook a study of the temperature dependence of x-ray diffraction from a single crystal with particular emphasis on the region around the *(0 0 20)* reflection, in order to confirm another study[24] which showed a crystallographic structural change around T_c. Their study showed no lattice constant or reflection intensity anomalies at T_c but they noted that the **b**-axis satellite intensities did show some unexplained thermal dependence below T_c. Shi *et al.*[25] saw splitting of the **a**- and **b**-axis parameters on a twinned crystal for two narrow temperature ranges around 156 and 220 K in a study over the range 77–300 K using x-ray diffraction. They concluded that this structural transformation confirms observations of internal friction and positron annihilation. They claim also to have observed a broadening of the *(0 4 0)* peak at 91 K indicating a structural change at T_c, but no quantitative analysis was undertaken.

We are able to further extend our knowledge in relation to the controversies surrounding the inherent crystallographic structural properties of this material given that we have access to high-quality Bi-2212 material[26–29] of both large single crystalline and polycrystalline nature and that we have undertaken neutron-diffraction studies. We consider the uncertainties to arise mostly from using samples of lower quality indicated by extra phases in published powder pattern fits, high Rw in refinements and diffuse features around main diffraction peaks, and from processing variations. Our high-quality samples confirm that the average structure is identical to that previously determined by the majority of authors.[30] We have then undertaken a temperature-dependent study using neutron powder diffraction to try to resolve the cause of the crystallographic structural modulation in Bi-2212 and to correlate possible linkages between the structural changes and the superconducting characteristics of the Bi-2212 material.

EXPERIMENT

The Bi-2212 samples were cleaved from polycrystalline ''as-grown'' rods which had been prepared by the floating zone method (Gu *et al.*[26]) and lightly powdered to minimize defects. The cleaved samples were similar to those used by Anderson *et al.*[31] in their acoustic vibration studies. The superconducting transition temperature of the samples was found to have a 91-K onset with a sharp 2-K width. Single-crystal neutron-diffraction measurements from crystals cleaved from rods of the same batch showed that the material is of exceptional quality with few defects as measured by diffuse neutron scattering at forbidden reflection positions determined from the $N\ \ Bbmb/\mathbf{\bar{1}11}$ space group.[27–29]

The powdered sample was measured at the HIFAR facility at Lucas Heights (Australia) using the MRPD neutron diffractometer. Temperature measurements were obtained by placing the sample in a Heliplex cryorefrigerator which was set at various temperatures with an error of ±1 K between 10 and 320 K. Powder diffraction patterns were taken at a wavelength 1.3179(1) Å at intervals of 0.1° for the 2θ range 4–102°. The combination of acicular and platelike shapes of the crystallites resulted in a strong preferred orientation in the powdered sample. To minimize the effects of this preferred orientation the sample was rotated through 180° in ω for each step in 2θ.

The temperature measurements were repeated to ensure reproducibility of the data and detect any irreversible changes.

The analysis was performed using a modified Rietveld analysis program written by Yamamoto *et al.*[12] which includes the structure factor calculations from the modulated atom positions (as discussed above) and periodic vacancies or inclusions. Instrument parameters such as neutron wavelength and peak widths were determined by refinement of the data from a standard rutile (Ti-O) sample, and were not varied in the refinement. Up to 60 refinement parameters were allowed to vary including atom positions, first- and second-order atom modulation displacements, and isotropic thermal parameters. In particular, the lattice parameters **a**, **b**, and **c** as well as the modulation vector **q*** were refined along with an estimate of their respective errors.

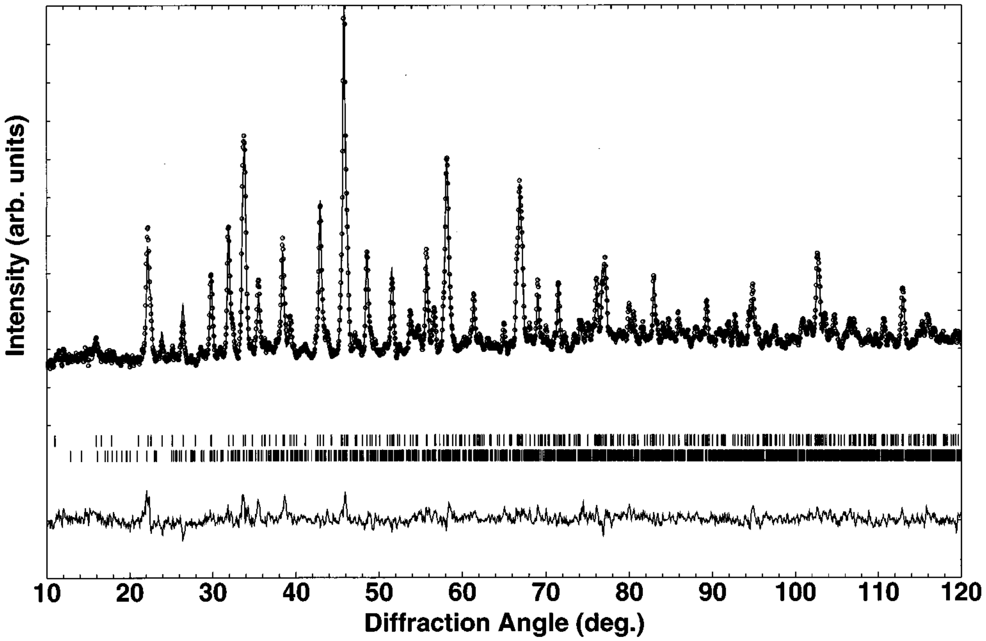

FIG. 1. An example of the fit of the data using four-dimensional Rietveld refinement as a function of 2θ. The data (+) and refined fit (solid line) are on top with the difference between the data and fit below. The vertical markers indicate the positions of the main reflections, first- and second-order satellites, respectively.

RESULTS AND DISCUSSION

Figure 1 is an example after analysis of the observed and calculated intensities and has a weighted R value (R_w) $=4.5\%$, which is typical of the refinements performed at each temperature. This R factor obtained is similar to that obtained for the standard rutile (Ti-O_2) sample under the same conditions in line with the resolution of the instrument. First- and second-order satellites were included in the refinement and the results are consistent with analysis of single-crystal neutron-diffraction data which were collected at room temperature. The positions of the main reflections and of first- and second-order satellite reflections are indicated separately by vertical bars below the difference plot.

Figure 2(a) shows the results for the **a**-axis lattice parameter variation as a function of temperature. This curve is consistent with the work of Yang *et al.*[22] The most significant features are the broad minima in the lattice parameter observed below ~90 K and around 220 K.

Figure 2(b) shows the **c**-axis lattice parameter variation, again the curve is consistent with the work of Yang *et al.*[22] with a broad minimum below ~50 K. A small discontinuity at the temperature of 160 K is also evident. A similar point is also evident in Yang's data but not commented upon.

Figure 2(c) shows the **b**-axis lattice parameter variation with temperature. There is a pronounced dip at 160 K which is consistent with the acoustic measurements of Anderson *et al.* [31] Further, a broader thermal history-dependent change was observed between 220 and 260 K for this axis. This latter observation seems to indicate a slow diffusion of oxygen atoms and is also consistent with the acoustic data where sample and thermal history dependence play an important role in any measurements in this temperature region.

Figure 3 shows a plot of the modulation period, in numbers of unit cells, along the **b** axis. This a real-space representation of the reciprocal space modulation vector $\mathbf{q}^* \cong 0{,}21\mathbf{b}^*$. There is a pronounced peak in the modulation at the 160 K structural change as well as minima at ~220 K and $\sim T_c$. The temperature of the dip at 220 K was found to vary with thermal history from between 220 and 260 K. This variation is consistent with reports of a broad feature seen in acoustic studies,[31] or, in some cases, a dip found in resistivity measurements,[32] and which can be ascribed to structural adjustments. Another interesting feature of the data is the change in slope at ~40 K where we have identified a sharp change in the flux lattice relaxation rates using neutron depolarization.[33] The flux lattice is found to change from a three-dimensional ''solid'' to a ''viscous liquid'' at 40 K in applied magnetic fields greater than 600 Oe.[34] As well, the structural changes associated with the b axis and modulation period for temperatures in the range $\widetilde{T}_c < T < 200$ could provide an alternative explanation for recently reported results from angle-resolved photoemission studies (ARPES) by Ding *et al.*[35] where it is claimed that a pseudogap exists.

In a recent study Kambe *et al.*[36] compared the valence of the Bi ions, extra oxygen and the modulation period at room temperature in an attempt to understand the cause of the modulation. They did this by substituting Pb for Bi, La for Sr, and Y for Ca. This indirectly changes the oxygen content and the Bi valence by changing the valence of the cations, rather than directly varying the oxygen by annealing at high temperatures. They observed an affect on the modulation period and related it to the oxygen content, thus concluding that the modulation was caused by the insertion of extra oxygen atoms in the Bi-O lattice. However, by changing the perovskite layer with the insertion of yttrium, and the rocksalt layer with insertion of Pb and La they were also varying the inherent relative lattice parameters of these two layers and thus affecting the mismatch between these two sublattices. Their dismissal of the mismatch between these layers as a

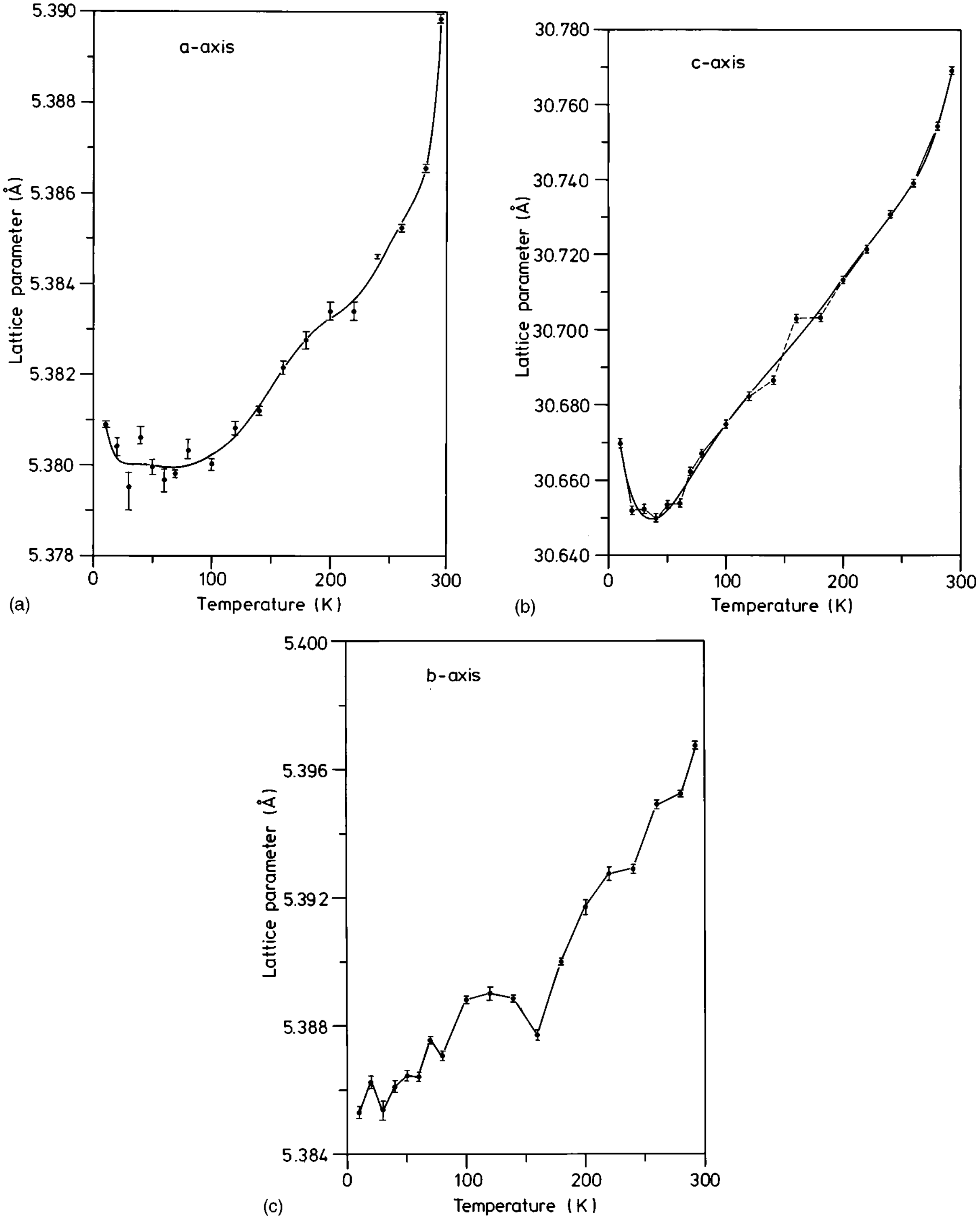

FIG. 2. Variation of the **a**-, **b**-, and **c**-axis lattice parameters as a function of temperature. The **a**-axis and **c**-axis lattice parameters show a broad minimum around 50 K. The **b**-axis lattice parameter shows a sharp minimum at 160 K in agreement with acoustic measurements.

possible cause of the modulation is open to question.

Our samples are oxygen deficient ($x \cong 0.0$) with a T_c of 91 K, whereas most other reports studying this structure have used oxygen excess samples ($x \sim 0.2$) with a T_c of ~84 K. As both sets of samples have a period of ~4.75**b**, we submit that the extra oxygen cannot be the cause of the modulation. In the results of Kambe *et al.*, where the modulation period was determined by looking at one peak rather than refinement of a large number of peaks as in our case, they saw a rough linear correlation between the modulation vector and oxygen content. Our results do not confirm this correlation.

The mismatch between the Bi-O rocksalt lattice and the Cu-O perovskite lattice can be readily seen in the paper by Shi *et al.*[25] where they show splitting of the *(400)/(040)* reflection from a poor sample with structural changes evident at temperatures ~220 and 156 K in a 2θ scan.

This mismatch between the Bi-O and Cu-O sublattices causes the Bi-O layers to buckle up in order to relieve the

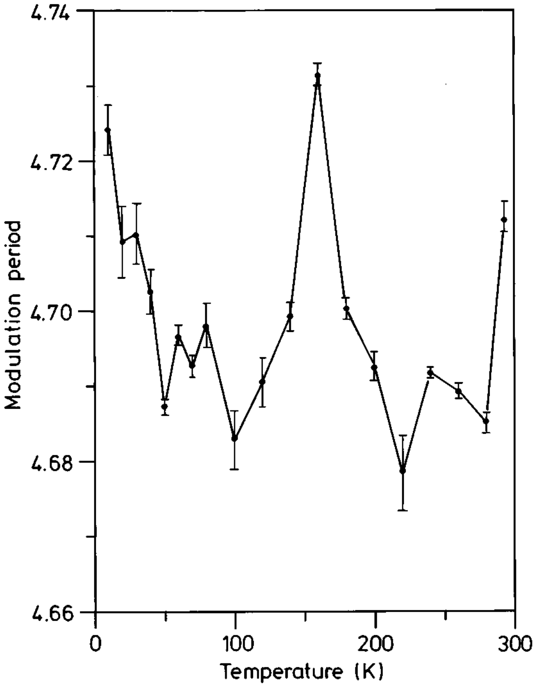

FIG. 3. The refined incommensurate modulation period along the **b** axis as a function of temperature. A pronounced peak is clear at 160 K in agreement with acoustic measurements as well as minima at ~220 K and ~100 K. There is also a change of slope below 40 K.

stress. As a consequence, defects occur which may be partially filled with extra oxygen. As the temperature changes, the differential expansion causes the mismatch to change the period slightly, especially where the defects have not been filled with extra oxygen. This explains our results with the structural changes being inherent with the mismatch changes which show up as changes in the modulation period.

This interpretation also explains most of the sample-dependent results that have been previously reported in the literature. With excess oxygen, especially after annealing, the periodic defects caused by the mismatch are filled with oxygen. This produces extra stresses on the lattice and the system then relies on oxygen diffusion to relieve this stress and return to equilibrium. This results in sample and thermal history-dependent data, especially for acoustic measurements. The as-grown, oxygen-deficient samples are more able to relieve stress with a change in the modulation period as the temperature changes, which results from mismatch changes (between the layers) due to differential thermal expansion of the Bi-O and Cu-O sublattices.

CONCLUSION

We have used neutron powder diffraction to investigate temperature-dependent changes in the modulation in the Bi-2212 system. We have found anomalies at certain temperatures where subtle structural changes occur especially at 160 K and between 220 and 260 K, coinciding with acoustic observations, the pseudogap region above T_c found in ARPES, and a $\leqslant$40 K, coinciding with polarized neutron measurements of the reversibility line in similar material at low fields. We also consider that this evidence points towards a possible model for the cause of the modulation that involves a mismatch between the Bi-O and Cu-O sublattices.

Further work[30] is being undertaken on changes in atom positions as a function of temperature and the structural changes detected will be reported.

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