

Pressure-induced self-insertion reaction in CoSb₃

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The thermoelectric material CoSb₃, with skutterudite structure, was subjected to high pressures using a diamond anvil cell up to 40 GPa. Above 20 GPa this compound undergoes an irreversible isosymmetric transition to a phase that, upon pressure release, exhibits a volume greater than that of pristine CoSb₃. Experimental evidences are shown that allow us to interpret this anomalous behavior as a kind of pressure-induced insertion reaction.

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Filled skutterudite compounds have been considered as potential candidates for thermoelectric applications.¹⁻⁴ These cubic compounds (space group $Im\bar{3}$) have a general formula $\square MX_3$, where M is a d -group metal (e.g., Co, Fe, Ir, Rh, occupying site $8c$) and $X=P$, As, or Sb (site $24g$). The symbol \square represents a vacancy (site $2a$, situated in a cage formed by the atoms in the $8c$ and $24g$ sites—see Fig. 1), which can be empty (as in the binary skutterudites) or partially occupied by rare-earth ions and other electropositive elements such as Na, K, or Ba. Rare-earth filled skutterudites are a physical realization of the *electron crystal and phonon glass concept*.^{1,5} In fact, the rare-earth ions inside the oversized cages in the skutterudite framework rattle around the equilibrium positions, incoherently scattering phonons and thus reducing the lattice thermal conductivity of the filled skutterudites. Owing to this reduced thermal conductivity, the thermoelectric figure-of-merit (ZT) for filled skutterudites such as LaFe₃CoSb₁₂ reaches values near one, for temperatures around 800 K.⁶ It has been argued that a ZT of about 3 would be necessary in order to make thermoelectric refrigeration competitive with today's technology.^{7,8} Nowadays, semiconductor nanostructures and thin-film superlattices with ZT \approx 2 at room temperature are state-of-art thermoelectric materials.⁸⁻¹⁰

Because of their relatively open structures, skutterudite compounds are expected to exhibit interesting behavior under high pressure. Despite that, the literature on the high pressure phase stability of skutterudite compounds is relatively scarce.¹¹⁻¹³ In a previous work we have determined the isothermal equations of state for two skutterudites, namely CoSb₃ and LaFe₃CoSb₁₂.¹¹ No phase transition was observed for CoSb₃ and LaFe₃CoSb₁₂ up to 20 GPa and also for IrSb₃ up to 42 GPa.¹¹⁻¹³ The general conclusion from these earlier studies is that, despite their open structures, the binary skutterudites are quite stable under high pressure. However, in this paper, we will show that above 20 GPa cobalt antimonide undergoes an irreversible transition to another phase, isosymmetric to CoSb₃, with a volume at ambient pressure greater than that of pristine CoSb₃. A similar result was obtained with samples submitted simultaneously to high pressure and high temperatures. This anomalous behavior, to the best of our knowledge never observed before, can be interpreted as a pressure-induced self-insertion reaction of cobalt

antimonide, in which antimony atoms from the compound framework partially fill the $2a$ site.

The sample of CoSb₃ used in this work was prepared according to the synthesis procedure described in detail by Sales *et al.*⁵ The x-ray powder diffraction pattern of the synthesis product revealed no contaminant phase. Pristine CoSb₃ is also compositionally homogeneous, as could be verified by energy-dispersive electron microprobe analysis. The lattice parameter at room pressure [$a_0=9.036(5)$ Å] compares well with the values reported in literature.¹⁴ A series of high pressure energy dispersive x-ray diffraction spectra (EDXRD) was obtained in the pressure range up to 40 GPa using a diamond anvil cell (DAC).¹⁵ The samples of CoSb₃ were contained into a 250 μ m diameter hole drilled in a tungsten gasket, along with a small ruby chip as a pressure gauge.¹⁶ We have used a mixture of methanol-ethanol-water (16:3:1) as pressure transmitting medium. Energy dispersive x-ray diffraction (EDXRD) experiments were performed with an intrinsic germanium detector, fixed at $2\theta=14^\circ$ ($E_d=50.87$ keV Å), using radiation from a tungsten x-ray tube operating at 45 kV and 20 mA. Peak positions in the ruby fluorescence and in the EDXRD spectra were determined by fitting Gaussian profiles to the peaks using the XRDA program.¹⁷ Some representative EDXRD spectra are shown in Fig. 2. No appreciable change in the EDXRD spectra that could suggest any departure from cubic symmetry was observed within this pressure range. Figure 3 shows the relative volume of cobalt antimonide *versus* pressure, obtained from several high pressure experiments carried out with different samples, both at increasing and decreasing pressures. As previously reported,¹¹ nothing unusual was observed while the maximum pressure remained below 20 GPa. A fitting of the Birch-Murnaghan equation-of-state (BM-EOS) to the data shown in Fig. 3 up to 20 GPa yields a bulk modulus at zero pressure $B_0=93(6)$ GPa and a bulk modulus pressure derivative $B'_0=5(1)$, in good agreement with previous results.^{11,12} Above 20 GPa, upon increasing pressure, the volume reduction with pressure becomes less pronounced, perhaps due to the increasingly nonhydrostaticity of the pressure medium, and the fitting of a single BM-EOS to the whole data set yields unreasonable results [$B_0=50(16)$ GPa and $B'_0=23(10)$]. It is noteworthy that, upon pressure release from above 20 GPa, a hysteresis was observed in which the unit

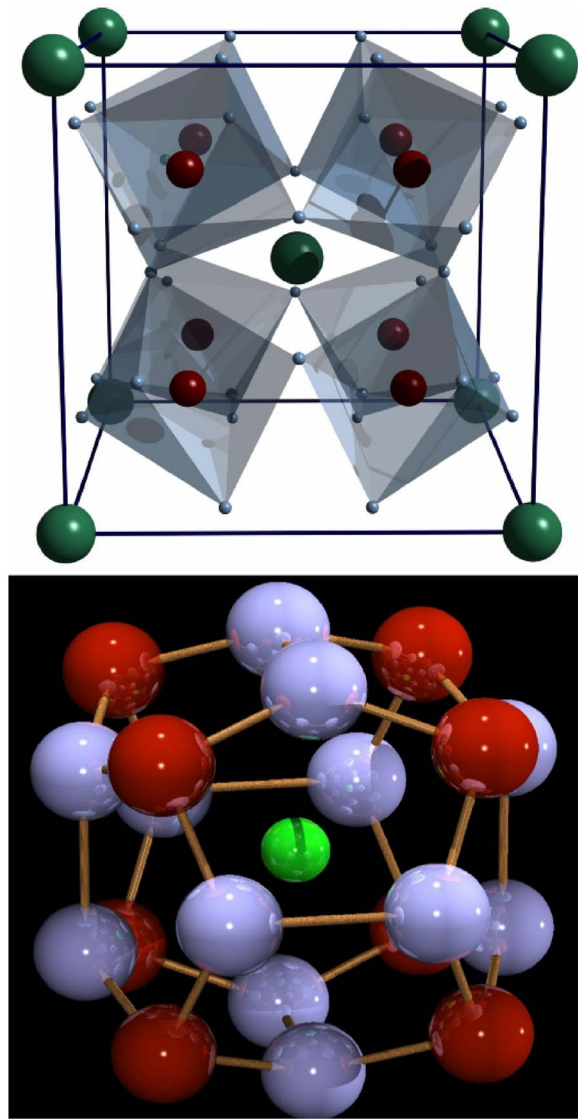


FIG. 1. (Color online) Schematic representation of the CoSb_3 crystal structure, showing the tridimensional arrangement of CoSb_6 octahedra (above) and the cage formed by the Co and Sb atoms around the $2a$ site (below). Cobalt, antimony, and the vacancy at the $2a$ site are represented by red, blue, and green spheres, respectively.

cell volume becomes greater than that observed at increasing pressure. This effect is irreversible, and the sample recovered at room conditions exhibits a volume about 2.5% greater than that of pristine CoSb_3 .

A small portion of cobalt antimonide previously submitted to 35 GPa in the DAC was taken for an *ex situ* analysis by angle-dispersive x-ray diffraction in the XDP beamline at D10B in the Laboratório Nacional de Luz Síncrotron (LNLS) (Campinas, Brazil).¹⁸ In this experiment, synchrotron radiation was monochromatized by a double-bounce Si(111) monochromator. The sample, mounted on the tip of a capillary tube, was attached to a goniometer head with four adjustable axes on a Huber 4+2 circle diffractometer. The wavelength [$\lambda=1.3791(5)$ Å] was determined from the analysis of the Bragg peaks from a sample of silicon standard (NIST SRM640c). Due to the very small amount of

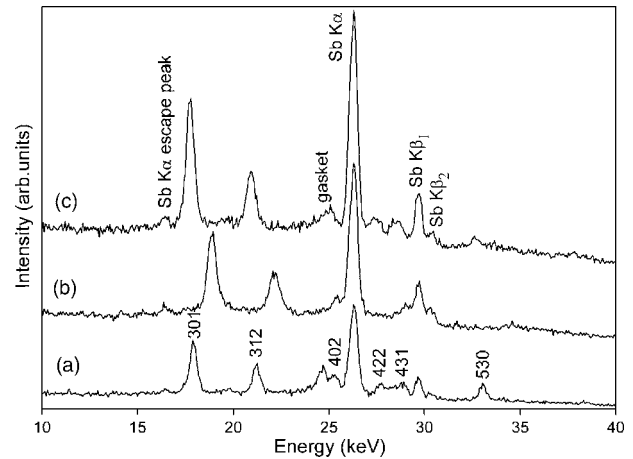


FIG. 2. Some representative energy-dispersive x-ray diffraction spectra of CoSb_3 in a DAC at (a) 2.7(1) GPa, (b) 39.7(3) GPa, and (c) 1.8(1) GPa (this last at decreasing pressure). The Miller index of the Bragg peaks and other major features are labeled in the spectra.

sample available for analysis, a (002) highly oriented pyrolytic graphite analyzer was employed to have a better signal-to-noise ratio. Even so, only the profile of the three more intense peaks could be measured within the available beam time. As can be seen in Fig. 4, the 310, 312, and 420 (not shown) peak profiles indicate that this sample actually has two phases. From the peak positions and assuming cubic symmetry, the lattice parameter of the phase with small width Bragg peaks [$a_0=9.033(2)$ Å] is the same as CoSb_3 pristine, while the second phase has $a_0=9.062(2)$ Å. From now on we will refer to the high pressure phase of cobalt antimonide as CoSb_3^* .

Pressure-induced volume increase has been previously

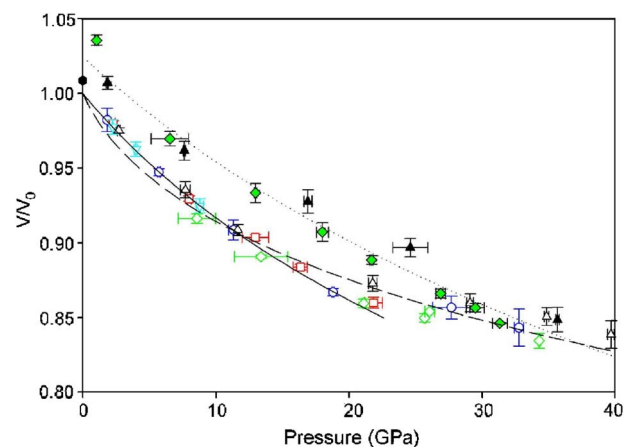


FIG. 3. (Color online) Pressure dependence of the relative volume for cobalt antimonide. Open and solid symbols refer to increasing and decreasing pressure runs, respectively. Solid and dashed lines represent the fitting of a BM-EOS to data below 20 GPa and to the whole set of data acquired upon pressure increase, respectively. The dotted line is plotted to guide the eye through the data obtained upon decreasing pressure from above 20 GPa. The solid hexagon at $P=0$ represents the relative volume of a sample previously submitted to 35 GPa, as measured at ambient conditions in the LNLS.

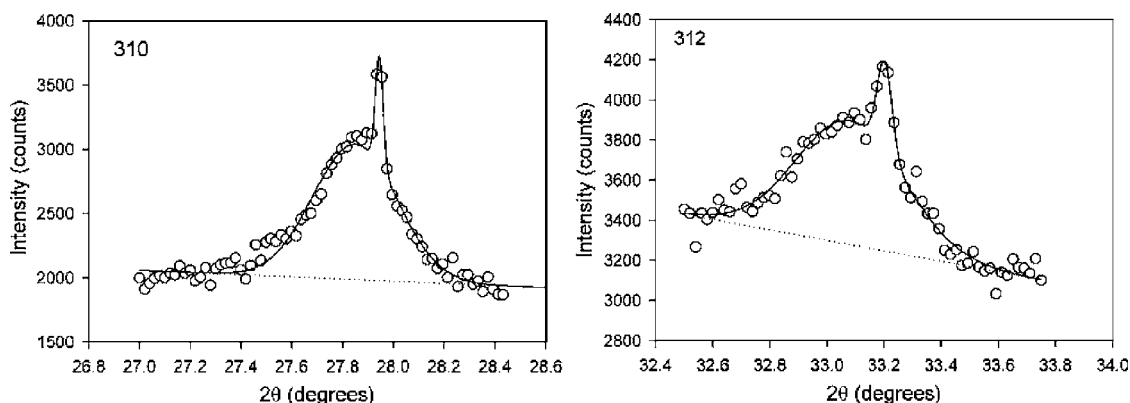


FIG. 4. Synchrotron radiation XRD profiles at room conditions of the Bragg peaks 310 and 312 for a sample of CoSb_3 previously submitted to 35 GPa in a DAC. Experimental data (open circles) and the fitted sum of two Gaussian profiles (full line) plus a linear background (dotted line).

observed as the result of the insertion of molecules from the pressure transmitting medium (see, e.g., Refs. 19–21 and references therein). As a necessary condition, the host compound should possess channels with a diameter large enough to allow the diffusion of some component from the pressure medium, and this is not the case for cobalt antimonide. However, the hypothesis of volume increase due to the insertion of a chemical species can still stand if we consider the possibility of insertion into the cages of atoms from the CoSb_3 framework itself.

Any insertion reaction involves diffusion processes and its rate can be increased at higher temperatures. Accordingly, in principle CoSb_3^* could be prepared at lower pressures and temperatures above ambient. To test this hypothesis, high pressure and high temperature experiments were conducted on a toroidal high pressure cell.^{22,23} In these experiments, a cylindrical sample of CoSb_3 (3 mm diameter and 5 mm high) was enclosed into a hexagonal boron nitride capsule to ensure *quasi*-hydrostatic conditions. Heating was provided by a graphite furnace. The pressure on the sample was calibrated against the fixed points of bismuth and ytterbium²³ and temperature was determined from the electrical power supplied to the graphite furnace, as previously calibrated against temperature as measured by a Pt-Pt 13% Rh thermocouple. Two samples of CoSb_3 were submitted to 7.7 GPa and then heated to 550 °C and 300 °C, respectively, for fifteen minutes, after which they were brought to ambient temperature and finally pressure was released. Cobalt antimonide decomposes partially at 7.7 GPa when heated to 550 °C and, to a minor proportion, at 300 °C. As can be seen in Fig. 5, the XRD pattern of the sample submitted to 7.7 GPa and 550 °C exhibits the same set of Bragg peaks as that of pristine CoSb_3 . These peaks, however, appear doubled and displaced toward lower angles [see the inset in Fig. 5(a)]. The same phenomenon observed at high pressure and room temperature in the DAC seems to be occurring also at lower pressures and higher temperatures. In fact, the set of displaced Bragg peaks shown in Fig. 5(b) was indexed in the same way as the parent cubic cobalt antimonide, yielding lattice parameters of 9.1372(3) Å and 9.0721(6) Å, both larger than that of pristine CoSb_3 . All these suggests we are observing here the same phase produced in the DAC. Fur-

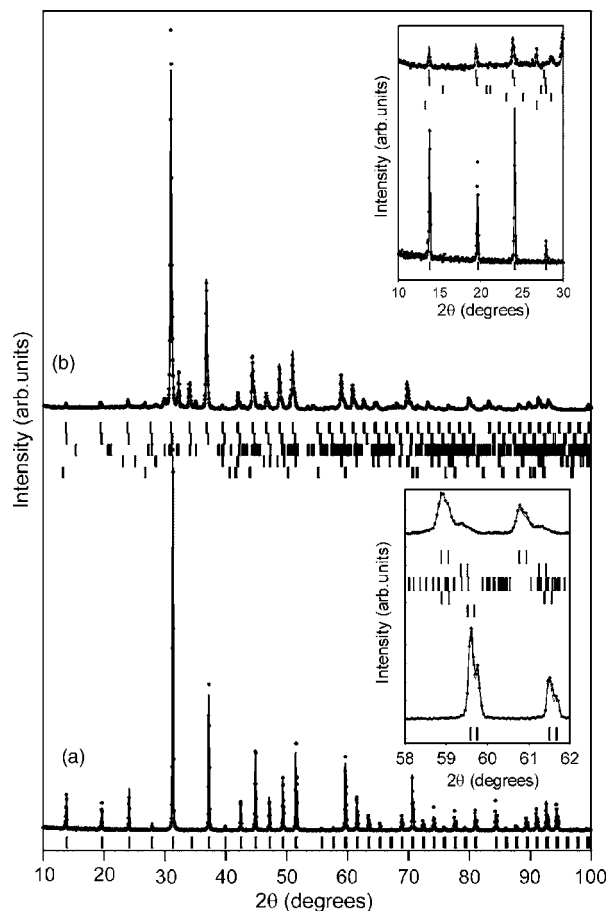


FIG. 5. X-ray powder diffraction patterns at room conditions of (a) CoSb_3 pristine and (b) CoSb_3 after pressed to 7.7 GPa and 550 °C. Dots indicate the raw data points and the solid line is the refined profile. Intensities were normalized with respect to the amplitude of the (most intense) 312 Bragg peak. The tick marks indicate the expected positions of Bragg peaks from (a) CoSb_3 and, in (b), from top to bottom, CoSb_3^* (phases 1 and 2), CoSb_2 , antimony, and hBN. The inset in (a) shows two peaks of pristine CoSb_3 (bottom) and the corresponding peaks in the pattern from the sample treated at 7.7 GPa and 550 °C, which appear doubled and displaced toward lower angles. The inset in (b) shows the intensity reduction of 110, 200, 211, and 220 Bragg peaks upon Sb insertion at high pressure and high temperature.

thermore, the Rietveld analysis of the XRD powder pattern shown in Fig. 5(b) reveals that this pattern can be modeled with two phases isosymmetric to CoSb_3 (plus CoSb_2 , antimony, and a small contamination of hexagonal boron nitride, hBN).^{24,25} In other words, the transition $\text{CoSb}_3 \rightarrow \text{CoSb}_3^*$ does not lead to any observable lowering of symmetry and thus there is no ambiguity in the indexing of the peaks in the high pressure EDXRD spectra and, consequently, in the calculation of the unit cell volume.

One possible mechanism behind the irreversible pressure-induced volume increase of CoSb_3 involves a two step process: Decomposition of cobalt antimonide according to $\text{CoSb}_3 \rightarrow \text{CoSb}_2 + \text{Sb}$, followed by diffusion and insertion of antimony into a nearby cage, $\text{CoSb}_3 + \text{Sb} \rightarrow \text{CoSb}_3^*$. In fact, CoSb_2 is observed in the XRD patterns shown in Fig. 5. However, the proportion of CoSb_2 to CoSb_3^* in the samples processed at 550 °C and 300 °C is very different, effectively ruling out this decomposition/insertion mechanism. Furthermore, no sign of the most intense peak of CoSb_2 could be found in the XRD analysis conducted in the LNLS with the sample of CoSb_3 previously processed at 35 GPa and room temperature.

We thus propose that all experimental findings reported in this paper can be interpreted in terms of a pressure-induced insertion reaction. According to this, above 20 GPa, at room temperature (and at lower pressures and higher temperatures), some atom of the skutterudite framework (most probably antimony) collapses into the cage, occupying the $2a$ site. Hence the CoSb_3^* phase formed at high pressures can be identified as $\text{Sb}_x\text{CoSb}_{3-x}$, with $x \leq 0.25$. Besides the increase of the unit cell volume, the striking reduction of the intensity of 110, 200, 211, and 220 Bragg peaks, shown in the inset in Fig. 5(b), also gives support to the hypothesis of pressure-induced insertion of antimony. In fact, under the assumption that CoSb_3^* is isosymmetric to CoSb_3 , there is no alternative way to explain this intensity reduction but to assume that some atom (and, particularly, antimony) partially occupies

the $2a$ site in the CoSb_3^* structure.²⁶ The greater volume of the phase recovered upon pressure release should be the result of the chemical pressure exerted by the antimony inserted into the cages of the skutterudite framework. The calculated density for the sample recovered from 7.7 GPa and 550 °C, 7.64 g cm^{-3} (estimated by supposing that the high pressure phase of CoSb_3 is actually $\text{Sb}_x\text{CoSb}_{3-x}$, and taking into account the sample's composition as determined by Rietveld analysis of the x-ray powder diffraction pattern), agrees very well with the experimental value of $7.6(2) \text{ g cm}^{-3}$, thus giving further support to the hypothesis of pressure-induced insertion reaction. Despite the lack of the same direct experimental evidence of antimony insertion, it seems reasonable to admit we are observing essentially the same phenomenon in the experiments carried out in a DAC.

The analysis of data shown in Fig. 3 suggests that the transition $\text{CoSb}_3 \rightarrow \text{Sb}_x\text{CoSb}_{3-x}$ takes place with no volume discontinuity. The increase of entropy following partial occupancy of the $2a$ site (concomitant with the creation of vacancies in the CoSb_3 framework) should be part of the driven force behind this transition. $\text{Sb}_x\text{CoSb}_{3-x}$ remains metastable at ambient pressure and converts back (exothermically) to CoSb_3 by heating to 250 °C.

To conclude, taken as a whole, the experimental findings reported in this paper give support to the conclusion that cobalt antimonide exhibits a self-insertion reaction at elevated pressures. A more detailed description of the microscopic mechanism behind this transition, as well as the effects of such insertion reaction on the transport properties of cobalt antimonide, should be subjects of further studies.

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¹G. S. Nolas, D. T. Morelli, and T. M. Tritt, *Annu. Rev. Mater. Sci.* **29**, 89 (1999).

²G. P. Meisner, D. T. Morelli, S. Hu, J. Yang, and C. Uher, *Phys. Rev. Lett.* **80**, 3551 (1998).

³G. Chen, M. S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial, and T. Caillat, *Int. Mater. Rev.* **48**, 45 (2003).

⁴G. D. Mahan, *Solid State Phys.* **51**, 81 (1998).

⁵B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, *Phys. Rev. B* **56**, 15081 (1997).

⁶B. C. Sales, D. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).

⁷F. J. DiSalvo, *Science* **285**, 703 (1999).

⁸A. Majumdar, *Science* **303**, 777 (2004).

⁹K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, and M. G. Kanatzidis, *Science* **303**, 818 (2004).

¹⁰R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn,

Nature (London) **413**, 597 (2001).

¹¹A. C. Kraemer, C. A. Perottoni, and J. A. H. da Jornada, *Solid State Commun.* **133**, 173 (2005).

¹²I. Shirovani, T. Noro, J. Hayashi, C. Sekine, R. Giri, and T. Kikegawa, *J. Phys.: Condens. Matter* **16**, 7853 (2004).

¹³T. S. Snider, J. V. Badding, S. B. Schujman, and G. A. Slack, *Chem. Mater.* **12**, 697 (2000).

¹⁴T. Schmidt, G. Kliche, and H. D. Lutz, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **43**, 1678 (1987).

¹⁵G. J. Piermarini and S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975).

¹⁶G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).

¹⁷S. Desgreniers and K. Lagarec, *J. Appl. Crystallogr.* **27**, 432 (1994).

¹⁸F. F. Ferreira, E. Granado, W. Carvalho, Jr., S. W. Kycia, D. Bruno, and R. Droppa, Jr., *J. Synchrotron Radiat.* **13**, 46 (2006).

¹⁹R. M. Hazen and L. W. Finger, *J. Appl. Phys.* **56**, 1838 (1984).

²⁰C. A. Perottoni and J. A. H. da Jornada, *Phys. Rev. Lett.* **78**, 2991

- (1997).
- ²¹P. W. Barnes, P. M. Woodward, Y. Lee, T. Vogt, and J. A. Hriljac, *J. Am. Chem. Soc.* **125**, 4572 (2003).
- ²²L. G. Khvostantsev, *High Temp. - High Press.* **16**, 165 (1984).
- ²³W. F. Sherman and A. A. Stadtmuller, *Experimental Techniques in High-Pressure Research* (Wiley, London, 1987).
- ²⁴Rietveld analysis was performed with the Fullprof suite (Ref. 25).
The x-ray powder diffraction data were acquired using Cu $K\alpha$ radiation on a Siemens D500 diffractometer. Peak intensities were corrected for the presence of a graphite monochromator in the secondary beam. The step size was 0.05° and counting time was 2 s per step. The number of refined parameters for the pristine CoSb_3 powder pattern (single phase) and for the sample of CoSb_3 processed at 7.7 GPa and 550°C (five phases) were 13 and 36, respectively. The resulting χ^2 for the refined powder patterns were 2.35 and 4.64, respectively.
- ²⁵J. Rodriguez-Carvajal, in *Abstracts, Satellite Meeting on Powder Diffraction, XVth Conference of the International Union of Crystallography*, Toulouse, France, 1990 (unpublished), p. 127.
- ²⁶With a structural model based on $\text{Sb}_x\text{CoSb}_{3-x}$, the Rietveld analysis of the XRD powder pattern of the sample processed at 7.7 GPa and 550°C gives $x=0.16(1)$ and $x=0.06(1)$ for the phases with lattice parameters equal to $9.1372(3)\text{ \AA}$ and $9.0721(6)\text{ \AA}$, respectively. For the sample processed at 7.7 GPa and 300°C , $x=0.12(1)$ and the lattice parameter is $9.1308(8)\text{ \AA}$. Owing to Vegard's law, these results allow us to estimate that $x\approx 0.04$ for the sample processed at room temperature and 35 GPa in the DAC.