

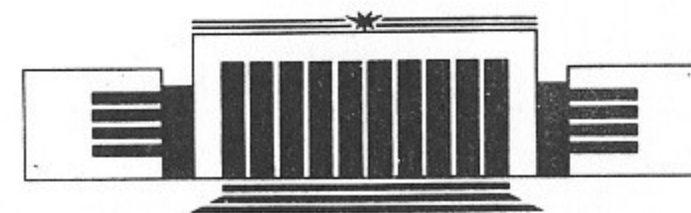


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ИНСТИТУТ ЯДЕРНОЙ ФИЗИКИ
им. Г.И. Будкера СО РАН

B.P. Tolochko, S.V. Chernov,
S.G. Nikitenko, D.R. Whitcomb

DETERMINATION OF THE CRYSTAL
STRUCTURE OF SILVER STEARATE
AND ITS TEMPERATURE CHANGES
BY AG K-EXAFS SPECTROSCOPY

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НОВОСИБИРСК

Determination of the Crystal Structure of Silver Stearate
and its Temperature Changes by Ag K-Exafs Spectroscopy

B.P. Tolochko, S.V. Chernov, S.G. Nikitenko, D.R. Whitcomb
Budker Institute of Nuclear Physics
630090, Novosibirsk, Russia

Abstract

Structure of silver stearate has been refined using Ag K-EXAFS spectroscopy and known unit cell parameters. The positions of the atoms of unit cell and silver-atom bond distances and angles have been determined: the silver carboxylate complex is similar to other short chain silver carboxylate and is a dimer formed from an 8-membered ring comprised of two silver atoms bridged by two carboxylate from the stearate molecules. The Ag-Ag distance is 2.9 Å, similar to the bond distance in metallic silver. Temperature significantly affects the structure, based on the data it is proposed that the silver atoms shift to new positions as the temperature is increased. Upon further increase, these positions become unstable, which appears to give rise to new constructions with the Ag-Ag distances at 4.2 Å.

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1. Introduction

The unit cell of silver stearate, and other carboxylate having long alkyl chains, has been known for a long time [1], however, until now, the coordinates of atoms located inside the unit cell, and particularly those of silver coordination sphere, have remained completely unknown. This problem normally would be solved by x-ray structural analysis of a single crystal, but it has not possible to grow a silver stearate single crystal sufficiently large with adequate quality for this technique. In this work, the Ag K-EXAFS spectroscopy has been used to determine the spacing between the silver atoms and their nearest neighbors, oxygen and carbon atoms. Proceeding from these spacings and the geometry of the molecule, we have determined the positions of the atoms in the unite cell. In this case, the angular characteristics of the atomic positions were chosen so that these would be similar to those typical of the known chemical compounds with similar spacings and the way the atoms are bonded.

Also, in this work, the changes in the positions of the silver atoms as function of temperature were followed using Ag K-EXAFS spectra taken at 25, 70, 100 and 120 C°. An analysis of temperature changes in the amplitude of the EXAFS signals and associated distances suggests that temperature has an effect on the silver atoms positions. At high temperatures (100 and 120 C°) the character of EXAFS signals indicates that a some of the silver stearate molecules rearrange to form new complexes with a spacing between the silver atoms of 4.20 Å.

Chapter 2 gives the procedure whereby the positions of the stearate atoms

inside the unit cell were determined EXAFS-spectrum taken at room temperature. Chapter 3 gives an analysis of the EXAFS-spectrum at 70 C° and new unstable positions of silver in the unit cell. In Chapter 4 the high-temperature EXAFS-spectra at 100 and 120 C° are discussed and a proposal is made that silver atoms are released from the stearate molecules to form the new molecule constructions with the Ag-Ag distances at 4.2 Å.

2. Positions of atoms in silver stearate unit cell

EXAFS-spectra were obtained on EXAFS-station of the storing ring of VEPP-3 at the Siberian Synchrotron Radiation Center of Institute of Nuclear Physics of Siberian Branch of Russian Academy of Science. The beam energy was 2 GeV and the current was 100 mA. Measurements were conducted according to a "transmission" procedure. A double modular crystal Si(111) monochromator was used [2]. EXAFS spectra were recorded by the *K*-edge of absorption of silver at a spacing of ~1.37 eV. In this operating region, the contribution of high harmonics is insignificant, therefore the effect of these was neglected. Ionization chambers filled with argon were used as detectors.

The oscillating member — $\chi(k)$ was derived according to a conventional procedure. The region near the Ag *K*-edge was extrapolated to the region of EXAFS oscillation by the Victoreen type polynomials. The fair region of the adsorption spectra was constructed as a combination of smoothing cubic splines. Radial distribution function were obtained using the Fourier-transformation of $k\chi(k)$ in the range 2.5 — 11.5(1/Å).

As is well known, the positions of the peaks of radial distribution functions only approximately correspond to the spacing between the excited atom and its neighbors. To obtain the actual distances, a phase shift typical of each sort of atoms should be added to the distance determined from the radial distribution function. The nature of the shift is associated with an additional displacement of phases as the wave of an excited electron is scattering in the potential of atoms. The phase shifts are determined most reliably in experiment using a reference. For this purpose, silver acetate with a well known arrangement of atoms inside its unit cell was used. A good coincidence of the model and experimental spectra was obtained. The phase shifts were as follows: 0.7 Å for carbon, 0.6 Å for oxygen, 0.2 Å for silver. Since the value of phase shifts is independent of the chemical state of atoms, these values were used for the interpretation of the EXAFS spectra of silver in the structure of silver stearate at all the temperatures: 25, 70, 100 and 120 C° (Fig. 1).

The structure of a number of silver carboxylates, Ag(O₂CR) has been

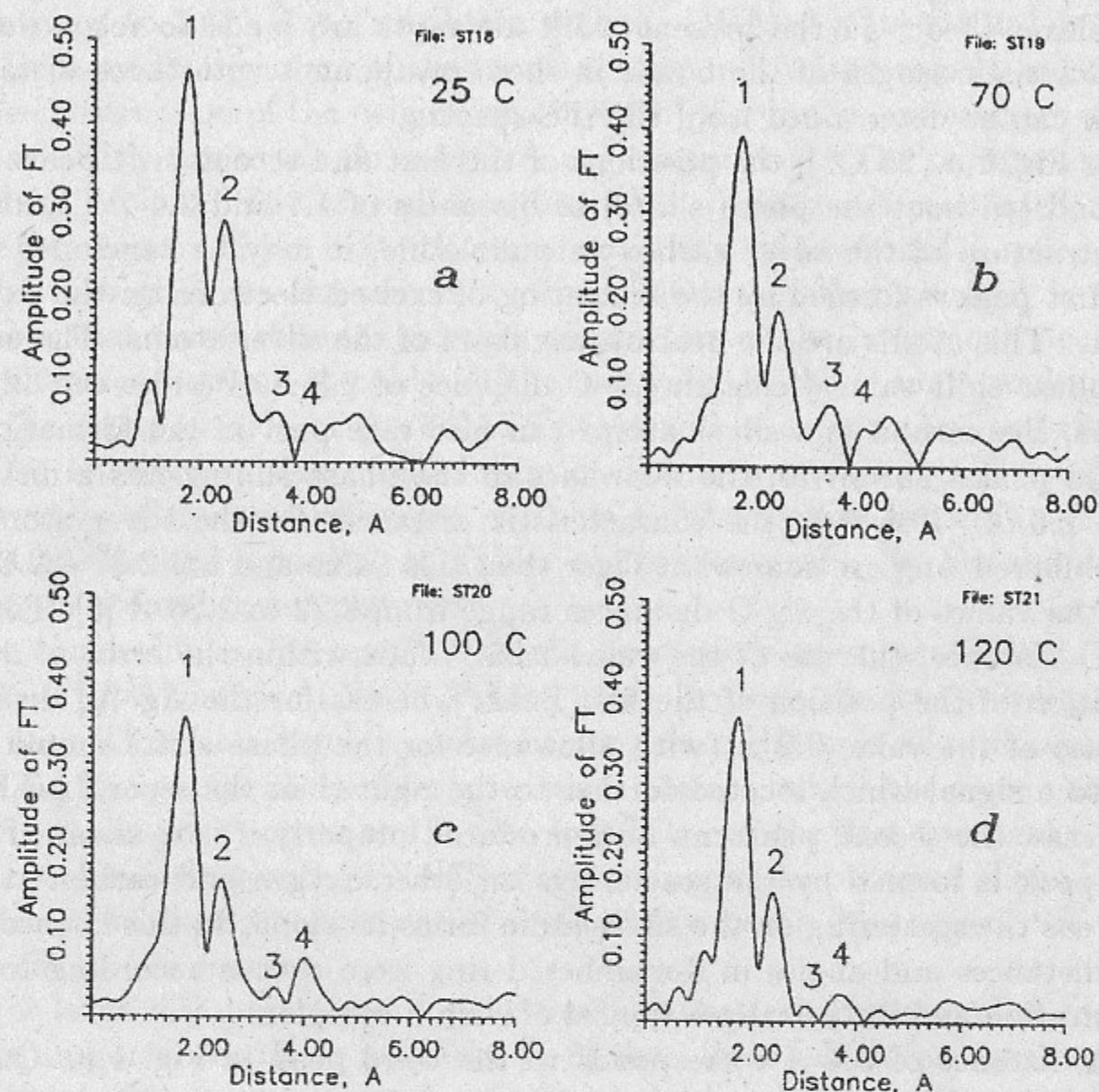


Fig. 1. The Fourier transform of Ag *K*-edge EXAFS (without phase correction) from washed silver stearate (powder) at the temperatures: a) 25 C°, b) 70 C°, c) 100 C°, d) 120 C°.

studied elsewhere [1]. *R* is a hydrocarbon (methylene) chain with different number of carbon atoms. For silver stearate, this number is 18. The silver carboxylates studied in [1] has triclinic layered structure with two molecules in the unit cell. At 20 C°, the parameters of the unit cell of silver stearate are as follows: $a = 4.693 \text{ \AA}$, $b = 4.120 \text{ \AA}$, $c = 50.35 \text{ \AA}$, $\alpha = 104^\circ 35'$, $\beta = 93^\circ 56'$, $\gamma = 76^\circ 1'$. To interpret the EXAFS-spectra at 25 C°, it has been suggested that hydrogen atoms are in the plane of the zigzag of carbon atoms of the methylene tail, and the silver, carbon and oxygen atoms of two molecules form the [Ag(O₂CR)]₂ dimer through an 8-membered ring in the

same plane. A lot of structural works have shown that the formation of 8-membered ring with the participation of two silver atoms is typical for similar complexes [3-5]. In the present work attempts are made to reconcile the characteristic length of the bonds in these compounds with those distances which can be determined from EXAFS-spectra.

In Fig. 1,*a* (25 C°), the positions of the first and second true peaks correspond (without the phase shifts) to distances of 1.7 and 2.4 Å. Knowing the structure of the silver carboxylate molecule, it may be concluded that the first peak is formed by the scattering of excited electrons on the oxygen atoms. These atoms are the nearest neighbors of the silver atoms. The use of the phase shift value yields an Ag-O distance of 2.3 Å. Besides the oxygen atoms, the carbon and silver atoms can also take part in the formation of second peak. For silver, the allowance of the phase shift yields a distance of ~ 2.6 Å. However, the characteristic distances for the silver atoms in 8-membered ring are somewhat larger than this value and are 2.87 - 2.97 Å, and the values of the Ag-O distances range from 2.22 to 2.25 Å [5]. For the Ag-O distance, the use of the value 2.25 Å falls within the error of determination of the position of the first peak, whereas for the Ag-Ag distance the use of the value 2.9 Å (with allowance for the phase shift) should give rise to a signal which is located further to the right than the second peak. In this case, the second peak can be reproduced properly if it is assumed that this peak is formed by the scatterings on other oxygen and carbon atoms, whereas the scattering on the silver atom forms its slope. In this connection, the distances and angles in 8-membered ring were chosen according to this assumption and in the ranges typical of such a complex.

A distance of 3.4 Å corresponds to the third peak in Fig. 1,*a*. On the assumption that this is associated with the scattering on the silver atom of the neighboring dimer, one more Ag-Ag distance of 3.6 Å is obtained. This distance is typical of 4-membered ring composed of two silver atoms and two oxygen atoms [6]. Thus, our following suggestion is that silver stearate dimers are bonded with each other in one plane via such 4-membered rings. Further, the distances and angles between the atoms were chosen in such a way as to satisfy better the positions of the peaks in Fig. 1,*a*. At the same time, these distances and angles should fall within the range of values typical of 4-membered ring.

The results of this are given in Tables 1-3 and in Fig. 2. It should be noted that the construction of neighboring dimers cannot be made without changing the angle γ . Otherwise, as the Ag(3)-Ag(2a) distance Fig. 2 remains 3.60 Å, the Ag(2a) and O1(3) atoms should locate improbably close to each other, and the O1(3)-Ag(2a)-O1(2a) angle should be considerably smaller

than a typical value of ~ 83 - 84° [6]. By choosing the Ag(2a)-O1(3) distance equal to 2.625 Å [6], we obtain that the O1(3)-Ag(2a)-O1(2a) angle is 84°. Such an arrangement of the atoms corresponds to the value $\gamma = 82^\circ 25'$. In the construction of the neighboring layers of the dimers, parameters of the unit cell with this new value of the γ angle were used. The parameters are listed in Table 4. The crystallographic $d(h, k, l)$ distances calculated using these parameters of the unit cell agree with their values from [1] even somewhat better than for the previous γ angle. On the other hand, it is quite possible that small changes in other parameters of the lattice can decrease the difference between the old and the new value of the γ angle, and in this case the interpretation of the EXAFS peaks will be satisfactory, as before.

The relative position of the layers of dimers was constructed using the parameters of the unit cell given in Table 4. The view of the unit cell with the atoms located according to Tables 1-3 is given in Fig. 3. For simplicity, hydrogen atoms are not pictured.

In conclusion, some remarks should be made concerning Table 1. The Ag(3)-O1(2a) distance (N_2 in Table 1) falls between the first two peaks in Fig. 1,*a*. This fact is not a contradiction, since this was also the case for the EXAFS spectra of the reference, silver acetate, where the same value of the Ag-O distance occurs and it also falls between the first two peaks. The numerical modeling of the EXAFS spectra support the observed shape of the spectra. The close arrangement of the first two peaks "slurs over" the peak from the above distance.

For large distances (> 4 Å), the multiple scattering effects is of considerable importance. It is noted in [7-8] that these effects are particularly significant if there are atoms located near the line between the central and back scattering atoms. It is suggested that such an effect brings about the screening of the $N_{20, 21}$ and N_{22} distances (Table 1) which are somewhat large than the distances corresponding to peak 6 (Fig. 1,*a*). Thus, if the change in the phase shift for the Ag(3)-Ag(2) distance due to the screening of Ag(2) by the O1(2a) oxygen (Fig. 2) is roughly estimated by a direct addition of the phase shifts of these atoms: $d = 0.2 + 0.6$ Å, the position of the EXAFS peak will be $5.82\text{Å} - d = 5.02$ Å, which coincides well with the position of the sixth peak in Fig. 1,*a* (~ 4.9 Å). Besides, another reason for which this explanation seems to be proper is that at 70 C°, a shift of the sixth peak by 0.7 Å (4.9 → 5.6 Å) is observed in Fig. 1,*b*, which appears to be associated with a considerable decrease in the screening of the Ag(2) atom due to the relative temperature shift of the oxygen and silver atoms. Analogous estimation of the screening of the Ag(2)-C2(3) and Ag(2)-C3(3a) distances show that these occur on the slope of the sixth EXAFS peak.

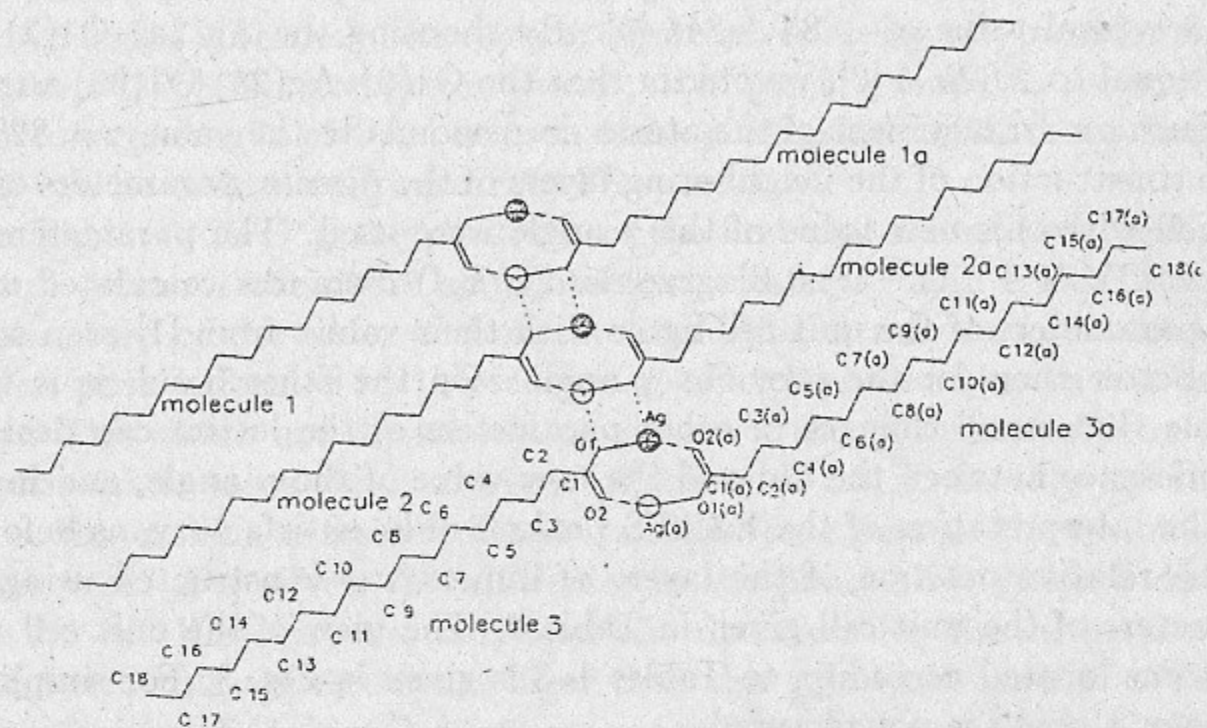


Fig. 2. The displacement of atoms in one layer of silver stearate crystal at room temperature (20 C°).

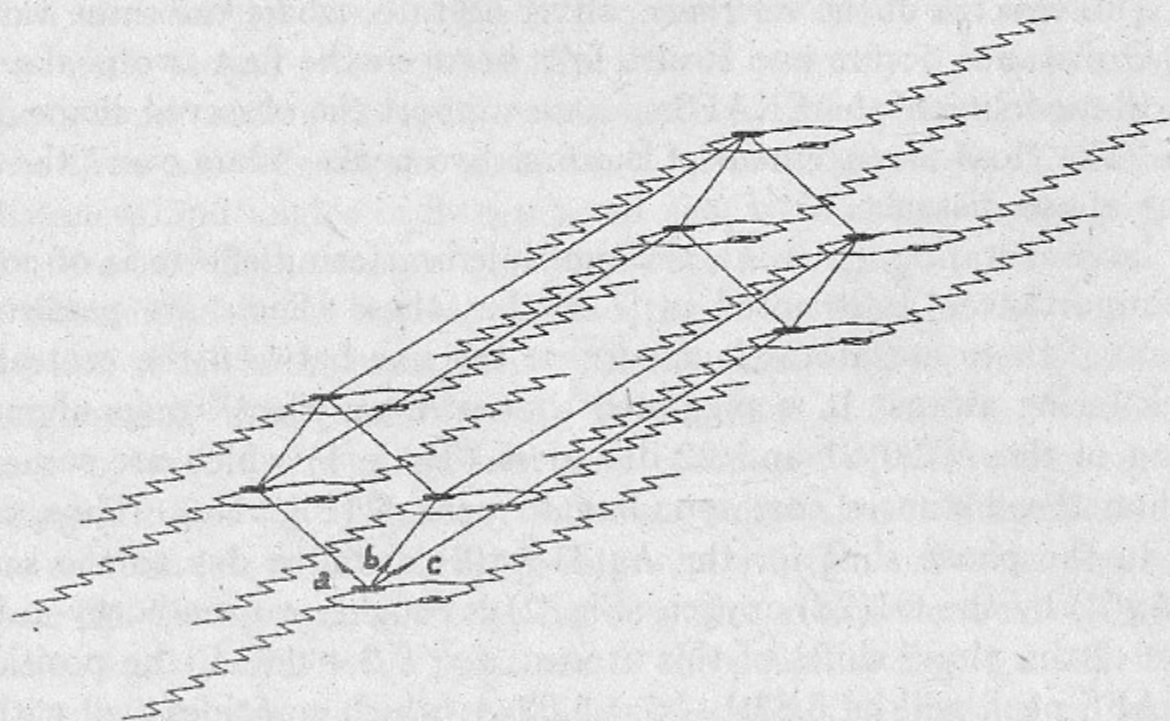


Fig. 3. The 3-dimensional unit cell of silver stearate.

3. Temperature changes in structure of silver stearate

A comparison of the EXAFS spectra of silver stearate at 25 and 70 C° (Fig. 1, (a-b)) shows that there are changes which cannot be explained only by a temperature decrease in the amplitude of the spectra. Thus, at 70 C° EXAFS peaks 2 and 3 are more clearly separated one from the other, and the amplitude of peak 3 increases in comparison to peak 1. At the same time, the right slope of peak 2 disappears. This can be accounted for by an increase in the spacing of the silver atoms, due to which the associated EXAFS signal is separated from the second peak and merges with the third peak. In this case the Ag(3)-Ag(3a) distance increases from 2.9 Å to ~ 3.6 Å (in Fig. 1, b - $3.45 + 0.2 = 3.65$ Å).

It should be noted that as the distance increases, the amplitude of the EXAFS signals rapidly decreases, as $\sim 1/R$. Therefore marked peaks can be formed either from a group of atoms with appropriate spacings or from an atom with large nuclear charge Z . In the present case, Ag with $Z = 47$ is such an atom. Therefore the suggestion that the increase of peak 3 with respect to 2 is predominantly associated with a shift of the Ag atom appears to be reasonable. The same is supported by a comparison of the values from Table 1 and Fig. 1, a. The position of any silver atoms corresponds to each peak at long distances.

To account for the entire character of the EXAFS spectra, attempts have been made to understand the possible temperature shift of the silver atom to a new position, proceeding from the shape of the unit cell obtained in the previous Chapter (Fig. 1-2). The shift of the silver atoms is due to their close arrangement in the dimer: the Ag(3)-Ag(3a) distance is ~ 2.9 Å. This distance is typical of silver atoms in metals. It is associated with a considerable interaction of these atoms and should increase with a rise in temperature. In turn, in the structure shown in Fig. 2 almost an equivalent position of silver atoms exist from the viewpoint of the nearest oxygen-carbon surrounding. In Fig. 4 these positions are demonstrated and new distances are given in Table 4. For these positions, the Ag(3)-Ag(3a) and Ag(2a)-Ag(3) distances are the same and are equal to 3.6 Å. The new Ag(3)-O1(2a), Ag(3)-O(3a) and Ag(2a)-Ag(3) distances are equivalent to the distances in 8-membered ring of the dimer (see Tables 1 and 4). The O-Ag-O and Ag-O-C angles also have similar values. Such a displacement of the silver atoms indicates the cleavage of the bond of the silver with the oxygen and the formation of an equivalent bond of silver with a new. In this case, the old oxygen bond is saturated with another silver atom, i.e. the silver atoms exchange the oxygen atoms. This displacement of silver atoms appears to proceed synchronously

not only for two molecules of the dimer, but also for several molecules of the neighboring dimers at once. The process propagates further to new regions, since small energy is required to initiate the collective displacement process. It is suggested therewith that the dimensions and shape of the (O_2CR) — carboxylate complex are essentially unchanged because of the strong bond among the atoms. It is believed that as a result of such a displacement of silver atoms, this complex would turn out to be in an unstable state with respect to the turn, which can restore the position of $C1(3a)$ and $O_2(3a)$ relative to $Ag(3)$, analogous to their position in 8-membered ring. Conceivably, this might further bring about the rotation of the hydrocarbon chains, as noted in an experimental study of the temperature transformations in silver stearate [9].

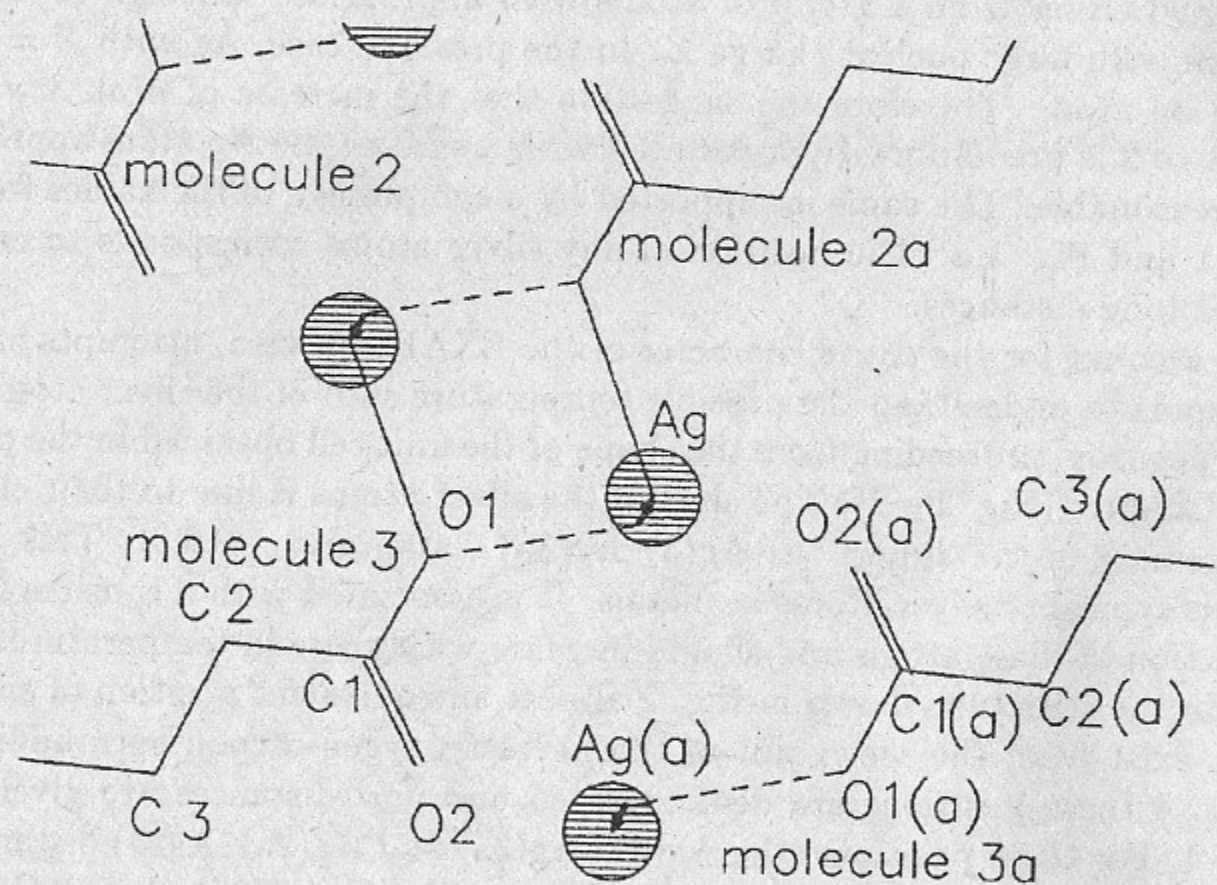


Fig. 4. The shift of the silver atom in the new positions at 70 C°. Arrows show the temperature shifts of the silver atom.

4. High-temperature transformations

A comparison of changes in the amplitudes of peaks 3 and 4 (Fig. 1, b and 1, c) shows that at 100 C°, a certain amount of silver stearate molecules break down to form some new compounds with a characteristic spacing between silver atoms of 4.20 Å. The first two peaks are indicative of the presence of silver stearate molecules. In this case, two peaks associated with two nearest spacings of silver and the oxygen and carbon atoms are observed, as before. The absence of regular peaks of marked amplitude at long distances, as was the case at 25 and 75 C°, points to a severe disordering of the structure. More distant peaks of this molecule do not correspond to the positions of the silver atoms and therefore these are considerably decreased due to both long distances and the temperature factor. The third peak at a distance of 4.0 Å at 100 C° can be associated only with silver. With allowance for the phase correction, the Ag-Ag distance is ~ 4.2 Å. Since this distance is much greater than the characteristic distances in metallic silver, the silver atoms should be bonded through a certain mediator. It is suggested that this mediator can be the oxygen and carbon atoms of carboxylate complex turned from the layer of dimers. In this case, the silver atoms of new complex are in different layers.

At 130 C° two peaks are observed in Fig. 1, d as before, which is indicative of the presence of silver stearate molecules. At the same time, the rest of the structure is severely suppressed by the temperature factor and provides no possibilities for analysis.

5. Conclusion

The atomic positions of silver stearate molecules have been determined by Ag K-EXAFS spectra, the silver atoms are bridged by the carboxylate in the form of dimers in an 8-membered ring, and the dimers are further bonded to each other by longer Ag-O bonds forming 4-membered rings. The γ angle of unit cell has been corrected to take the molecular structure into consideration, otherwise, the length of the bond between the silver and oxygen atoms in a silver stearate molecule would be larger than that between the same silver atom and oxygen atom of the neighboring dimer. While the EXAFS approach used herein cannot compete in accuracy with the diffraction method the important atomic bond distances and angles of significant structural problems, such as that described above, can be resolved with reasonable error limits. The above considerations are based on the interpretation of characteristic dimensions, which can be derived from the position of EXAFS signals, and on a comparison of these with the geometry of known structures. Also, at

70 C°, the displacement of silver in the silver stearate structure into a new position occurs in another way.

References

- [1] V. Vand, A. Aitken. Campbell R.K. Acta Cryst. v.2, (1949), 398.
- [2] V.A. Chernov, I.B. Drobyazko, S.G. Nikitenko. SSRC Activity Report-1990. INP, Novosibirsk, p.114-115, (1991).
- [3] C.B. Acland, H.C. Freeman. Chem. Commun. N17, (1971), 1016.
- [4] M. Hedrich, H. Hartl. Acta Cryst. C39, (1983), 1649
- [5] B.T. Usubaliev, E.M. Movsumov and et.al. Zurnal structurnoyi himii (Russ.) v.22(1), (1981), 98.
- [6] M. Hedrich, H. Hartl. Acta Cryst. C39, (1983), 1649.
- [7] G. Bunker, E.A. Stern. Phys. Rev. Lett. v.52, (1984), 1990.
- [8] B.K. Teo. J. Am. Chem. Soc. v.103, (1981), 3990.
- [9] V.M. Andreev, L.P. Burleva, V.V. Boldyrev. Izvestiya Vusov SO AN SSSR: Him. nauk. v.5, (1984), 3.

Table 1.

The atomic distances of the nearest neighbors of the silver atom in silver stearate at the temperature of 25 C°.

n	couple	distance (Å)	number of atoms	EXAFS peak number
1	Ag(3)-O1(3)	2.25	2	1
2	Ag(3)-O1(2a)	2.625	1	(between 1 and 2)
3	Ag(3)-O2(3)	3.34	2	2
4	Ag(3)-C1(3)	3.135	2	2
5	Ag(3)-Ag(3a)	2.90	1	2
6	Ag(3)-C1(2a)	3.59	1	2
				(right slope)
7	Ag(2a)-Ag(2)(A) (from A layer)	3.22	1	(between 2 and 3)
8	Ag(3)-C2(2a)	3.73	1	(between 2 and 3)
9	Ag(3)-Ag(2a)	3.60	1	3
10	Ag(2a)-Ag(3)(C)	4.03	1	4
11	Ag(3)-Ag(3)(A,C)	4.12	2	4
12	Ag(3)-O2(2a)	4.69	1	4
13	Ag(3)-C2(3a)	4.59	1	4
14	Ag(3)-Ag(2)(A,C)	4.69	2	5
15	Ag(3)-C3(3a)	5.00	1	5
16	Ag(3)-C3(2a)	5.27	1	5
17	Ag(3)-C3(3)	5.68	1	6
18	Ag(3)-C4(2)	5.94	1	6
19	Ag(3)-O2(2)	5.72	1	6
20	Ag(3)-Ag(2)	5.82	2	6
21	Ag(2)-C2(3)	6.52	1	6
22	Ag(2)-C3(3a)	6.54	1	6

Examples of

designation (see Fig. 2-3):

1) C3(2a) — Atom C3 of 2a molecule from B (middle) layer.

2) Ag(3)(A,C) — Atom Ag of 3 molecule on Fig. 2 from A (downer) and C (upper) layers of dimers on Fig. 3.

Table 2.

Atomic distances in the silver stearate molecule at the temperature of 25 C°
(Fig. 2)

N	Atoms	Distance (Å)
1	Ag-O1	2.25
2	Ag - O2(a)	2.25
3	Ag - Ag(a)	2.90
4	Ag(a) - O2	2.25
5	Ag(a) - O2(a)	2.25
6	O1 - C1	1.20
7	O2 - C1	1.20
8	C1 - C2	1.54
9	C2 - C3	1.54
...		

Table 3.

Atomic angles in the silver stearate molecule at the temperature of 25 C°.
In the bracket there is the number of a molecule on Fig. 2

N	Atoms	Angle (grad)
1	Ag(3)-O1(3)-C1(3)	128°
2	O1(3)-Ag(3)-O2(3a)	160°
3	O1(3)-Ag(3)-O1(2a)	84°
4	C3(3)-C2(3)-C1(3)	112°
5	C1(3)-O1(3)-Ag(3)	128°
6	O1(3)-C1(3)-C2(3)	113°
7	C1(3a)-C1(3)-C3(3)	151°

Table 4.

Parameters of the unit cell of silver stearate crystal

a=	4.69 (Å)
b=	4.12 (Å)
c=	50.35 (Å)
α=	104°35'
β=	93°56'
γ=	82°25'

Table 5.

The atomic distances of the nearest neighbors of the silver atom in silver stearate at the temperature of 70 C°.

N	Couple	Distance (Å)	Quantity of neighbors	Number of EXAFS peak
1	Ag(3) - O2(3a)	2.2	1	1
2	Ag(3) - O1(2a)	2.3	1	1
3	Ag(3) - O1(3)	2.5	1	1
4	Ag(3) - C1(3a)	3.2	1	2
5	Ag(3) - C1(2a)	3.2	1	2
6	Ag(3) - C2(2a)	3.4	1	2
7	Ag(3) - C1(3)	3.5	1	2
8	Ag(3) - O1(3a)	3.5	1	right slope between 2 and 3
9	Ag(2a)-Ag(2)(A)	3.1	1	between 2 and 3
10	Ag(3) - Ag(3)	3.6	1	3
11	Ag(3) - Ag(2a)	3.6	1	3
12	Ag(3) - O2(3)	3.7	1	3
13	Ag(3) - C2(3a)	4.1	2	3
14	Ag(3) - O2(2a)	4.3	1	3
15	Ag(3)-Ag(3)(A,C)	4.2	2	4
16	Ag(2a)-Ag(3)(C)	4.1	2	4
17	Ag(3) - C3(2a)	4.9	1	4
18	Ag(3) - C3(3a)	4.8	1	4
19	Ag(3) - C2(3)	4.8	1	4
20	Ag(3)-Ag(2)(A,C)	4.7	2	5
21	Ag(3) - Ag(2)	5.75	1	6

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*Б.П. Толочко, С.В. Чернов,
С.Г. Никитенко, Д.Р. Виткомб*

**Кристаллическая структура стеарата серебра
и ее температурные изменения, определенные по EXAFS**

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