COOPERATIVE TUNNEL EFFECT IN SEMICONDUCTING ANTIMONY COMPOUNDS HAVING A MIXED VALENCE

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It was shown in [1] that a second-order phase transition (of the electronic "order-disorder" type) with two-electron tunnel transport can occur in semiconducting crystals with mixed valence. Our theoretical model of a second-order phase transition, using as an example a strong anisotropic (quasi-one-dimensional) alternating crystal, is illustrated in Fig. 1. In the high-temperature phase there is one electron for each center and the electrons are delocalized, while in the low-temperature phase the electrons are localized with a certain difference in the electron density $z = p_i - p_j$ at the even (i) and odd (j) centers.

We report here observation of this phenomenon with the aid of the Mossbauer effect in the dark-violet isotropic crystals Cs_2SbCl_6 (A) and $RbSbCl_6 \cdot 2Rb_3SbCl_6$ (B).

The Mossbauer spectra were plotted in the temperature interval 77 - 150°K using a $^{121}SnO_2$ source (absorber thickness 5 - 7 mg/cm^2 equivalent of Sb). The samples were synthesized by Day and Atkinson at Oxford. The spectra of crystals (A) and (B) are shown in Fig. 2.

A study of the resonance-absorption spectra leads to the following conclusions: 1) two peaks corresponding in magnitude to the isomer shifts of Sb^{III} and Sb^{V} are observed for an investigated compounds; 2) each compound has also in intermediate peak whose intensity increases with increasing temperature, whereas the peaks corresponding to Sb^{III} and Sb^{V} decreases, and this process is reversible; 3) all peaks have a hyperfine structure due to the quadrupole interaction. Unlike the spectra given here, the brown modifications of (A) and (B) have no intermediate peak in the investigated temperature range [2]. The appearance of the latter and its increase with temperature point to the occurrence of Sb atoms of a new kind, in a valence

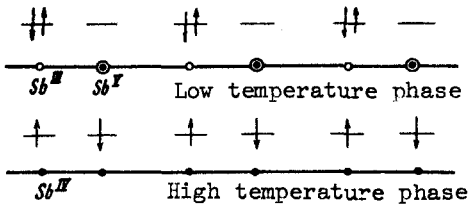

Fig. 1

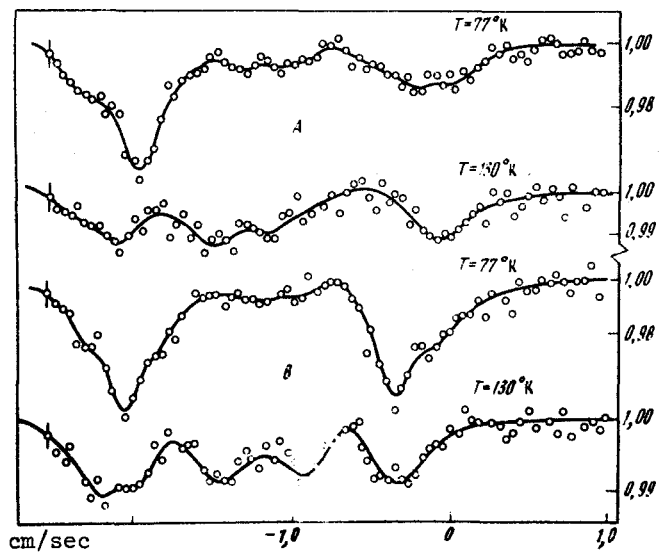

Fig. 2

state that differs from that of III or V. The isomer shift of this state lies in the region of the values proposed for Sb^{IV}.

Using the data on the Mossbauer spectra, we can estimate the relative number of Sb^{IV} atoms at 130°K. If we assume that the value of the Mossbauer effect does not depend on the electronic structure of the Sb atoms and is determined only by the lattice structure, then the relative number of Sb^{IV} atoms (n_{IV}) is $\eta = n_{IV}(130°K)/n_{III}(77°K) = 0.35$. The concentration of the Sb^{IV} atoms, as given by the Mossbauer data, is so high that it cannot be attributed to a temperature-induced excitation of the electrons from the valence band into the conduction band at a forbidden band width $\sim$1.5 eV [3]. Measurement of the concentration of the unpaired electrons in the conduction band by the EPR method, which was carried out by us, as well as the data on the electronic conductivity of the single crystals (A) [3], yield a value $\sim 10^{18}$ spin/deg, which is smaller by two orders of magnitude than the value obtained from the Mossbauer spectra. Thus, the occurrence of Sb^{IV} can be explained only within the framework of the "order-disorder" model of second-order phase transitions [1], with a fast exchange of a pair of electrons within a time shorter than the lifetime 3.5×10^{-9} sec of the Sb^{121m} nucleus. We note that crystal (A) is diamagnetic with $\chi = (-0.1 - 0.34) \times 10^{-6}$ deg^{-1} in the interval from 1.5 to 300°K. The last fact excludes the possibility of localized states, and the electrons are delocalized in the entire system.

A first-order phase transition is eliminated on the basis of the performed calorimetric measurements in the temperature interval 77 - 300°K.

The temperature of the "order-disorder" phase transition is given by $kT_n \sim V_z$ [1]. Extrapolation of the temperature dependence of the Sb^{IV} effect to lower temperatures yields a value of T_n in the region of 60°K. Calculation of the interaction potential entails great mathematical difficulties analogous to those encountered in the calculation of the interaction potential between electrons in the theory of superconductivity. Since $T_n \sim 60°K$, V is of the order of 10^2 cm^{-1} at $z \sim 1.8 - 2.0$ V. A similar phenomenon is apparently observed in the dark-violet crystal (B).

In conclusion, we thank Day and Pritchard for the samples, V.I. Gol'danskii for support, V.I. Trofimov, A.V. Zavarykin, V.B. Stryukov, and A.P. Shvedchikov for help with the experiment, and G.V. Ionov and N.A. Aleksandrov for a discussion of the work.

[1] S.P. Popov, G.V. Ionova, V.M. Lyubimov, and A.Yu. Aleksandrov, ZhETF Pis. Red. 12, 544 (1971) [JETP Lett. 12, 386 (1971)].
[2] A.Yu. Aleksandrov, S.P. Ionov, A.M. Pritchard, and V.I. Gol'danskii, ibid. 13, 13 (1971) [13, 8 (1971)].
[3] L. Atkinson and P. Day, J. Chem. Soc. (A) 16, 2432 (1969).

E R R A T A

Article by A. Yu. Aleksandrov et al., Vol. 16, No. 4:

On p. 147, lines 17 - 18 from top, read ...Cs_2SbCl_6(B) and $RbSbCl_6 \cdot 2Rb_3SbCl_6$(A).... instead of ... Cs_2SbCl_6(A) and $RbSbCl_6 \cdot 2Rb_3SbCl_6$(B).

On p. 148, lines 16 - 17 from the bottom, read ...$kT_n \sim Vz$... instead of ...$kT_n \sim V_z$...

Article by L. E. Gendenshtein and A. B. Kaidalov, Vol. 16, No. 4:

On p. 177, line 22 from top, read ... $C_R \approx 1/30 C_l \approx 5C_p$ ... instead of $C_R \approx 1/30$, $C_l \approx 5C_p$.