Van Vleck's contribution to the magnetic susceptibility in the $CuTa_2O_6$:Sb semiconductors

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A substitutional solid solution with the general formula $CuTa_{2-x}Sb_xO_6$ and a limited range of homogeneity ($0 < x \leq 0.5$) is formed in the $CuTa_2O_6$–$CuSb_2O_6$ system [1]. The $CuTa_{2-x}Sb_xO_6$ solid solution crystallizes in a tetragonal system and adopts the $CuTa_2O_6$ structure. The maximum replacement of Ta^{5+} ions by Sb^{5+} ones reaches at least 25 mol%. The $CuTa_{2-x}Sb_xO_6$ phase was obtained by solid-state reactions both from oxides: CuO, α-Sb_2O_4 and Ta_2O_5, as well as from separately obtained compounds: $CuSb_2O_6$ and $CuTa_2O_6$. Heating of the samples in air was carried out in several 12-hour stages in the temperature range 700°C -1150°C. The band gaps estimated by the Kubelka-Munk method decreased with increasing antimony ions from $E_g = 2.94$ eV for x = 0.0 to $E_g = 2.64$ eV for x = 0.5 [1].

Static magnetic susceptibility was measured at 5 kOe and in the temperature range 4-300 K, and magnetization isotherms up to 70 kOe and at 5, 10, 20, 40, 60 and 300 K, using a PPMS platform equipped with a vibrating sample magnetometer (VSM) option (Quantum Design, San Diego, California, USA). Electrical conductivity σ(T) of the samples under study was measured by the DC method using a KEITHLEY 6517B Electrometer/High Resistance Meter (Keithley Instruments, LLC, Solon, OH, USA) and within the temperature range of 100-400 K. For the electrical measurements, the powder samples were compacted in a disc form (10 mm in diameter and 1-2 mm thick) using the pressure of 18 MPa; then, they were sintered for 2 h at 873 K.

Electrical conductivity measurements showed that all samples are characterized by strong thermal activation of 0.7 eV in the intrinsic region, i.e. above room temperature, and its absence in the extrinsic one. The magnetic parameters listed in Table 1 are determined after taking into account the contribution of Van Vleck's magnetic susceptibility (χ_0). They show that the magnetic moments come exclusively from Cu^{2+} ions, whose effective moments (μ_{eff}) are close to the effective number of Bohr magnetons (p_{eff}). The oxides under study do not saturate at 70 kOe, and in the Curie Weiss region they are paramagnetic. They are characterized by short-range antiferromagnetic and long-range ferrimagnetic interactions.

Table 1. Magnetic parameters of solid solution $CuTa_{2-x}Sb_xO_6$: *C* is the Curie constant, θ is the Curie-Weiss temperature, μ_{eff} is the effective magnetic moment, *M* is the magnetization at 5 K and at 70 kOe, p_{eff} is the effective number of Bohr magetons, χ_0 is the slope and *b* is the intercept of the linear function of $\chi T=\chi_0 T+b$.

x	C (emu·K/mol)	θ (K)	μ_{eff} (μ_B/f.u.)	$M_{(5K)}$ (μ_B/f.u.)	p_{eff}	χ_0 (emu/mol)	b (emu·K /mol)
0	0.416	-14.2	1.823	0.110	1.732	0.00136	0.39351
0.1	0.333	-35.7	1.631	0.158	1.732	0.00279	0.25106
0.2	0.394	-7.8	1.774	0.246	1.732	0.00204	0.38074
0.3	0.401	-7.1	1.792	0.272	1.732	0.00108	0.38975
0.5	0.430	-8.4	1.855	0.277	1.732	0.00184	0.41576

[1] G. Dąbrowska, and E. Filipek, *Solid State Science* **119**, 106686 (2021).