Unusual Chemical Behavior for Potassium under Pressure: Potassium−Silver Compounds

T. Atou, M. Hasegawa, L. J. Parker, and J. V. Badding*

Contribution from the Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

Received August 2, 1996[⊗]

Abstract: At high pressures, there are large changes in the size and electron concentration of the alkali metals. As a result, significant changes should occur in the solid-state chemistry of these elements, allowing the formation of alkali metal−transition metal compounds. The formation of two alkali metal−transition metal compounds, K_3Ag and K_2Ag, is reported. These compounds rapidly form at room temperature upon compression of stoichiometric mixtures of the elements. K_3Ag has a BiF_3-type structure related to the *bcc* structure of potassium, with silver replacing some of the *bcc* potassium sites. The anisotropic ω-phase structure of K_2Ag consists of graphite-like layers of potassium atoms with silver atoms between the layers. At ambient pressure, lithium is the only alkali metal that forms compounds with silver. Thus, under pressure, potassium can exhibit chemical behavior exhibited by lithium at atmospheric pressure.

Introduction

Compounds formed between the alkali metals and other metals and metalloids form a class of materials of considerable technological and scientific interest. For example, Zintl compounds, which obey traditional chemical valence rules, have had a major impact on our understanding of bonding in the solid state.[1−3] Many Zintl compounds, such as NaTl, are formed between alkali metals and the elements on the right side of the periodic table. Compounds between cesium and gold, in which gold behaves as an auride (Au^-), are the only known examples of ionic compounds formed between two metals.[1,4] No compounds have been reported to form between the alkali metals potassium, rubidium, or cesium and the transition metals above and to the left of gold in the periodic table.[5] Sodium forms compounds with platinum, the metal next to gold in the periodic table.[6,7]

Pressure can have a profound effect on chemical reactivity because it can induce large changes in electronic structure, size, and Gibbs free energy.[8] We are systematically exploring the chemistry of the "new" elements formed under pressure.[8] We have found that the chemistry of the alkali metals can be considerably extended under pressure, such that they react with transition metals. At pressures in the range of 30 GPa (1 GPa $\sim$ 10 000 atm), potassium transforms into a metal having a d^1 electron configuration (the s-to-d transition[9−11]) that exhibits transition metal-like chemical behavior and reacts with the transition metal nickel.[12] Formation of these compounds has implications for the chemistry of Earth's core.[13−15] Here we report that at more moderate pressures in the range of 4 to 8 GPa (below the s-to-d transition) large changes still occur in the chemical behavior of potassium. Specifically, we have found compounds that form between the transition metal silver and alkali metal potassium that have stoichiometries K_3Ag and K_2Ag. One of these compounds, K_2Ag, has an anisotropic (ω-phase) structure consisting of graphite-like layers of potassium, an unusual chemistry for this element. At ambient pressures, lithium is the only alkali metal that forms compounds with silver.[5] Surprisingly, the kinetics of the solid state reactions to form these compounds are rapid at room temperature.

The effect of pressure on reactions between alkali metals and transition metals can be predicted[8,12] by adapting simple semiempirical rules that accurately predict at ambient pressure whether a transition metal will form compounds with another metal.[16,17] According to Miedema's rules, small differences in electron charge density and large differences in electronegativity (or work function) between two metals favor compound formation. Though large amounts of charge transfer are certainly not involved in the formation of intermetallic compounds, it is not surprising that large differences in electronegativity favor compound formation. Large differences in charge density tend to inhibit compound formation because there is a substantial energetic cost in compressing low charge density metals to the density of an intermetallic compound, which is generally intermediate in charge density between its constituent elements.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984.

(2) von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 33−51.

(3) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383−397.

(4) Batchelor, R.; Birchall, T.; Burns, R. *Inorg. Chem.* **1986**, *25*, 2009−2015.

(5) Massalski, T. B.; Okamoto, H.; Subramanian, P. R. Kacprzak, L. *Binary Alloy Phase Diagrams*; ASM International: Materials Park, OH, 1990.

(6) Nash, C. P.; Booyden, F. M.; Whittig, L. D. *J. Am. Chem. Soc.* **1960**, *82*, 6203−6204.

(7) Range, K. J.; Rau, F.; Klement, U. *Acta Crystallogr.* **1989**, *45C*, 1069−1070.

(8) Badding, J. V.; Parker, L. J.; Nesting, D. C. *J. Solid State Chem.* **1995**, *117*, 229−235.

(9) Young, D. A. *Phase Diagrams of the Elements*; University of California Press: Berkeley, 1991.

(10) Sternheimer, R. M. *Phys. Rev.* **1950**, *78*, 235−243.

(11) Drickamer, H. G. In *Solid State Physics*; Seitz, F., Turnbull, D., Eds.; Academic Press: New York, 1965; pp 1−145.

(12) Parker, L. J.; Atou, T.; Badding, J. V. *Science* **1996**, *273*, 95−97.

(13) Bukowinski, M. S. T.; Knopoff, L. In *High-Pressure Research—Applications in Geophysics*; Manghanani, M. H., Akimito, S., Eds.; Academic Press: New York, 1977; pp 367−387.

(14) Bukowinski, M. S. T. In *High Pressure Science and Technology*; Timmerhaus, K. D., Barber, M. S., Eds.; Plenum: New York, 1979; pp 237−244.

(15) Goettel, K. *Geophys. Surv.* **1976**, *2*, 369−397.

(16) Pettifor, D. G. *Solid State Phys.* **1987**, *40*, 4392−4440.

(17) Miedema, A. R.; de Chatel, P. F.; de Boer, F. R. *Physica* **1980**, *100B*, 1−28.

S0002-7863(96)02700-X CCC: $12.00

The electronegativities of the alkali metals and the late transition metals differ considerably (1 to 1.75 Pauling units). However, the differences in charge density (n) are too large for compound formation (in terms of $n^{1/3}$, which is used in Miedema's model, they range from ~0.6 to 1.3 in units of $(10^{23}$ electrons/cm$^3)^{1/3}$). Gold forms compounds with the alkali metals because its charge density is lower than the charge density of much of the rest of the transition series and it has the highest electronegativity of any metal (2.4).[16,17] Because they are compressible, under pressure the charge densities of the alkali metals increase rapidly. Therefore, according to Miedema's rules the boundary separating the metals that do react with potassium, rubidium, and cesium under pressure (e.g., gold, cadmium, and zinc) with those that do not (the rest of the transition series) should move to the left with an increase in pressure.[8,12] The formation of the potassium–silver compounds reported here is in agreement with these predictions.

Experimental Section

A Mao-Bell megabar-type diamond anvil cell was used for the high-pressure syntheses.[18] Pressure was measured by ruby fluorescence collected with a Dilor XY triple stage spectrometer equipped with a Princeton Instruments liquid nitrogen cooled TKB1024 CCD detector. The 514.5 nm line of a Spectra-Physics model 164 argon ion laser at 35° incidence was used to excite the ruby fluorescence.

Powder diffraction patterns were collected at high pressures with a diffraction system that utilizes a Johansson–Guinier quartz monochromator to focus an X-ray beam onto the sample.[19] The focused beam is nearly monochromatic ($I_{K\alpha 2} \cong 0.12 I_{K\alpha 1}$) and is collimated to a low divergence, allowing high-quality, high-resolution diffraction data to be collected. The X-ray source was a Rigaku RU-200H rotating anode generator with a 0.1 × 1 mm molybdenum fine focus target ($\lambda_{K\alpha 1}$ = 0.7093 Å). Stepper motor driven x, y, and z stages allowed precise positioning of the sample with respect to the incident beam. Diffraction patterns were collected in a Debye–Scherrer configuration using DEF-392 X-ray film.[18] In these experiments, the diffraction ring profiles on the film were smooth, indicating that a large number of crystallites contributed to the diffraction patterns. The diffraction patterns were scanned into a Macintosh computer and were collapsed into diffraction profiles using the program of Nguyen and Jeanloz, which gives accurate intensity information.[20] The intensities obtained were corrected by calibration of the relationship between film density and exposure. To check for systematic errors in this procedure, a Rietveld analysis[21,22] was performed on a diffraction pattern collected from silver metal contained within the diamond cell, which gave excellent agreement factors: $R_{wp} = 0.0397$, $\chi^2 = 3.684$, and $R_{F^2} = 0.0241$. The interplanar spacings obtained by this procedure are accurate to within 0.1%. The major contribution to the background intensity is Compton scattering from the single crystal diamond anvils.

Potassium metal and silver powder were loaded in a series of experiments (nominal molar ratios of potassium:silver from 1:0 to 1:2) into the Mao-Bell cell to explore the formation of phases. Loading was performed under a high-purity argon atmosphere contained within a Vacuum Atmospheres glovebox. The holes in the rhenium or T301 stainless steel gaskets used to contain the sample were approximately 150 μm in diameter. After compression, diffraction peaks other than those of potassium and silver appeared, revealing that new intermetallic compounds were formed.

Results

When a sample of the nominal composition of K_3Ag was compressed to 6.4 GPa, formation of a compound with the same stoichiometry was observed (Figure 1). Small variations of the molar ratio of silver to potassium lead to the appearance of diffraction lines due to other phases, allowing unambiguous assignment of the diffraction lines due to K_3Ag. No variation in lattice parameter was observed as the potassium to silver ratio was varied, indicating that K_3Ag is a stoichiometric phase.

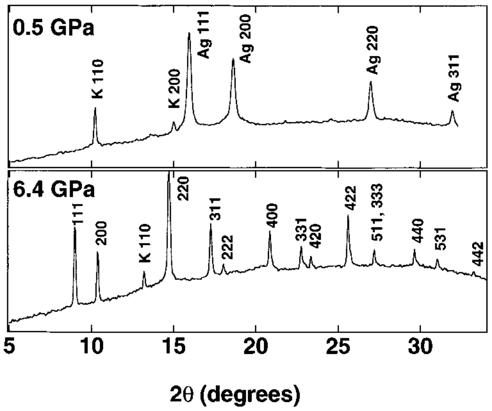

Figure 1. Diffraction patterns for a potassium–silver mixture (3:1) before reaction (0.5 GPa) and after reaction (6.4 GPa) to form K_3Ag.

The reaction to form K_3Ag was rapid at room temperature. Upon release of pressure to 0.5 GPa, K_3Ag decomposed into the elements. In view of the low decomposition pressure, it is likely that, like many transition metal hydrides synthesized at high pressure,[23] K_3Ag could be quenched to ambient pressure at a lower temperature. K_3Ag exhibits a silver luster, similar to elemental potassium.

The diffraction lines of the K_3Ag phase were indexed by a cubic unit cell with a lattice parameter of 7.8370(2) Å at 6.4 GPa (Figure 1). The indices satisfy the extinctions for a face centered lattice and additional extinctions $k,l = 2n + 1$ for $0kl$, $h + l = 2n + 1$ for hhl, and $l = 2n + 1$ for $00l$. Thus possible space groups are $F23$, $Fm3$, $F432$, $F43c$, and $Fm3m$. The volume of one formula unit of the elemental reactants (Ag + 3K) at 6.4 GPa is 140.1 Å^3. Because the unit cell volume of the K_3Ag compound is 481.0 Å^3 and the volume of the products in a pressure-induced reaction must be less than the volume of the reactants, the number of formula units (Z) in the unit cell must be four or more (4 × 140.1 = 560.4 Å^3). If $Z = 4$ is assumed, the volume decrease after reaction is 14.2%, a reasonable value for a pressure-induced chemical reaction. In Pearson's handbook of intermetallic compounds, BiF_3 is the only structure type that is face-centered cubic and has $Z = 4$ with a stoichiometry MN_3.[24] We conclude that K_3Ag is isotypic with BiF_3, which has space group $Fm3m$.

To confirm the structural assignment, a Rietveld analysis using the program GSAS was performed on the K_3Ag diffraction pattern.[21,22] The refinement included scale, background, lattice, profile, preferred orientation, and isotropic thermal parameters. The peak shapes were modeled using the psuedo-Voigt profile function of Thompson, Cox, and Hastings.[25] The preferred orientation model was that of Dollase and March.[26] Only a moderate amount of preferred orientation was noted. The refinement converged with agreement factors $R_{wp} = 0.0454$, $R_p = 0.0318$, $\chi^2 = 1.3$, and $R_{F^2} = 0.130$. A plot of the calculated and observed diffraction profiles is shown in Figure 2.

---

[18] Jephcoat, A. P.; Mao, H. K.; Bell, P. M. In *Hydrothermal Experimental Techniques*; Ulmer, G. C., Barnes, H. L., Eds.; Wiley-Interscience: New York, 1987; pp 469-506.

[19] Atou, T.; Badding, J. V. *Rev. Sci. Instrum.* **1995**, *66*, 4496–4500.

[20] Nguyen, J.; Jeanloz, R. *Rev. Sci. Instrum.* **1993**, *64*, 3456–3461.

[21] Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65–71.

[22] Larson, A. C.; Von Dreele, R. B. *Report LAUR 86*–748, GSAS: General Structure Analysis System; Los Alamos National Laboratory: Los Alamos, NM, 1994.

[23] Badding, J. V.; Hemley, R. J.; Mao, H. K. *Science* **1991**, *253*, 421–424.

[24] Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; ASTM International: Newbury, OH, 1991.

[25] Thompson, P.; Cox, D. E.; Hastings, J. B. *J. Appl. Crystallogr.* **1987**, *20*, 79–83.

[26] Dollase, W. A. *J. Appl. Crystallogr.* **1986**, *19*, 267–272.

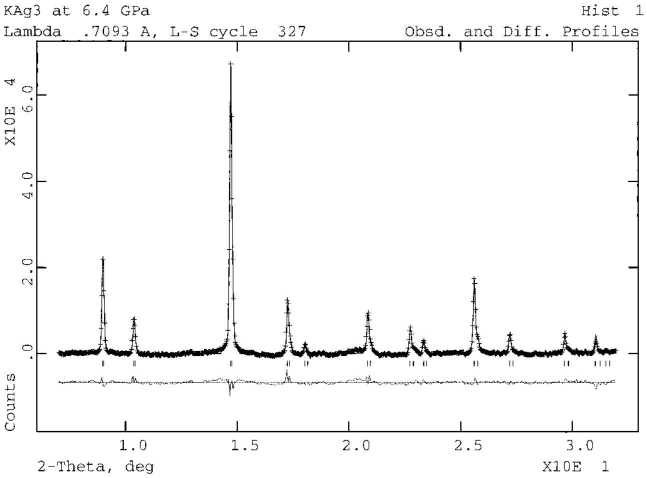

Figure 2. Diffraction pattern for a potassium−silver mixture (3:1) at 6.4 GPa after reaction to form K_3Ag. Observed, calculated, and difference profiles are shown. The fitted background has been subtracted. Vertical lines mark the positions expected for the diffraction peaks.

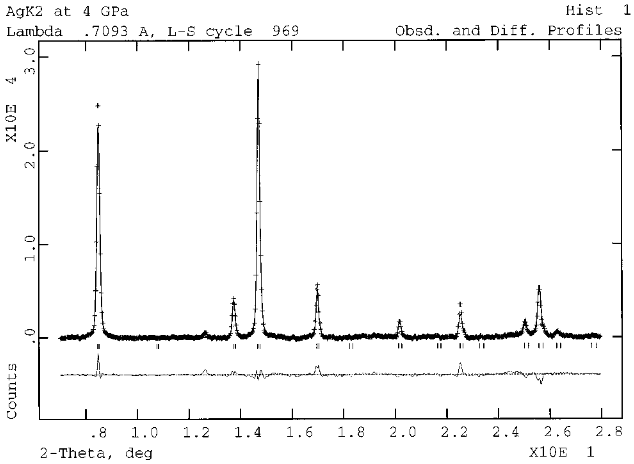

Figure 3. Diffraction pattern for a potassium−silver mixture (2:1) at 4.1 GPa after reaction to form K_2Ag. Observed, calculated, and difference profiles are shown. The fitted background has been subtracted. Vertical lines mark the positions expected for the diffraction peaks. The second and sixth pair of lines are for the 001 and 002 reflections, which have negligible intensity due to preferred orientation.

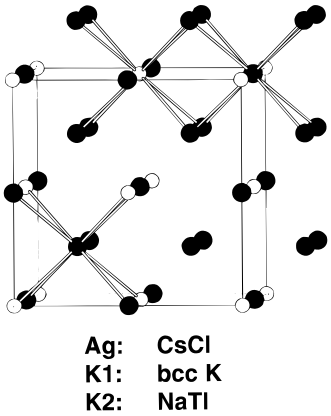

Figure 4. Crystal structure of BiF_3 type K_3Ag, which has space group $Fm3m$. The silver atoms (unshaded) are in the 4a (0, 0, 0) positions and the potassium atoms (black), K1 and K2, are in the 4b ($^1/_2$, $^1/_2$, $^1/_2$) and 8c (1/4,1/4,1/4) positions, respectively.

As the silver to potassium ratio was increased, thermodynamic equilibrium was more difficult to achieve at room temperature, likely because of the high melting point of silver compared to potassium. A sample with initial stoichiometry K_2Ag exhibited a very complex diffraction pattern at 6.1 GPa, indicating the existence of several phases. Nearly single phase material (of one of the phases present at 6.1 GPa) could be obtained by compression to 35 GPa at room temperature (the diamonds, which have a high thermal conductivity, constrain the sample to constant temperature), followed by release to 6.1 GPa. Diffraction data were also collected at 4.0 GPa (Figure 3) and 8.2 GPa. Two very weak peaks at $2\theta = 12.60°$ and $16.04°$ due to a small amount of impurity phase were present (Figure 3). These peaks could be unambiguously identified by noting the effect on the diffraction intensities of varying the silver to potassium ratio. The diffraction lines could be indexed with a hexagonal unit cell with $a = 5.5434(2)$ Å, $c = 3.770(1)$ Å at 4.0 GPa. No systematic extinctions were observed, but the 00*l* lines were absent. By comparison of the volume at 6.1 GPa of one formula unit (98.71 Å^3) of the elements (Ag + 2K) with the unit cell volume of K_2Ag (91.44 Å^3), it can be concluded that the primitive unit cell contains one formula unit. The volume decrease after reaction at this pressure is 7.4%.

The ω-phase structure provides the best match to the diffraction data.[24,27] It has a *c*/*a* ratio close to 0.6, similar to that observed for K_2Ag. It is known to form with stoichiometry MN_2 with one formula unit in a primitive hexagonal unit cell ($Z = 1$). The structure has space group $P6/mmm$, with silver atoms in the 1a (0, 0, 0) positions and potassium atoms in the 2d ($^1/_3$, $^2/_3$, $^1/_2$) positions. It is anisotropic, with the silver and potassium atoms forming layers along the *c* axis. As will be discussed below, upon compression, the *c*/*a* ratio of K_2Ag changes rapidly, providing experimental evidence that structural anisotropy is present. The presence of this anisotropy further supports the structural assignment. The absence of the 00*l* lines in the diffraction pattern is also consistent with the presence of structural anisotropy; when compressed, anisotropic materials tend to align with the unique axis perpendicular to the applied load, a texture that reduces the intensity of the 00*l* lines.

A Rietveld analysis was also performed on the K_2Ag diffraction pattern.[21,22] The refinement and peak shape parameters were similar to those used in the K_3Ag refinement. The preferred orientation model was that of Popa, which is based on an expansion in spherical harmonics.[28] The refinement rapidly converged, with agreement factors $R_{wp} = 0.0183$, $R_p = 0.0125$, $\chi^2 = 3.1$, and $R_F{}^2 = 0.116$. Because of the large amount of preferred orientation, small deviations from the ideal ω-phase structure, such as the existence of a superlattice, cannot be ruled out. A plot of the calculated and observed diffraction profiles is shown in Figure 3.

Like K_3Ag, K_2Ag decomposed into the elements upon decompression to 0.5 GPa and would likely be quenchable at lower temperatures. In contrast to the elemental reactants, K_2Ag exhibits a strong golden luster.

Discussion

The K_3Ag structure can be derived by replacement of half of the body-centered sites of elemental potassium with silver to form a stoichiometry K_3Ag (Figure 4).[1] The replacement doubles the lattice parameter of the simple *bcc* structure. The K2 atoms form a primitive cubic lattice with body-centered sites alternately occupied by Ag and K1. K2 is in a NaTl type coordination environment surrounded by four silver and four potassium nearest neighbors. Ag is in a CsCl type coordination environment, surrounded by eight potassiums.

---

(27) Pearson, W. B. *Proc. R. Soc. London* **1979**, *A365*, 523−535.
(28) Popa, N. C. *J. Appl. Crystallogr.* **1992**, *25*, 611−616.

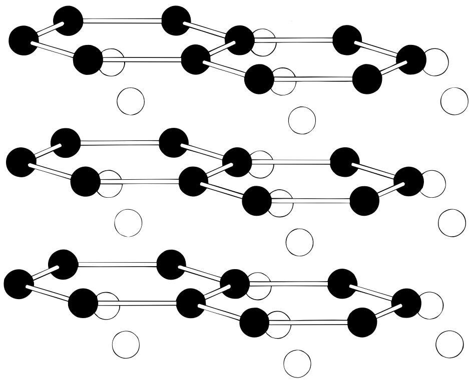

Figure 5. Crystal structure of hexagonal ω-phase type K_2Ag. The *c* axis is near vertical. The structure consists of graphite-like layers of K atoms (black) with Ag atoms (unshaded) between the layers in the center of the K hexagons. The distance between K planes is the same as the *c* axis lattice parameter, 3.605 Å at 6.1 GPa. Closest K−Ag distances are 3.628 Å.

The nearest neighbor interatomic distances (K1−Ag, K1−K2) in K_3Ag are 3.39 Å at 6.4 GPa. The atomic radii of elemental silver and potassium at 6.4 GPa are 1.41 and 1.89 Å, respectively. The Ag−K1 distance is similar to the sum of the atomic radii (3.30 Å). However, the K1−K2 distance is 10% shorter. This substantial decrease in interatomic distance is similar to the behavior observed in many polar intermetallic compounds and Zintl phases. The interatomic distances in NaTl, for example, are 12% less than the sum of the atomic radii derived from the elemental sodium and thallium.[1] Thus the "chemical pressure" due to incorporation into the *bcc* potassium lattice of the more electronegative silver atom is substantial.

Many other intermetallic and Zintl compounds form with the BiF_3 structure at ambient pressure, but those formed with potassium and the heavier alkali metals can only be found with elements farther to the right in the periodic table than silver. Lithium forms a compound with silver with a stoichiometry that varies between Li_3Ag and Li_2Ag that, like K_3Ag, can be derived by substitution of Ag atoms into a *bcc* alkali metal structure.[5] Miedema's rules predict that at ambient pressure lithium, but not sodium or potassium, will form compounds with silver.[16] By a pressure of 6 GPa, the charge density of potassium increases sufficiently to allow the formation of compounds. The charge density of potassium at 6 GPa exceeds the charge density of sodium at ambient pressure, explaining why potassium forms compounds, but sodium does not. Thus, under pressure potassium has sufficient charge density to form compounds with silver similar in composition and structure to those formed by lithium with silver at ambient pressure.

The ω-phase structure adopted by K_2Ag consists of a graphite-like network of potassium atoms with silver atoms interleaved between the layers and centered in the hexagons of the network (Figure 5). It is adopted by titanium at high pressure and is closely related to the well-known AlB_2 structure, except that the c/a ratio is smaller ($\sim$0.6 vs $\sim$1.1).[27] Other than lithium, no alkali metals form compounds with the ω-phase structure and the alkali metal in the graphite-like (4d) positions, again demonstrating how potassium under pressure can perform some of the same chemistry as lithium.

The potassium atoms in the layers are compressed significantly. At 6.1 GPa the distance between potassiums in the plane of the graphite-like network is 3.13 Å (Figure 5), considerably smaller than the nearest neighbor distance of 3.82 Å in pure potassium at this pressure. The coordination around the K atoms is a tri-capped trigonal prism, coordination number 9. The Ag atoms lie in a distorted cubic polyhedron.

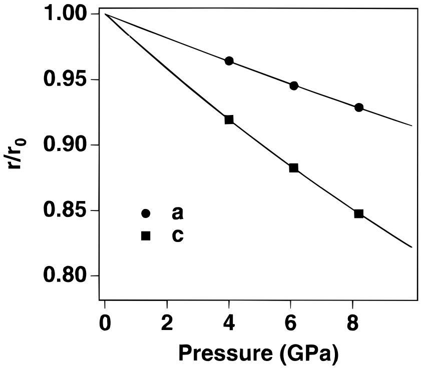

Figure 6. Normalized lattice parameters (*a* and *c*) of K_2Ag as a function of pressure. The lines are a fit to a linear Murnahgan equation of state.[29]

The most striking feature of K_2Ag is its graphite-like network of potassium atoms, which give rise to a structural anisotropy. The *c* axis collapses more rapidly with pressure than the *a* axis (Figure 5). The lattice parameters were fit to a one-dimensional Murnaghan equation of state:

$$r/r_0 = [(\beta'/\beta_0)P + 1]^{-1/\beta'}$$

which provides an approximation for the relationship between normalized lattice parameters, r/r_0, and pressure, P.[29] Here, r is a lattice parameter at high pressure, r_0 is a lattice parameter at ambient pressure, $\beta_0^{-1} = -(\mathrm{d}\ \ln r/\mathrm{d}P)$ is the linear compressibility at $P = 0$, and β' is the pressure derivative of β. β' was constrained to be 1 in this fit. For K_2Ag, β_0 is 107 GPa along the *a* axis and 46 GPa along the *c* axis. Thus K_2Ag is more than twice as compressible along the *c* axis as along the *a* axis, a substantial anisotropy that indicates that the bonding in the potassium layers is stronger than the bonding between them. For comparison, the reciprocal compressibilities for the anisotropic layered compound TiS_2 differ by a factor of 3 (*c* axis $\beta_0 = 58$ GPa, *a* axis $\beta_0 = 178$ GPa).[30]

At pressures above the s-to-d transition in elemental alkali metals, open structures are found that exhibit unusual structural features and novel, more covalent and directional bonding.[9] In elemental titanium, for example, the s-to-d transition under pressure induces the transition to the ω-phase.[9] Elemental cesium undergoes a transition at 4.2 GPa from a *fcc* structure to a structure containing trigonal prisms that is isostructural with the thorium atoms in the Zintl compound α-$ThSi_2$.[31,32] Electronic structure calculations indicate that the valence electron density is concentrated in the same positions in the α-$ThSi_2$ structure as the silicon atoms, which are located within the trigonal prisms.[32] It has been argued that this is a very unusual bonding situation—an electride, consisting of e^- anions and Cs^+ ions.[32] As a result of the change to d-electron bonding, at 10 GPa elemental cesium becomes a superconductor.[33]

Alkali metal rich compounds prepared under pressure may exhibit similar or other types of unusual bonding. We note the possibility that d-electron bonding may influence the structure of K_2Ag, where the distances between the potassium atoms within the graphite-like layers at 6.1 GPa are 3.13 Å, comparable to those in elemental potassium at 44 GPa, a pressure above

---

(29) Murnaghan, F. D. *Proc. Natl. Acad. Sci. U.S.A.* **1944**, *30*, 244−254.

(30) Zhou, O.; Fischer, J. E. *Phys. Rev. B* **1991**, *44*, 7243−7247.

(31) Takemura, K.; Minomura, S.; Shimomura, O. *Phys. Rev. Lett.* **1982**, *49*, 1772−1775.

(32) von Schnering, H. G.; Nesper, R. *Angew. Chem.* **1987**, *26*, 1059−1200.

(33) Wittig, J. *Phys. Rev. Lett.* **1970**, *24*, 812−815.

the s-to-d transition.[9] As mentioned previously, at the pressures used for synthesis (4 to 8 GPa) elemental potassium does not yet exhibit d-electron bonding. The decrease in the potassium interatomic distances in K_2Ag is due to the "chemical pressure" induced by compound formation. The golden color of K_2Ag is suggestive of an electronic structure more complex than that of simple s-electron metals, which exhibit a silver luster (elemental Cs at ambient pressure is an s-electron metal that exhibits a slight gold cast due to the presence of empty d-bands just above the Fermi energy; as it develops d-character under pressure, the golden color becomes much richer[34]). Elemental potassium above the s-d transition is also golden, as a result of interband transitions that arise because of the d^1 electron configuration.[9] Further investigation with electronic structure calculations will be necessary to determine if the bonding in K_2Ag exhibits d-character or if (like the ω-phases containing lithium) it is essentially s-electron.

Diffraction patterns collected at other molar ratios of potassium to silver exhibited diffraction peaks indicative of the formation of several additional phases with a wide range of stoichiometries. Thus, the application of pressure to potassium allows a much richer chemistry with silver (and also with nickel[12]). Many of the other transition elements should react with the alkali metals under pressure, allowing the synthesis of other alkali metal−transition metal compounds. Some of these compounds, like K_2Ag, should exhibit unusual chemical behavior for the alkali metal component. Compounds between the alkali metals and the higher melting transition elements will likely be quenchable in metastable form to ambient pressure.[12] Finally, the large changes in electronic structure (e.g., large changes in charge density, availability of d orbitals at sufficiently high pressures) and free energy induced in the alkali metals by pressure should allow new alkali metal chemistry with some of the nonmetallic elements and many compounds, many of which should also be quenchable to ambient pressure.[8]

Acknowledgment. This work was supported by a National Science Foundation Young Investigator award to J.V.B., the donors of the Petroleum Research Fund (administered by the American Chemical Society), and a David and Lucile Packard Foundation Fellowship to J.V.B. We thank John Parise for valuable discussions about Rietveld analysis.

JA9627003

---

(34) Syassen, K. *Phys. Rev. Lett.* **1982**, *49*, 1776−1779.