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Transition-Metal Electron States in Imperfect Ga_2S_3 Crystals

By

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The Ga_2S_3 compound is representative of $A_2^{III}B_3^{VI}$ imperfect crystals and crystallizes into the wurtzite-type lattice /1/. Every third lattice site in the cationic sublattice of Ga_2S_3 is vacant so that defects of 10^{21} cm^{-3} concentration are found in these structures /2/.

The literature data /3 to 6/ on the impurity behaviour in $A_2^{III}B_3^{VI}$ compounds (In_2Te_3, Ga_2Te_3) are contradictory. So far no transition-metal impurity effect on the physical properties of $A_2^{III}B_3^{VI}$ compounds has been reported.

Our Mössbauer and magnetic measurements on Ga_2Se_3:^{57}Fe favour the conclusion that iron ions are incorporated in this compound and form chemical bonds with the matrix atoms /7/. The authors of /8/ prove convincingly that electrically inactive iron atoms are incorporated into the In_2Te_3 lattice as Fe^{2+} and form chemical bonds with Te atoms.

There are just a few works on transition-metal impurity states in Ga_2S_3 compounds /9, 10/.

Resonance techniques and, in particular, electron paramagnetic resonance (EPR) and γ-resonance (GR) are the most informative ones for the interpretation of the impurity character in defect semiconductors. These methods give information on the spatial distribution of paramagnetic ions, on the chemical bond nature, and on the charge state of the atoms under study and their electronic structure.

Ga_2S_3 defect crystals were studied by EPR and GR within the 77 to 300 K range, to determine the electronic states of Mn and Fe impurity atoms.

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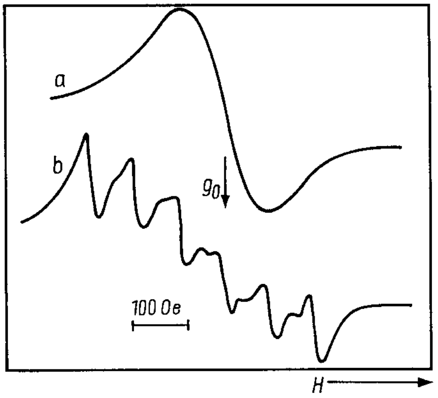

Fig. 1. EPR spectra of Ga_2S_3 (0.01 at% Mn) at 300 K a) before and b) after annealing

Transition-metal-doped Ga_2S_3 was obtained by the vacuum technique in quartz tubes at 1400 K for 8 h. The approach to the equilibrium state was controlled by X-ray phase analysis (XPA), microstructural analysis (MSA), and microhardness measurements.

The EPR spectra of manganese in non-thermally treated Ga_2S_3 following its long-term annealing (at 1250 K for 540 h) reveal significant differences in absorption line shapes (Fig. 1) in specimens with 0.01 at% impurity content. Non-treated specimens give dipole-dipole broadened EPR lines at 77 and 300 K resulting from the $3d^5$ Mn^{2+} ion configurations with linewidth $\Delta H = 143$ Oe and effective g-factor of 1.995 (Fig. 1, curve a). The same treated specimens show a hyperfine structure (HFS) (Fig. 1, curve b) of EPR spectra ($S = 5/2$, $I = 5/2$) associated with Mn^{2+} localization in lattice centres conditioned by the strong field. It might be due to the fact that annealing results in an ordering of the nearest environment of the paramagnetic ion. The available isotropic HFS EPR spectra yield $A = 81$ Oe, $g = 2.003$. The occurrence of HFS EPR spectra at room temperature might be attributed to a large separation of the lower and higher levels of the split d-energy term.

^{57}Fe Mössbauer spectra are recorded by the GRS-4m spectrometer at 80 and 300 K with ^{57}Co source in chromium. Isomer shifts are given with respect to this source. Mössbauer spectra of Ga_2S_3 (3 at% Fe) are plotted in Fig. 2 at various temperatures and exhibit quadrupole doublet lines. Their isomer shift, representative of the Fe valence state, is 0.60 mm/s, while the line separation, i.e. the quadrupole splitting, is 3.4 mm/s at 80 K. The greater the iron concentration and the measurement temperature the higher the relative spectral intensity is. The spectral isomer shift is within the range of overlapping shift regions for typical Fe^{2+} and Fe^{3+} compounds. However, the large spectral quadrupole splittings enable their attribution to the Fe^{2+} state.

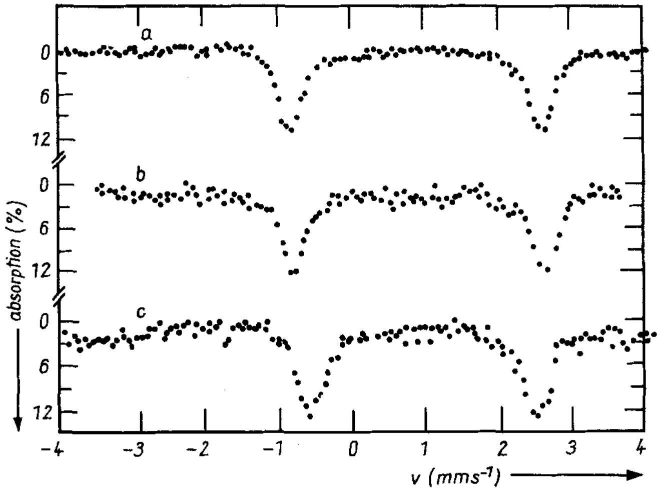

Fig. 2. Mössbauer spectrum of Ga_2S_3 (3 at% Fe) at various temperatures: a) 80, b) 180, c) 300 K

Moreover, the isomer shift value ($\delta \approx 0.90$ mm/s at 80 K) proves that Fe^{2+} atoms are chemically bonded to sulphur atoms within the Ga_2S_3 lattice. The spectral quadrupole splitting might be due to Fe^{2+} being associated with stoichiometric vacancies. In this case, the electron state degeneracy is relieved, and an electric field gradient appears at the Fe nuclei.

Our attempt to find an Fe EPR spectrum in Ga_2S_3 has failed. This can be accounted for by the disappearance of the EPR signal due to impurity atoms with even 3d-shell electrons, which relate to the Fe-group charge state. It also confirms the bivalency of the Fe impurity in Ga_2S_3.

Hence, the analysis of EPR and Mössbauer spectra reveals that electrically inactive Fe atoms are incorporated as Fe^{2+} into the Ga_2S_3 lattice and form chemical bonds with S atoms.

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