PHYSICAL REVIEW B VOLUME 61, NUMBER 5 1 FEBRUARY 2000-I

Observation of the incommensurate barium-IV structure in strontium phase V

M. I. McMahon, T. Bovornratanaraks, D. R. Allan, S. A. Belmonte, and R. J. Nelmes
Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom

(Received 12 July 1999)

A previously unknown type of elemental structure has been discovered recently in barium, phase IV. The structure is composed of a ‘‘host’’ and two or more ‘‘guest’’ components made up of chains that lie in channels in the host, and form structures that are incommensurate with the host. This implies a segregation into different electronic species. The same structure has now been found in phase V of Sr above 45 GPa.

Under pressure, Sr transforms from the ambient-pressure face-centred cubic (fcc) phase, to a body-centred cubic (bcc) structure at 3.5 GPa. This phase is stable up to 24 GPa, where there is a transition to Sr-III.[1] On further compression, there are transitions to Sr-IV at 35 GPa, and to Sr-V at 46 GPa.[2] There is a long established interest in these phases of Sr and other alkaline earth metals as a manifestation of $s \rightarrow d$ electron transfer under pressure.[3]

The structure of Sr-III was initially reported to be distorted simple cubic[2] and then, more recently, orthorhombic (spacegroup *Imma*) from energy-dispersive powder diffraction data.[4] However, with two-dimensional data collected with angle-dispersive (AD) techniques, we were able to show that the *Imma* solution was misled by the presence of an as yet unidentified contaminant phase that we have also found in most of our data—though sometimes it is almost absent.[1] If the contaminant is excluded, Sr-III is found to be tetragonal, with the β-tin structure[1]—the first observation of this structure in a nongroup IV element. The structure of Sr-IV is known to be complex and has long resisted solution.[2] Sr-V also gives a complex diffraction pattern, that has been noted to be similar to that of the (also long-unsolved) structure of Ba-IV.[2]

Recently, we have found Ba-IV to have a remarkable self-hosting structure, comprising a tetragonal host with chains of guest atoms contained in channels running along the fourfold axis of the host.[5] The chain atoms form two different structures, both of which are incommensurate with the host, and one of which is disordered and gives rise to strong diffuse scattering. One of the guest structures was also found to undergo a structural phase transition without any accompanying structural change in the host structure. The reported similarities in the diffraction patterns of Ba-IV and Sr-V have led us to reexamine Sr-V, and indeed we find it to have the Ba-IV-type structure. This is thus emerging as a radically new type of elemental structure, stable over wide pressure ranges in both barium and strontium, that may be found in other elements.

The samples of Sr were small pieces cut from starting material of 99.95% purity purchased from the Aldrich Chemical Company. To prevent oxidation, the samples were cut while completely immersed in dry mineral oil. Then, still enveloped in oil, they were loaded into Diacell DXR5 and DXR6 diamond-anvil pressure cells, with a small chip of ruby for pressure measurement. The mineral oil also provided a quasi-hydrostatic pressure transmitting medium. Diffraction patterns collected after loading revealed no peaks from SrO. Data were collected to 56 GPa on station 9.1 at SRS Daresbury, and to 74 GPa on beamline ID9 at the European Synchrotron Radiation Facility (ESRF), Grenoble, using image-plate area detectors.[6,7] The incident wavelengths were 0.4654(1) Å and 0.45115 Å, at SRS and ESRF, respectively. Structural information was obtained from Rietveld refinement of the integrated profiles using the program MPROF.[8]

Diffraction peaks from Sr-V were observed on pressure increase at 49.0(7) GPa. Whereas the diffraction pattern from Sr-IV was that of a highly textured powder sample, with short arcs of intensity, the diffraction patterns from Sr-V consisted of many strong, quite sharp, spots, indicating that recrystallisation of the sample occurs at the IV-to-V transition. Similar recrystallisation effects were observed at the Ba II-to-IV transition.[5] However, attempts to grow a single crystal of Sr-V by annealing a partially recrystallised sample at 373 K for 2 h were unsuccessful, and resulted, instead, in a sample with *smoother* diffraction rings. Data were collected from several other samples that gave the same diffraction peaks, but this annealed, smoothed, sample was used for structure refinement.

Figure 1 shows the integrated diffraction profile obtained from Sr-V at 56 GPa, compared with a profile from Ba-IV at 12.9 GPa. The relative intensities and spacings of the strongest peaks in each pattern (numbered 1 to 8) are clearly very similar, as was rather less certainly apparent before.[2] In Ba-IV, these peaks all arise principally from the body-centred tetragonal (*I*) host structure. They can be interpreted the same way in Sr-V, with lattice parameters $a_I = 6.958(2)$ Å and $c_I = 3.959(2)$ Å, giving a c_I/a_I ratio of 0.569(1) compared with 0.563(1) in Ba-IV at 12.9 GPa. However, as in Ba-IV, this cell could not index all the reflections; some 15 weak reflections remained unindexed, of which the ten lowest-angle ones are marked in the inset to Fig. 1. Of these, one (labeled G) arises from the tungsten gasket, and five—those marked with asterisks—are from the unidentified contaminant phase discussed above.[1] This phase appears at the II-to-III transition, and produces very smooth diffraction rings—see Fig. 1 of Ref. 1— which are thus readily distinguishable from the textured diffraction rings of Sr-III, IV and V. The contaminant phase is unchanged at the III-IV and IV-V transitions, and the peaks marked with asterisks in Fig. 1 are the same as those marked with arrows in Fig. 3 of Ref. 1. (The strongest contaminant peak, at 10.5° in the inset to

0163-1829/2000/61(5)/3135(4)/$15.00

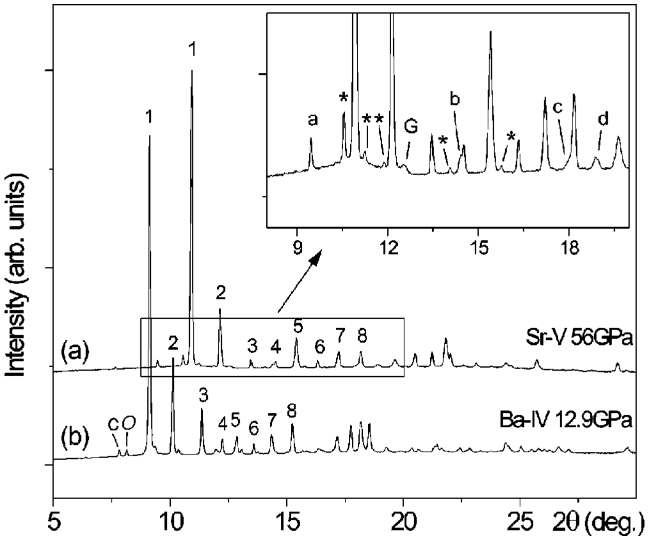

FIG. 1. Integrated 1D profiles from Sr phase V at 56 GPa and Ba phase IV at 12.9 GPa. The lowest angle *I*-lattice peaks are numbered in each profile. The inset shows an enlarged view of part of the Sr-V profile. Peaks marked with asterisks are from a contaminant phase, peak G is from the gasket, and the peaks marked a to d are from the guest component. The lowest-angle peaks from the *C* and *O* structures in Ba-IV are labeled. The first of these corresponds to peak a in the Sr-V profile.

Fig. 1, is the one that led Winzenick and Holzapfel to misassign the structure of Sr-III as orthorhombic *Imma*,[4] as already discussed.)

The remaining weak peaks unaccounted for by the *I* lattice (a, b, c, and d in Fig. 1 and others at higher angles) are clearly in the same relative positions as reflections from the *C*-face-centred tetragonal (*C*) guest phase observed in Ba-IV.[5] From the measured positions of 7 such peaks, the refined lattice parameters are $a_C=6.961(3)$ Å and $c_C=2.820(1)$ Å at 56.0 GPa. As in the case of Ba-IV, the *C* lattice is commensurate with the host *I* lattice in the ab plane, but incommensurate with it along *c*. The c_I/c_C ratio is 1.404(1), similar to the value of 1.378(1) in Ba-IV at 12.9 GPa.

The host *I* structure is shown by the dark colored symbols in Fig. 2, in a *c*-axis projection. The *C* structure formed by the (light colored) guest chains at $x,y=(0,0)$ and $(\frac{1}{2},\frac{1}{2})$ is shown in inset (i). Figure 3 shows a Rietveld refinement fit with these structures to the diffraction pattern in Fig. 1. The non-$hk0$ *I*-lattice reflections can be fitted with atoms in the $8h$ sites of spacegroup $I4/mcm$, at $x,y=x+0.5$ and $z=0$, with $x\sim0.15$. To fit the $hk0$ reflections, which include contributions from both *I* and *C* components, guest atoms were placed at (0,0,0) and $(\frac{1}{2},\frac{1}{2},0)$ with very large thermal motion along c so that they model uniform rods of density and contribute only to the $hk0$ reflections. The non-$hk0$ *C*-phase reflections were fitted as a second separate ''phase,'' the contributions of which to the $hk0$ reflections had to be deleted from the fit as they were already given by the first composite ''phase.'' The fit can be seen to be very good. There are some small displacements in peak positions of a magnitude to be expected with a solidified pressure medium at such a high pressure. Significant preferred orientation is included in the fit, in accord with the evidently strong texturing of the sample. The refined value of the *I*-structure *x* coordinate was 0.1460(2), compared with 0.1484(3) in Ba-IV at 12.9 GPa.

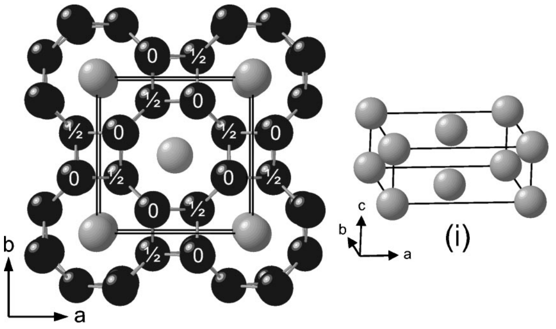

FIG. 2. Structure of Sr phase V. The host *I* structure (dark symbols) with guest chains (light symbols) is shown in a *c*-axis projection. The *I* structure atoms are labelled with their *z* coordinates. Inset (i) shows the *C* guest structure.

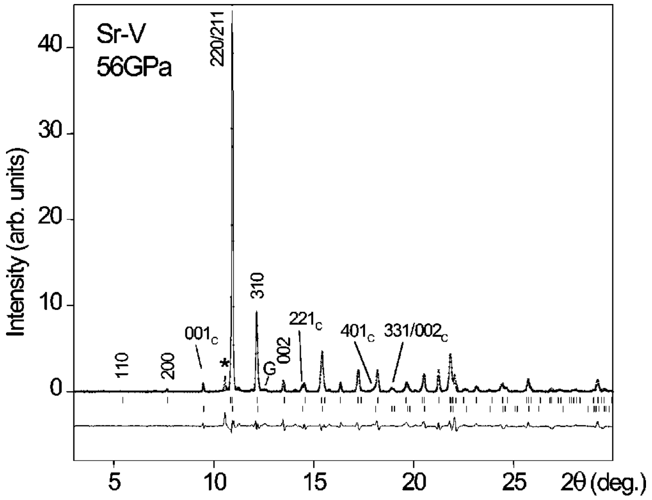

FIG. 3. Rietveld refinement of the Sr-V profile at 56 GPa. The tick marks below the profile show the peak positions from (upper set) the *I* structure with *C* rods to fit the $hk0$ reflections (see text) and (lower set) the *C* structure with its $hk0$ reflections deleted. Indices are given for the a, b, c, and d *C*-structure peaks of Fig. 1, and also the lowest-angle *I*-structure peaks. Below the tick marks is the difference between the observed and calculated profiles.

In Ba-IV, the availability of accurate single-crystal data enabled the occupancy of the guest sites to be refined as 100% within less than 1%.[5] We do not have a sample of Sr-V that is sufficiently well recrystallised to obtain single crystal data. At the same time, the strongly textured nature of the sample limits the accuracy with which the guest site occupancy can be refined from the powder data, and it can be shown to be 100% to within only ~30%. However, the great similarity to Ba-IV in atomic coordinates, c_I/c_C and c_I/a_I as well as considerations of structural stability, all strongly, suggest that the occupancy is 100%. (It is a curious feature of this type of structure that the density thus cannot be determined with complete certainty even though the lattice parameters and atomic coordinates are known.) If 100% occupancy is assumed, there are then $c_I/c_C=1.404$ guest atoms in each of the two channels in the host *I* unit cell at 56 GPa,

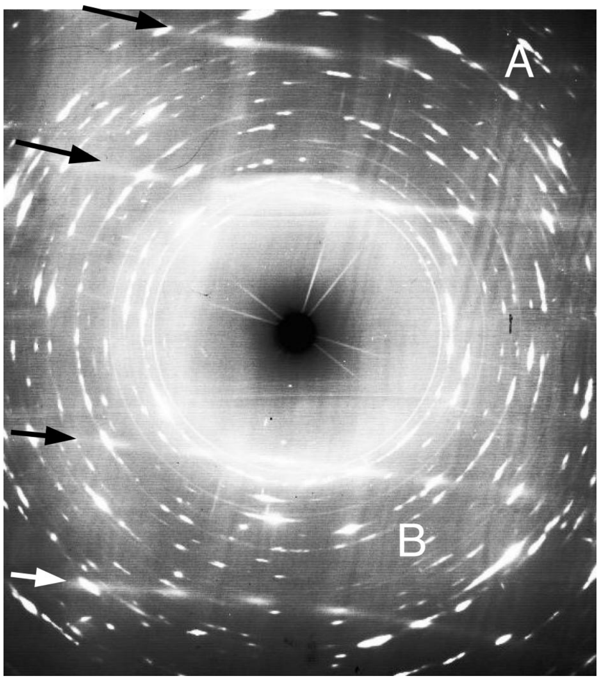

FIG. 4. 2D image from Sr-V at 70 GPa showing $l \neq 0$ lines of diffuse scattering, as marked by arrows. The streaks along the AB direction are an artefact of the image-plate reader.

and hence a total of 10.808 atoms in the volume of the *I* cell.

In Ba-IV, we identified three different guest structures *C*, as in Fig. 2(i), a monoclinic distortion of it (M), and an orthorhombic distortion of it (O). *C* and *M* coexist from 12.0 to 12.6 GPa (Ba-IVa); *M* transforms to *O* at 12.6 GPa (Ba-IVb); and there is a further transformation in the guest structure at 18 GPa (Ba-IVc)—and maybe yet further transformations occur at higher pressures beyond the range of our studies.[5] Forms IVa, IVb, and IVc all have the same $(I4/mcm)$ host structure, which can be identified in data from earlier work[9,10] across the whole range of phase IV to 45 GPa. In addition, we observed strong diffuse scattering, in at least forms IVa and IVb, that signal a degree of random positional disordering of the guest chains along the *c* axis in the *C* structure. The Sr-V diffraction patterns collected up to 56 GPa at SRS showed no evidence of either diffuse scattering or transformations in the guest structure. We therefore conducted a detailed study of Sr-V to 74 GPa at the ESRF, to obtain increased sensitivity to weak diffraction features and extend the pressure range explored. The samples were prepared and loaded as already described.

Figure 4 shows an image recorded at 70 GPa, and lines of diffuse scattering are plainly visible, revealing the presence of one larger crystallite with its *c* axis in the plane of the image. The positions of these lines correspond to sheets of diffuse scattering that are coplanar with the $hk1, hk2$, etc., reciprocal-lattice layers of the *C* component, exactly as in Ba-IV. (There is no plane of diffuse scattering for $l=0$ because the chain displacements are along *c*.) In fact, the ESRF data reveal diffuse scattering at the pressures of the SRS data, but it becomes readily visible only at much higher pressures. This may be because of increasing disorder with increasing pressure, or because the crystallite giving the diffuse scattering in Fig. 4 grew larger with increasing pressure.

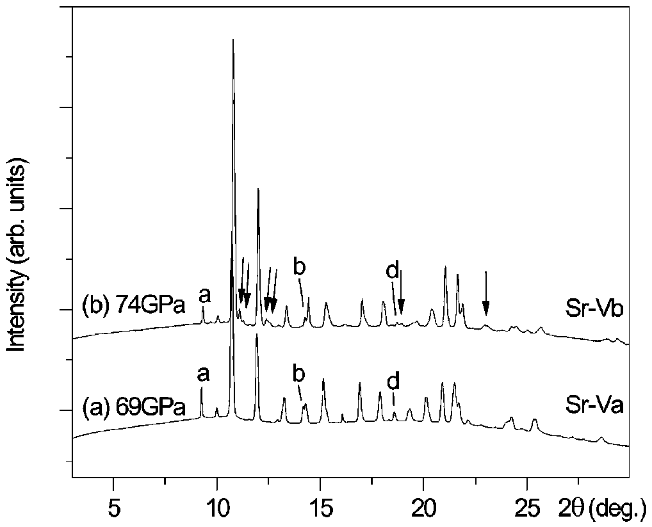

FIG. 5. Diffraction profiles from Sr-Va at 69 GPa and Sr-Vb (see text) at 74 GPa. The *C*-lattice reflections a, b, and d (see Fig. 1) are labeled in both profiles. Arrows in (b) mark new non-*I*-lattice reflections. (In these data, oversaturation of the strong reflections has enhanced the apparent magnitude of the weaker reflections compared to the true relative *I*- and *C*-lattice intensities in Figs. 1 and 3.)

Figure 5 shows integrated profiles collected at 69 and 74 GPa, the highest pressure reached. The *C* peaks a, b, and d (see Fig. 1; peak c has become too weak to detect) can be seen to have reduced markedly in intensity between 69 and 74 GPa, and several new weak diffraction peaks have appeared, as marked. But there is no discernible change in the *I*-lattice peaks. Because the *C* peaks are all weakened with respect to the (unaltered) *I*-lattice peaks, the most probable interpretation is that, like Ba-IV, Sr-V shows a transformation in its guest component—at 71(1) GPa. However, we cannot completely rule out the possibility that the weak new peaks mark the start of a transition to another phase, Sr-VI. So, we label the form below 71 GPa as Sr-Va, and that above 71 GPa as Sr-Vb, but only provisionally. Again, as with Ba-IV, the *C* form of the guest is associated with significant disorder of the chains in their positions along *c*. As said, it is impossible to compare the degree of this disorder with Ba because the strength of the diffuse scattering depends on crystallite size, and this is not known for the Sr sample.

We thus conclude that the structure and behavior of Sr-V is very similar to that of Ba-IV in all its principal features. There are some differences in detail in the nature of the guest component: Sr-Va has only the disordered *C* form (in the samples we have studied to date), whereas Ba-IVa and Ba-IVb, and probably Ba-IVc, have two forms; and Sr-Vb, if that is its correct designation, gives a guest-structure pattern unlike any of the Ba forms observed so far. However, the key characteristic of having an incommensurably self-hosting structure is the same, and suggests that there is a segregation into two different electronic species. This state is surprisingly stable in both metals; Ba-IV exists from 12 to 45 GPa and Sr-V from 48 to at least 74 GPa (the highest pressure yet reached in studies of Sr). In the host structure of Sr at 56 GPa, each Sr atom has four nearest neighbors at 2.837(1) Å, two at 2.847(1) Å, and one at 2.873(2) Å.

The atoms in the chains are separated along c by a similar distance of 2.82 Å. However, on the assumption that the chains are 100% occupied, as in Ba-IV, the chain atoms have a significantly shorter minimum approach to the host atoms of 2.664(1) Å, with a maximum distance from them of 2.842(1) Å. There is a commensurate prototype of the Ba-IV structure formed by M_2M' intermetallics such as Al_2Cu and Na_2Au,[11] in which the M atoms form the $I4/mcm$ host structure and the M' atoms occupy the chain sites. The M' atoms are the smaller in all cases.[11] This and the close chain-host approach in Ba-IV and Sr-V suggest that the Ba and Sr atoms in the chains have an electronic configuration with a smaller radius than those forming the host structure.

As discussed in Ref. 5, there are also interesting parallels to pursue with the remarkably similar phenomenology of organic inclusion compounds such as is formed by α,ω-dibromoalkane guest molecules in the channels of a urea host,[12] and with the disordered incommensurate Hg chains in $Hg_{3-\delta}AsF_6$.[13,14] However, these and the commensurate M_2M' prototype are all two-component systems; an incommensurate host-guest structure is very surprising in an element. But its emergence as a phase stable over 25 GPa or more in already two elements suggests that it may prove to be a ubiquitous new phenomenon.

We thank M. Hanfland for technical assistance in running the experiment on ID9 at ESRF, M.A. Roberts and A.A. Neild for technical support at SRS, C. Vanpeteghem for some assistance with data collection, and G.J. Ackland for helpful discussion. This work was supported by grants from the EPSRC, funding from the CCLRC, and facilities provided by Daresbury Laboratory. M.I.M. acknowledges support from the Royal Society.

---

[1] D.R. Allan, R.J. Nelmes, M.I. McMahon, S.A. Belmonte, and T. Bovornratanaraks, Rev. High Pressure Sci. Technol. **7**, 236 (1998).

[2] H. Olijnyk, and W.B. Holzapfel, Phys. Lett. **100A**, 191 (1984).

[3] B. Vasvari, A.O.E. Animalu, and V. Heine, Phys. Rev. **154**, 535 (1967); H.L. Skriver, Phys. Rev. Lett. **49**, 1768 (1982); H.L. Skriver, Phys. Rev. B **31**, 1909 (1985); R. Ahuja, B. Johansson, and O. Eriksson, *ibid.* **58**, 8152 (1998).

[4] M. Winzenick and W.B. Holzapfel, Phys. Rev. B **53**, 2151 (1996).

[5] R. J. Nelmes, D. R. Allan, M. I. McMahon, and S. A. Belmonte, Phys. Rev. Lett. **83**, 4081 (1999).

[6] R.J. Nelmes and M.I. McMahon, J. Synchrotron Radiat. **1**, 69 (1994).

[7] M. Hanfland, U. Schwarz, K. Syassen, and K. Takemura, Phys. Rev. Lett. **82**, 1197 (1999).

[8] A. N. Fitch and A. D. Murray (unpublished).

[9] K. Takemura, Phys. Rev. B **50**, 16 238 (1994).

[10] K. Takemura, in *High Pressure Science and Technology*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross (American Institute of Physics, New York, 1994), p. 417.

[11] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. 1, p. 361.

[12] K.D.M. Harris, S.P. Smart, and M.D. Hollingsworth, J. Chem. Soc., Faraday Trans. **87**, 3423 (1991).

[13] I.D. Brown, B.D. Cutforth, C.G. Davies, R.J. Gillespie, P.R. Ireland, and J.E. Vekris, Can. J. Phys. **52**, 791 (1974).

[14] J.M. Hastings, J.P. Pouget, G. Shirane, A.J. Heeger, N.D. Miro, and A.G. MacDiarmid, Phys. Rev. Lett. **39**, 1484 (1977).