

## Raman scattering behavior of hybrid polymeric complexes of polyvinyl alcohol with $\text{CuCl}_2$ and $\text{Cu}(\text{OH})_2/\text{CuO}$

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It is shown that Raman spectra of PVA- $\text{CuCl}_2$  and PVA- $\text{Cu}(\text{OH})_2/\text{CuO}$  complexes recorded at 514.5 nm excitation have similar shape with prominent background and broad band at  $1590\text{ cm}^{-1}$ . They are identical to spectra of PVA complexes' with other inorganic compounds, spectra of different carbonaceous materials — polyacetylene, graphite and nanotubes and PVA's SERS spectrum. This result is regarded as a consequence of one-dimensionality of investigated materials. Raman bands of PVA,  $\text{Cu}(\text{OH})_2/\text{CuO}$ , and CuO are present in PVA- $\text{Cu}(\text{OH})_2$  complexes' spectra at 1064 nm excitation.

**Keywords:** low-dimensional systems, SERS.

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### 1. Introduction

One-dimensional structures attract a lot of attention for their potential capabilities based on the manifestations of the quantization effect in their properties. One of these phenomena is — ballistic conduction [1]. Unfortunately, there is a lack of true one-dimensional polymer-like systems suitable for some practical applications. For example, it is relatively difficult to create polymers with high conductance and good (electro)luminescent characteristics. Currently, a small number of chain inorganic polymers are known, and the task of expanding their range is urgent. One of the ways to solve this problem [2] was previously proposed. It is based on the synthesis of hybrid interpolymer complexes with the participation of organic complexing polymers like polyvinyl alcohol (PVA). A well-known representative of such compounds is the PVA complex with iodine [3], in which iodine has the structure of linear polymer chains that form complexes with PVA chains like components of a DNA double helix. There was also the discussion of the hybrid interpolymer complex PVA- $\text{Cu}(\text{OH})_2$  [4,5]. There was an idea about the opportunity of synthesizing other similar hybrid interpolymer complexes [2]. Due to the lack of three-dimensional periodicity, confirmation of the polymer structure of materials is problematic. In this case, the Raman scattering (RS) spectroscopy can help. The Raman effect is due to the influence of molecular vibrations on the polarizability of molecules. This means that its singularities are determined by both vibrational modes and polarization properties of the material under study [6]. Therefore,

Raman spectroscopy provides additional opportunities to study the properties of a material compared to infrared spectroscopy. In particular, a method for identifying the polymer structure of an inorganic compound using the RS method [7,8] was previously proposed. It is based on the anisotropy of polarizability of conjugated polymers serving as substrates when observing an effect similar to SERS (Surface Enhanced Raman Scattering). In the SERS effect, as the name suggests, the enhancement of light scattering is due to the presence of a surface, i.e. two-dimensional heterogeneity of structure. In graphite, single carbon layers themselves can be considered such two-dimensional heterogeneities. Thus, graphite can be reviewed as a SERS substrate unto itself. In the same way, the one-dimensional polymer molecules in polyacetylene must themselves serve as a substrate for an effect similar to SERS, but now due to the one-dimensionality of the substrate. It could be called ChERS (Chain Enhanced Raman Scattering) by analogy. The Raman spectra of layered and chain carbon structures with conjugated bonds have common features:

1) similar general appearance with two main bands in the region  $1000\text{--}2000\text{ cm}^{-1}$ ;

2) relatively strong dependence of the position of these bands in the spectrum on the wavelength of the exciting radiation (tens  $\text{cm}^{-1}$  at the change of excitation from 514.5 nm to 1064 nm) [9,10].

The presence of these common features gives grounds to speak about a special mechanism for the formation of bands in the Raman spectra of anisotropic carbon structures with conjugated bonds. In this work, the RS method is

used to study the structure of the complexes PVA-CuCl<sub>2</sub> and PVA-Cu(OH)<sub>2</sub>/CuO. It is assumed that these complexes include inorganic coordination polymers that can serve as substrates to identify bands in the RS spectrum of an organic component (PVA). In other words, the complexes can be considered as solid solutions of inorganic polymers in an organic polymer. It is natural to expect that an inorganic polymer has very different polarizability components along and across the chain. In the presence of such a substrate, the Raman spectrum of PVA (or more precisely, the PVA complex) can have a characteristic appearance with bands similar to the D- and G-bands of carbon materials. The main goals of the work are to test this assumption, check the presence of the effect of frequency dispersion of the band positions, as well as search and interpret the vibrational bands of the inorganic component in the Raman spectra of the materials under consideration.

The PVA-CuCl<sub>2</sub> and PVA-Cu(OH)<sub>2</sub> complexes can be used as starting reagents in the synthesis of PVA complexes with copper chalcogenides (PVA-CuS, PVA-CuSe and PVA-CuTe) in accordance with the previously proposed method [2,11]. The PVA-CuO complex can be produced as a result of dehydration of the PVA-Cu(OH)<sub>2</sub> [12] complex. The linear CuO chain is a component of some high-temperature superconductors. Its isolation and study can be useful for establishing the nature of superconductivity.

## 2. Experimental

### 2.1. Preparation of samples

To prepare the samples we used: PVA of 18-88 grade, produced by BDH Chemicals Ltd, CuCl<sub>2</sub> · 2H<sub>2</sub>O, AlCl<sub>3</sub> · 6H<sub>2</sub>O and CuSO<sub>4</sub> · 5H<sub>2</sub>O of „analytically pure“ grade. Ammonia solution of Cu(OH)<sub>2</sub> was prepared by A.A. Sidelnikov, the senior staff scientist of Laboratory of Solid State Chemistry of the Institute of Solid State Chemistry and Mechanochemistry SB RAS.

The complexes with following stoichiometry were used in the measurements: 3 PVA units (–CH<sub>2</sub>–CHOH–) to 1 CuCl<sub>2</sub> or Cu(OH)<sub>2</sub>. An aqueous solution of CuCl<sub>2</sub> or an aqueous ammonia solution of Cu(OH)<sub>2</sub> was mixed with 10% wt. an aqueous solution of PVA in an appropriate proportion. This composition was poured onto a fluoroplastic plate and dried overnight at room temperature. After this, the films were separated from the plate. Heat treatment of the complex PVA-Cu(OH)<sub>2</sub> was carried out in a vacuum ~ 1 Pa at a temperature 150°C for 100 min with the aim of converting Cu(OH)<sub>2</sub> into CuO. The weight loss in this case was 12% instead of the calculated 8% (with the complete conversion of Cu(OH)<sub>2</sub> into CuO).

### 2.2. Specimen characterization

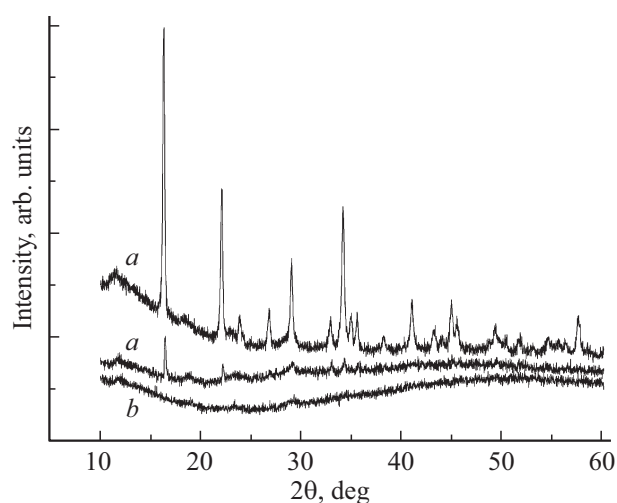
X-ray diffraction studies were carried out on a Bruker D8 Advance diffractometer using CuK<sub>α</sub> radiation.

The Raman spectra were studied using a Bruker RFS-100/S spectrometer equipped with a laser with a wavelength of 1064 nm and a Horiba Jobin-Yvon T64000 spectrometer equipped with a 514.5-nm laser. The resolution was 4 cm<sup>-1</sup>. All spectra were registered at room temperature. The measurement conditions excluded overheating of the sample by exciting radiation.

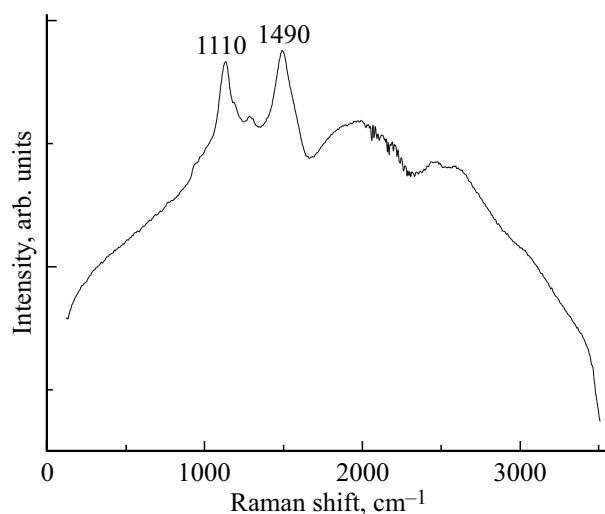
## 3. Results and discussion

The properties of the PVA-CuCl<sub>2</sub> complex have been previously studied [13,14], but its structure remains undetermined. To begin with, we determine the stoichiometric ratio of the components in the complex PVA-CuCl<sub>2</sub> constituting 3–4 of the PVA units (–CH<sub>2</sub>–CHOH) to the 1 molecular unit of CuCl<sub>2</sub> (~ 50% wt). At higher CuCl<sub>2</sub> contents, it is released as a crystalline phase of dried samples. At a lower content of CuCl<sub>2</sub>, an amorphous complex of nonstoichiometric composition is formed. Accordingly, X-ray diffraction analysis reveals the presence of a crystalline phase at a higher content of CuCl<sub>2</sub> (Figure 1). This result agrees with data from other authors [13]. There was also the effect of displacement of excess CuCl<sub>2</sub> from the forming complex upon drying of the samples. Thus, it follows from Figure 1 that two regions of the sample have different contents of the crystalline phase.

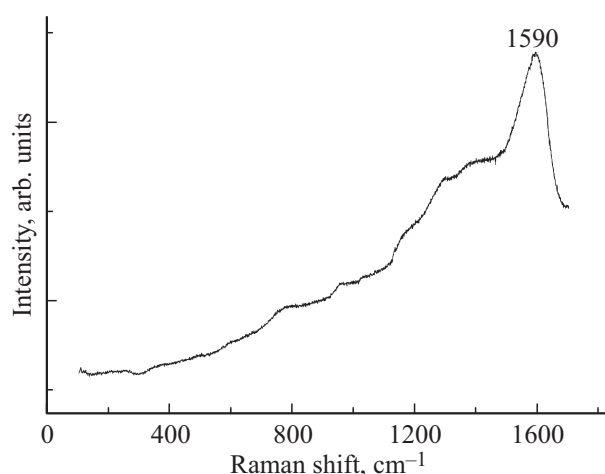
We did not manage to obtain the Raman spectrum of the PVA-CuCl<sub>2</sub> complex at the excitation by light with a wavelength of 1064 nm, since under the influence of such radiation there was either a change in the material (at a relatively high level of excitation) or no useful signal was detected. At a low level of excitation, the spectrum of the sample PVA-CuCl<sub>2</sub> with a 2% impurity AlCl<sub>3</sub> (relative to CuCl<sub>2</sub>) was managed to be recorded which turned out to be similar to the Raman spectra of graphite, polyacetylene [9],



**Figure 1.** Diffraction patterns of PVA-CuCl<sub>2</sub> samples with the ratio of components (number of PVA units to CuCl<sub>2</sub>) a) 2.5 : 1 (from different areas) and b) 3 : 1.



**Figure 2.** Raman spectrum of PVA-CuCl<sub>2</sub> sample with 2%AlCl<sub>3</sub> impurity. Excitation by low intensity radiation at a wavelength of 1064 nm.



**Figure 3.** Raman scattering spectrum of a PVA-CuCl<sub>2</sub> sample (with an admixture of 2% Al) upon excitation at a wavelength of 514.5 nm.

dehydrated PVA [15], a PVA complex with iodine [8] and a PVA-CdS [7] compound. It is possible that the sample changed under the influence of radiation, although no signs of heating were detected. The obtained spectrum contains an intense background and two bands in the region of 1110 and 1490 cm<sup>-1</sup> (as well as a weak band at 1290 cm<sup>-1</sup>) (Figure 2). In the case of layered carbon materials such as graphite, there are reasons for attributing the low-frequency band to vibrations localized near structural defects (D-band). This interpretation of the low-frequency band is not suitable for conjugated chain structures, since the influence of edge atoms on the spectrum in them can be neglected. The proposed interpretations of the high-frequency and low-frequency bands as appearances of stretching vibrations of fragments C=C and C-C [9] are

not compatible with ideas about the delocalization of bonds in conjugated chain polymers. We believe that this type of spectrum is caused by analogue of the SERS effect, and to some extent it reflects the function of the density of vibrational states of the material under study. The SERS substrate in this case is one of the components of the complex — under study polymer chains —(CuCl<sub>2</sub>)<sub>n</sub>—. At a high level of excitation, thermal destruction of PVA occurs, and the final spectrum of the sample takes on shape of an intense structureless background. This interpretation is supported by the similarity of the spectrum we obtained with the well-known SERS spectrum of PVA obtained on a traditional silver substrate [16].

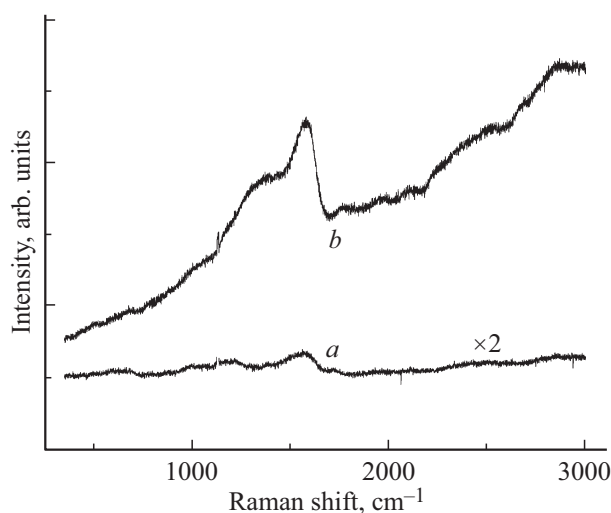
When excited at a wavelength of 514.5 nm, the Raman spectrum of the PVA-CuCl<sub>2</sub> sample doped with aluminum has the form of a structureless background with one noticeable band in the 1590 cm<sup>-1</sup> region (Figure 3), similar to the G-band of carbon materials. In general, it appears that we are seeing the same effect as one for polyacetylene, the PVA-iodine complex, and the PVA-CdS compound, where distinct bands similar to the carbon D and G bands are detected. Meanwhile, there are differences in their position. One important difference should be noted from the case with the PVA-CdS sample. The effect appears on the doped PVA-CuCl<sub>2</sub> sample, while it disappears on the aluminum-doped PVA-CdS sample. In other words, in the case of the PVA-CdS sample, it was found that the addition of aluminum (1%wt. AlCl<sub>3</sub> to the original CdCl<sub>2</sub>) results in the disappearance of the 1110 and 1490 cm<sup>-1</sup> bands and the appearance of PVA own bands in its Raman spectrum [7], which was explained by the breakage of inorganic polymer chains —S—Cd—S—Al=S, leading to a critical decrease of their longitudinal polarizability. In the case of PVA-CuCl<sub>2</sub>, the heterovalent additive does not result in termination of the polymer chain  $\text{>Cu}<\begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix}\text{>Al}<\begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix}\text{>Cu}<$ , but, ap-

parently, it can result in an increase of its longitudinal polarizability, just as the addition of a heterovalent impurity results in an increase of the conductance of semiconductors. In general, we believe that the results obtained confirm the formation of the structure of the linear coordination polymer —(CuCl<sub>2</sub>)<sub>n</sub>— as a component of the PVA-CuCl<sub>2</sub> complex and the similarity of its electronic properties to the properties of conjugated polymers, which determine the shape of their Raman spectra.

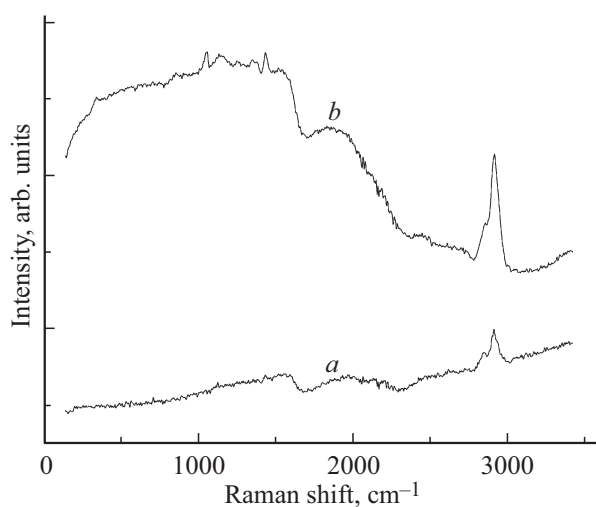
The PVA-Cu(OH)<sub>2</sub> complex is second only to the PVA-iodine complex, whose structure has been interpreted by other researchers as a form of hybrid interpolymer complex [4,5]. This provides grounds for testing our method for identifying the structure of hybrid interpolymer complexes from their Raman spectra. When determining the stoichiometric ratio of components in the PVA-Cu(OH)<sub>2</sub> complex using a method similar to that described above [12], it turned out that it is approximately the same as for the PVA-CuCl<sub>2</sub> complex — 3 units PVA (—CH<sub>2</sub>—CHOH—) to 1 molecular unit Cu(OH)<sub>2</sub>. After that, it was found

that when excited at a wavelength of 514.5 nm, the Raman spectrum of the PVA-Cu(OH)<sub>2</sub> complex is similar to the spectrum of the PVA-CuCl<sub>2</sub> complex, with a weak characteristic band in the region of 1590 cm<sup>-1</sup> (Figure 4). After heating the sample in a vacuum, its spectrum became more distinct, with a well-defined band similar to the G-band of carbon materials. When using exciting radiation with a wavelength of 1064 nm, the spectrum looks different (Figures 5–7). In this case, there are vibrational lines of the original PVA and the background. The difference in the spectra obtained upon excitation at different wavelengths can be explained by the spectral sensitivity of the SERS effect [17].

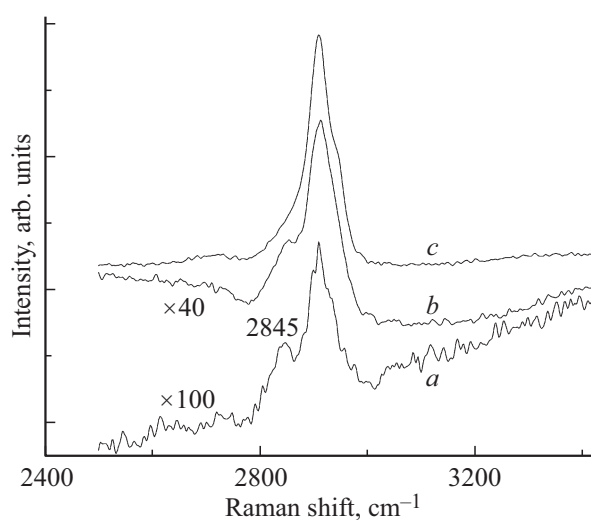
The characteristic band in the region of 2845 cm<sup>-1</sup> in the spectrum of the PVA-Cu(OH)<sub>2</sub> complex can be



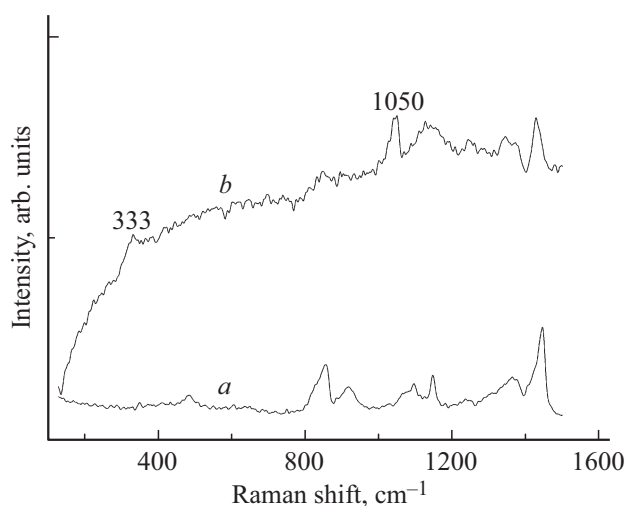
**Figure 4.** Raman spectrum of the PVA-Cu(OH)<sub>2</sub> complex *a*) before and *b*) after heating upon excitation at a wavelength of 514.5 nm.



**Figure 5.** Raman spectrum of the PVA-Cu(OH)<sub>2</sub> complex *a*) before and *b*) after heating. General view when excited at a wavelength of 1064 nm.



**Figure 6.** High-frequency region of the Raman spectrum of the PVA-Cu(OH)<sub>2</sub> complex *a*) before and *b*) after heating and *c*) the initial PVA upon excitation at wavelength 1064 nm.



**Figure 7.** Low- and mid-frequency regions of the Raman spectrum of *a*) original PVA and *b*) PVA-Cu(OH)<sub>2</sub> complex after heating with excitation at a wavelength of 1064 nm.

attributed to the stretching vibrations of the O–H group of copper hydroxide. Upon dehydration of the PVA-Cu(OH)<sub>2</sub> complex, it turns into „a shoulder“ on the PVA band (Figure 6). This means that the dehydration of Cu(OH)<sub>2</sub> in our case is incomplete. The band in the region of 1050 cm<sup>-1</sup> can be attributed to the residual impurity of the NO<sub>3</sub> group in Cu(OH)<sub>2</sub> synthesized from nitrate (Figure 7). Changes in the region 1050–1150 cm<sup>-1</sup> indicate the interaction of Cu(OH)<sub>2</sub>/CuO with the OH groups of PVA. There is also a clear decrease of the intensity of PVA bands in the 800–950 cm<sup>-1</sup> region. We attribute the band in the region of 333 cm<sup>-1</sup> to the polymer form of CuO. This band was previously detected in the spectra of nanostructures based on CuO [18–21]. However, it was weak in comparison

with other simultaneously observed nearby bands, the most intense among which was the band in the region 276 (282–288)  $\text{cm}^{-1}$ . The only band in the region of 276  $\text{cm}^{-1}$  was detected in  $\text{Cu}(\text{OH})_2$  [22].

#### 4. Conclusion

Based on a comparison of our results with the literature data, we can conclude that the spectra of the complexes PVA- $\text{CuCl}_2$  and PVA- $\text{Cu}(\text{OH})_2/\text{CuO}$  reveal features that allow them to be classified as hybrid interpolymer complexes, similar to the complex PVA-iodine. Namely:

- 1) the characteristic appearance of Raman spectra, in which there are two broad bands in the region 1000–2000  $\text{cm}^{-1}$ ;
- 2) a significant dependence of the position of the bands in the spectrum on the wavelength of the exciting radiation (frequency dispersion of the position of the bands);
- 3) influence of impurities
- and 4) the presence of the 333  $\text{cm}^{-1}$  band in the Raman spectra of the complexes.

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#### Conflict of interest

The authors declare that they have no conflict of interest.

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