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Intramolecular superconductivity and Raman scattering of dehydrated polyvinyl alcohol at room temperature

© I.Yu. Prosanov

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia

E-mail: prosanov@mail.ru

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Investigation of Raman scattering temperature dependence of dehydrated polyvinyl alcohol reveals a peculiarity at 340–380 K range which can be attributed to intramolecular superconducting transition.

Keywords: one-dimensional systems, Raman scattering, high-temperature superconductivity, polyacetylene.

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The author of the study of intramolecular diamagnetic currents in polyacetylenes in Ref. [1] believes that the corresponding superconducting transition in them can be observed at relatively high temperatures. Dehydrated polyvinyl alcohol (DPVA) is a type of polyacetylene $(-(CH{=}CH)_n-)$ [2]. It had specific electrical properties in the region of 320 K, which may be attributed to the occurrence of such a superconducting transition. It is known that the polarizability of some unsaturated compounds, which are polyacetylenes, cannot be calculated in the usual way as the sum of the polarizabilities of the constituent elements (individual atoms or bonds) [3]. This may be attributed to the displacement of valence electrons in an external electric field at distances exceeding the size of the atoms to which they originally belong. Thus, an intramolecular electric current, which can also be superconducting, contributes to the polarizability. This contribution is similar to the Maxwell–Wagner polarization mechanism for a dielectric containing conductive inclusions [4]. The surrounding space plays the role of a dielectric in this case. The flow of a through "intramolecular" current in the system is not possible due to the lack of chemical bonds between neighboring macromolecules. This is its difference from the usual electron current of fermions, which causes macroscopic conductivity, for which physical contact between conducting particles is sufficient. The molecular current is rather a plasmonic — an equivalent of plasma motion in metals and semiconductors [5]. Therefore, it should have other mechanisms of interaction with atomic vibrations that determine heat losses. Moreover, the scattering of the charge carrier at an angle to the initial direction of motion is not possible in one-dimensional systems such as polyacetylene, which leads to such effects as ballistic conductivity [6].

It is believed that the impact of atomic oscillations on substances's electronic polarization is the reason for the Raman scattering (RS) [7]. In this case, a change of the characteristics of the intramolecular current, such as, for example, a superconducting transition, should manifest itself in the RS. The expected decrease of the intensity of the RS signal during the transition from the superconducting state should be proportional to the contribution of the intramolecular polarization current to the total polarization current. We studied in this paper the change of the RS spectrum of the same DPVA sample in the same temperature range in which the peculiarity of its electrical properties was previously found [2] for establishing above mentioned correlation. The RS spectra were recorded using Bruker RFS 100/S spectrometer. $\lambda_{ex} = 1064$ nm laser was used to excite the RS spectra.

Figure 1 shows the RS spectra of the DPVA obtained at various temperatures. The spectra are shifted vertically for convenience, which avoids overlapping curves. Two characteristic bands of carbon materials are observed in these spectra in the region of 1110 and 1490 cm^{-1} [8], as well as an extended structureless background. This

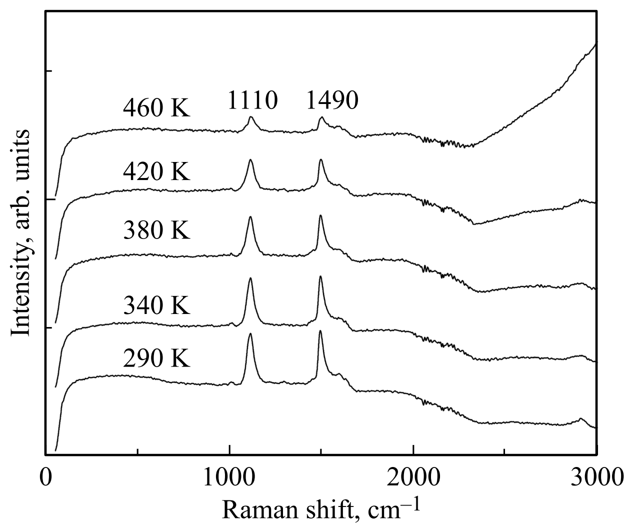

Figure 1. RS spectra of DPVA at various temperatures.

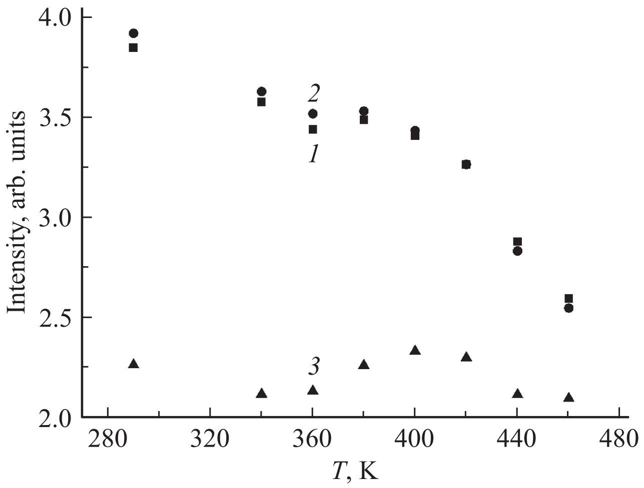

Figure 2. Temperature dependence of the intensity of characteristic bands at frequencies 1110 (*1*) and 1490 cm^{-1} (*2*), as well as the background at frequency 1330 cm^{-1} (*3*) in the RS spectrum of DPVA.

background may be caused by luminescence and it can also reflect a function of the density of vibrational states of a non-crystalline substance [9,10]. The luminescence intensity usually decreases when the sample is heated [11]. Figure 2 shows the dependence of the signal intensity in the maxima of the observed bands (the background was not subtracted), as well as the background at a frequency of 1330 cm^{-1}. This dependence is non-monotonic. It shows a „dip" in the temperature range of 340–380 K, more pronounced for the background than for the bands (with background addition). Thus, the desired correlation between the characteristics of RS and the electrical properties of the substance is revealed. The difference in the characteristic temperature values can be explained by measurement error. The presented data show that the superconducting transition affects a small (intramolecular) fraction (on the order of several percent) of the polarization current. The main part of it (intraatomic) remains superconducting. It cannot be different, since the energy of an applied low-frequency electric field cannot be converted into the energy of thermal motion in a monatomic system without changing this system. On the other hand, such systems cannot in principle be electrically conductive in the macroscopic sense, unlike molecular systems, to which, apparently, it is possible to create „contacts" for intermolecular transmission of „intramolecular" electric current. Such contacts should be based on chemical bonds, and not on physical proximity, as with conventional conductors. In other words, the electrical circuit should be a single macromolecule.

Various one-dimensional structures can be obtained based on polyvinyl alcohol (PVA) ($-(CH_2-CHOH)_n-$) [12]. The RS spectra of similar materials with polymeric copper(II) chloride, copper(II) and cadmium sulfides, and cadmium are similar to those of DPVA [12–15], which indicates the similarity of their electrical properties. Electrical measurements on these materials are complicated by the presence of orientational polarization in PVA (PVA has polar –OH groups in its structure, while DPVA does not) masking electronic polarization [2]. For this reason the Raman spectroscopy is becoming increasingly important for detecting intramolecular superconductivity in them and studying it.

Conflict of interest

The author declares that he has no conflict of interest.

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