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Neutron powder diffraction study of silver subfluoride

Arthur Williams

Low Alamos Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract. Neutron powder diffraction measurements have been made at a number of different temperatures from room temperature to 20 K on a sample of silver subfluoride. The anti-CdI₂ structure has been confirmed and no evidence of a crystallographic phase transformation was discovered. We report the first measurements of the thermal parameters, strain, grain size, thermal expansion coefficients and vacancy density in this peculiar compound.

1. Introduction

Shortly after the turn of the century a large number of sub-metal halides in which the metal appeared with half its normal valence continued to appear in the literature. Of all these materials, only the enigmatic Ag₂F has withstood the test of time, all others having been found under more careful investigation to be non-existent.

Silver subfluoride is a bright, brassy yellow material with a hexagonal crystal structure, consisting of close-packed layers in the sequence Ag–Ag–F–Ag–Ag–F. It can be prepared chemically [1] or electrolytically [2], but decomposes into Ag metal and AgF in the presence of moisture, ultraviolet light, or above 80 °C. The transport properties are very anisotropic, having a room-temperature resistivity parallel to the layers about two orders of magnitude less than that perpendicular to the layers [3]. While conduction parallel to the layers is clearly metallic, both semiconducting [3] and metallic [4] behaviour has been claimed for conduction along the *c* axis. Although band structure calculations [5] support the latter, photo-emission experiments [6] suggest that semiconducting behaviour is more likely. Below 66 mK the compound exhibits bulk superconductivity [7].

Only two structural studies have been made to date on this unusual compound, [8, 9] both with x-rays and both concluding the anti-CdI₂ structure, space group P $\bar{3}$ m1, shown in figure 1. For this structure, the two Ag atoms shown in the unit cell are in exactly equivalent positions. In view of this claim that all Ag atoms are identical, the radiographic studies by Bruno and Santoro [10] are of particular interest. In their first experiment they found that following the formation of Ag₂F from inactive AgF and radioactive ¹¹⁰Ag metal and subsequent decomposition in H₂O, the resulting Ag metal and AgF had equal activities. This is what would be expected given the equivalence of the silver atoms in the crystal structure. However, in a second experiment, in which natural Ag₂F was allowed to exchange with radioactive ¹¹⁰AgNO₃ in an acetone solution,

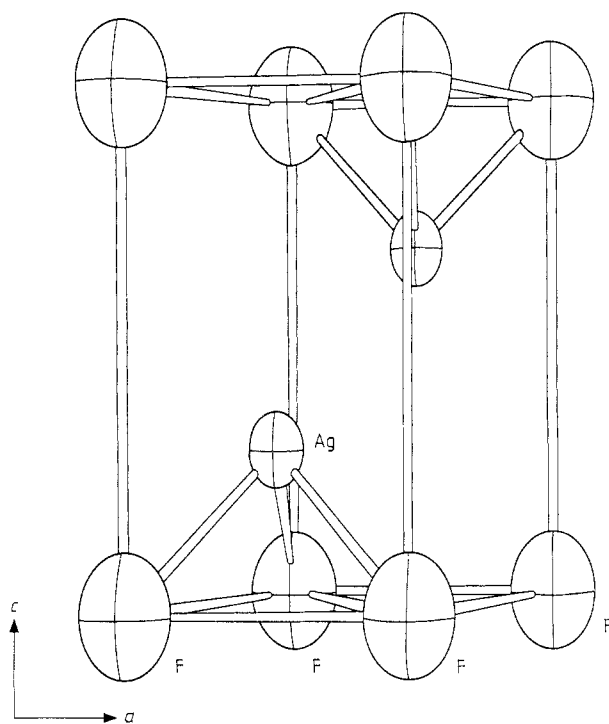


Figure 1. Ag₂F unit cell. The thermal ellipsoids are drawn as 99% probability surfaces for the refinement at 300 K.

all the ¹¹⁰Ag doped into the Ag₂F was recovered as Ag metal upon decomposition with H₂O. This latter result suggests the existence of two inequivalent crystallographic sites for Ag atoms in Ag₂F, which is inconsistent with the proposed anti-CdI₂ structure.

It is therefore of interest to make a more careful examination of the crystallography of silver subfluoride using modern neutron scattering and Rietveld refinement techniques. Using a pulsed spallation neutron source, the crystallographic parameters have been obtained over a wide temperature range. We also report the first thermal parameters, thermal expansion coefficients and estimate of the internal strain in chemically produced Ag₂F crystals.

2. Experimental

Silver subfluoride powder was prepared following the procedure described in [1]. The powder thus produced was carefully shielded from sources of ultraviolet light and protected from moisture in an inert-gas glove box equipped with a recirculating water vapour scrubber. Enough powder was made to completely fill a 9.5 mm diameter vanadium tube 50 mm long, which was sealed in dry helium gas with an indium O-ring seal. Neutron powder diffraction data was collected on the High Intensity Powder Diffractometer (HIPD), at the pulsed spallation neutron source at the Los Alamos Neutron Scattering Center (LANSCE). The sample tube was mounted to an Air Products recirculating ⁴He Displex refrigerator and the temperature monitored and con-

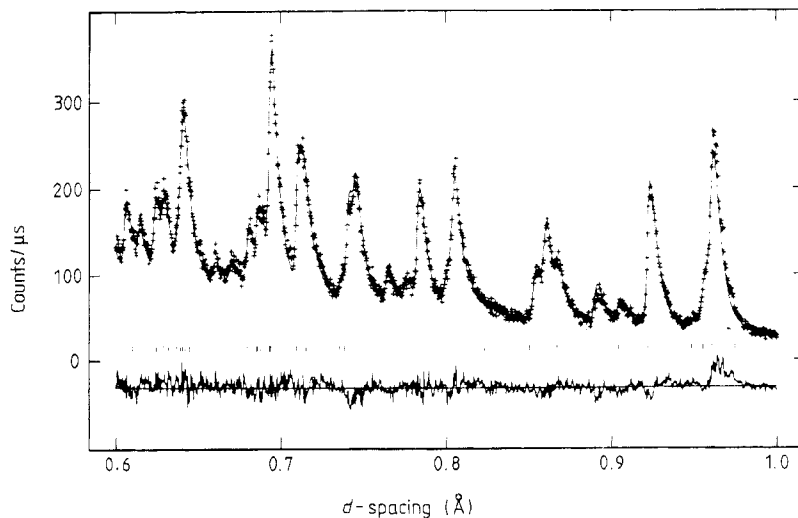


Figure 2. Partial neutron powder diffraction pattern of polycrystalline Ag_2F at 20 K. The crosses are the data from the $+153^\circ$ detector bank and the full curve through the data is the Rietveld refinement best fit to the model. The tick marks show the positions of reflections allowed by the structure, and the full curve at the bottom is the difference between the data and the fit.

trolled by a Lakeshore DRC-81C PID controller. Diffraction data was collected in four detector banks, ($\pm 153^\circ$ and $\pm 90^\circ$). The best resolution of the data obtained in these banks is about $\Delta d/d = 0.3\%$. The data acquisition program was set to hold at each temperature for one hour before beginning data collection in order for the rather massive sample to come to thermal equilibrium. Data collection times were about one hour for each temperature with LANSCE running at 805 MeV and 20–30 μA of proton current into the spallation target. The powder diffraction data was analysed using the General Structure Analysis System (GSAS) Rietveld refinement software package [11], using NBS silicon as an instrument calibration standard. The neutron powder peak profiles were modelled with the standard double-exponential–Gaussian convolution function [12].

3. Results

Figure 2 shows part of a typical diffraction pattern obtained from the polycrystalline Ag_2F sample. Also shown are the Rietveld refinement fit to the data and the residual. The fits were to the anti- CdI_2 structure and were in all cases found to be quite good with R -factors in the neighbourhood of 6 to 9% and reduced χ^2 very close to unity. No evidence of any other phases or of any crystallographic phase transformations was found. Table 1 shows the crystallographic parameters obtained from the Rietveld refinements as well as the unit cell volumes and c/a ratios at each of nine temperatures. The thermal expansion behaviour of this material is extremely anisotropic, with the linear expansion coefficient near room temperature in the ab plane being about $2.8 \times 10^{-5} \text{ K}^{-1}$, which is comparable to many metals, (1.9×10^{-5} for Ag for example). The linear expansion coefficient along the c axis is four to five times smaller than that perpendicular to

Table 1. Crystallographic parameters for silver subfluoride obtained from Rietveld refinement to neutron powder diffraction data. The number in parentheses are the ESDs for the values. The cell volume and c/a ratio are calculated from the values of the refined lattice parameters.

T (K)	a (Å)	c (Å)	c/a	Unit cell volume (Å ³)	z
300	2.998 77(5)	5.6950(2)	1.8991(1)	44.351(3)	0.3053(1)
250	2.994 56(5)	5.6932(2)	1.9012(1)	44.213(3)	0.3050(1)
200	2.989 55(4)	5.6910(2)	1.903 63(8)	44.049(2)	0.3051(1)
150	2.986 44(4)	5.6897(2)	1.905 17(8)	43.947(2)	0.3049(1)
100	2.982 80(4)	5.6881(2)	1.906 97(8)	43.828(2)	0.3049(1)
50	2.978 35(4)	5.6877(2)	1.909 66(8)	43.693(2)	0.304 81(9)
40	2.977 35(4)	5.6880(2)	1.910 43(8)	43.667(2)	0.304 90(8)
30	2.977 03(4)	5.6881(2)	1.910 66(8)	43.658(2)	0.305 01(9)
20	2.976 85(4)	5.6883(2)	1.910 88(8)	43.654(2)	0.305 01(8)

the c axis at room temperature and changes sign between 50 K and 100 K, although the behaviour of both the unit cell volume and c/a ratio is everywhere monotonic with temperature. The room-temperature volume thermal expansion coefficient, $(1/V)(\partial T/\partial T)$ is about $6.9 \times 10^{-5} \text{ K}^{-1}$, a value also typical of most metals and somewhat larger than that of silver, ($5.7 \times 10^{-5} \text{ K}^{-1}$). The atomic parameter, z , is nearly independent of temperature and has a value of 0.304, in good agreement with the previous estimates from x-ray diffraction work [8, 9].

The refinements of the peak profiles for this material exhibited no evidence for particle-size (Sherrer) broadening but a small amount of strain broadening. From the absence of any particle-size broadening and the limit of the resolution of the diffractometer, a lower limit of about 1000 Å can be placed on the crystallite size of this sample. The refinements gave no evidence of extinction, from which an upper limit on the grain size of about 3 μm can also be estimated. Refinement of the peak broadening contribution due to homogeneous isotropic strain in the sample consistently produced results between 0.2–0.3%, with a weak tendency to decrease with decreasing temperature. Since no processing of the sample was done other than running the as-prepared powder through a 120 mesh sieve, this strain represents that which is ‘grown in’ the polycrystalline Ag_2F during its synthesis. Production of the material electrochemically or by a different chemical means may result in different values for the strain.

Table 2 shows the anisotropic thermal parameters obtained for each temperature. The thermal ellipsoids for both Ag and F atoms clearly exhibit much larger excursions along the c axis than in the ab planes by about a factor of two at room temperature and nearly a factor of five at 20 K. The unit cell shown in figure 1 shows the actual thermal ellipsoids obtained from the refinement at 300 K. From the very large values of u_{33} for fluorine and its rapid increase with temperature it is not surprising that the compound decomposes at a relatively low temperature between 70 and 80 °C. At room temperature the u_{33} value corresponds to an RMS displacement of the fluorine atom of 0.18 Å, more than 10% of the distance between adjacent Ag–F layers. Apparently the Ag–F bonding is very weak. By comparison, the ionic compound AgF is extremely stable, melting at 435 °C and boiling at 1159 °C. The common claim [4, 6, 9, 13, 14] that Ag_2F is an example of a mixed metallic–ionic bonded ‘metal-salt’ based on the similarity of its Ag–F bond length to that in AgF is clearly a serious over-simplification. F atoms in the subfluoride have three Ag atoms coordinated both above and below at 2.45 Å and six coplanar F

Table 2. Anisotropic thermal parameters for silver subfluoride obtained from Rietveld refinement to neutron powder diffraction data. The numbers in parentheses are the ESDs for the values.

T (K)	F		Ag	
	u_{11}, u_{22} (\AA^2)	u_{33} (\AA^2)	u_{11}, u_{22} (\AA^2)	u_{33} (\AA^2)
300	0.0164(5)	0.0312(7)	0.0080(2)	0.0160(3)
250	0.0133(4)	0.0293(7)	0.0070(2)	0.0146(3)
200	0.0100(3)	0.0252(6)	0.0056(1)	0.0119(2)
150	0.0078(3)	0.0232(5)	0.0047(1)	0.0105(2)
100	0.0060(3)	0.0211(5)	0.0036(1)	0.0089(2)
50	0.0042(2)	0.0182(5)	0.00203(9)	0.0073(2)
40	0.0036(2)	0.0167(4)	0.00154(9)	0.0068(2)
30	0.0033(2)	0.0175(5)	0.00154(9)	0.0063(2)
20	0.0034(2)	0.0166(4)	0.00122(8)	0.0061(2)

atoms in a hexagonal arrangement at 3.00 \AA . The fluorine in AgF (NaCl structure) has only a symmetric octahedral coordination of six Ag atoms at 2.46 \AA , each having one valence electron to donate to a fluorine to fill its outer shell, resulting in strong ionic bonds. The mixed-valent character of the electronic structure of silver in Ag_2F on the other hand results in a structure with much weaker covalent Ag–F bonds.

Ido and co-workers [4] have reported a Debye temperature of 120 K for Ag_2F from fits of the Bloch–Grüneisen formula to their electrical resistivity data. Resistivity measurements both parallel to and perpendicular to the c axis of the single-crystal samples gave the same Debye temperature, suggesting that the scattering process is similar in both cases. From the temperature dependence of the thermal factors and the average atomic mass, it is also possible to make an estimate of the Debye temperature [15]. We obtain a value of 119 K from the values of u_{xx}, u_{yy} , in very good agreement with [4]. However, from the values of u_{zz} we obtain a Debye temperature of 81 K, indicative of the extremely anisotropic behaviour of this material. The resistivity, on the other hand, does not give a reliable indication of the vibrational anisotropy since it tends to weigh the higher energy phonons more strongly (which have a higher momentum to impart in a scattering event).

The density of Ag_2F has been measured by Terry and Diamond [9], who found that their experimentally obtained value, 8.64 g cm^{-3} , was somewhat lower than that obtained from a calculation using the lattice parameters which they determined from x-ray powder diffraction, 8.78 g cm^{-3} . Hettich [2] also reports a rather low value for the measured density, in his case 8.57 g cm^{-3} . In view of this we considered the possibility of the presence of defects in Ag_2F in the form of both F vacancies and Ag vacancies. We therefore performed Rietveld refinements of the occupations of both F and Ag at each temperature measured. No evidence of vacancies beyond the accuracy of the refined values of about one or two atomic per cent was observed. To account for the difference in measured and calculated densities reported by Terry and Diamond [9] the compound would require an average stoichiometry of $\text{Ag}_2\text{F}_{0.80}$ or $\text{Ag}_{1.93}\text{F}$ for strictly F or Ag vacancies respectively. Even if all the vacancies were Ag our results are not adequate to explain the low measured densities of Ag_2F by other experimenters [2]. Since the accuracy of both lattice parameter and density measurements is ordinarily quite high, this discrepancy remains a mystery unless a high density of some other form of defect

exists in the material or the density of the material is strongly dependent on the method of preparation.

4. Conclusions

We have confirmed the anti-CdI₂ structure for Ag₂F. In view of this the radiographic work of Bruno and Santoro [10] seems questionable. It is difficult to envisage a situation which would allow the complete separation of the ¹¹⁰Ag doped into the single existing crystallographic site of Ag₂F. No evidence for a structural phase transformation was found between 20 K and 300 K, although a pronounced minimum in the 'c' lattice parameter exists between 50 K and 100 K. The polycrystalline sample prepared in this study was found to have about 0.2% internal strain at room temperature and a grain size between 0.1 and 3 μm. As with the electrical resistivity, the thermal expansion and vibrational behaviour of this material is very anisotropic. The expansion coefficient is much smaller along the c axis than in the planes, while vibration amplitudes along the c axis are much larger than the in-plane amplitudes. The Ag-F bonding is much weaker than that found in AgF despite the similarity in their bond lengths. The claim by Pauling [13] and others [4, 6, 9, 14] that Ag₂F is a rare example of mixed metallic and ionic bonding is incorrect. While metallic behavior certainly exists in the Ag planes, the Ag-F bonding is intimately affected by the mixed-valent condition of the Ag.

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