Nuclear Gamma Resonances in Ga$_2$S$_3$:^{151}Eu Single Crystals

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The electron structure of impurity ^{151}Eu atoms in Ga$_2$S$_3$:Eu and Ga$_2$S$_3$:EuS single crystals has been studied by using the nuclear gamma resonance method at temperatures between 77 and 300 K by using different doping proportions of Eu atoms with Sm$_2$O$_3$ as the source. By investigating the Mössbauer spectra, we first determined the values of the isomer shift and then the charge states for Eu, which turned out to be a Eu^{2+}(4f^7) ion with spin $S = 7/2$. In this study, the Debye temperature, Θ_D, of the impurity ^{151}Eu atoms were calculated from the Debye-Waller factor. The results obtained were compared with those in other studies and were found to be in agreement.

I. INTRODUCTION

High native defect concentrations in A$_2^{III}$B$_3^{VI}$ [1–3] semiconductors (Ga$_2$Se$_3$, Ga$_2$S$_3$, Ga$_2$Te$_3$, In$_2$Te$_3$) allow large magnetic impurity solubility and possible preparation of semiconductor magnetics. Added interest about such systems can be explained by the statistical nature of the structural defects and by the resulting opportunity to obtain magnetic states of a spin glass type.

Published data on the chemical neutrality of the impurities ^{57}Fe and ^{119}Sn in In$_2$Te$_3$ and Ga$_2$Te$_3$ semiconducting compounds with a loose crystal lattice are very conflicting [4,5]. Nuclear gamma resonance (NGR) studies have shown that with ^{57}Fe and ^{119}Sn nuclei in In$_2$Te$_3$ and Ga$_2$Te$_3$, the electron density corresponds to the neutral state of those nuclei. This explains an unusual fact about semiconductors, namely, the absence of an impurity conductivity when In$_2$Te$_3$-type crystals are doped with elements of the same group of the periodic system.

The problem of "non-doping" in A$_2^{III}$B$_3^{VI}$ defect semiconductors represented here by Ga$_2$S$_3$, Ga$_2$Se$_3$ and In$_2$Te$_3$, was investigated by using Mössbauer studies [6–9]. In those studies, it was shown that impurity iron atoms in Ga$_2$S$_3$ and Ga$_2$Se$_3$ single crystals were in normal valent states and formed chemical bonds. The Ga$_2$S$_3$ compound, which crystallizes into wurtzite-type lattice [10], is a very promising material for blue-green light-emitting devices because of its wide direct band-gap. The polymorphism of Ga$_2$S$_3$ has been demonstrated by several studies [11]. Four different phases have been identified: α-Ga$_2$S$_3$ (hexagonal, space group p6$_1$ and p6$_5$); α'-Ga$_2$S$_3$ (monoclinic, space group Bb); β-Ga$_2$S$_3$ (hexagonal wurtzite structure p6$_3$mc); and γ-Ga$_2$S$_3$ (cubic sphalerite structure, F43m).

Experimental results for the fundamental absorption edge of a Ga$_2$S$_3$ single crystal [12], which was grown by using the closed tube chemical transport method, have been described. The properties of the absorption bands, along with the peak in the reflection spectrum, affirm that the structure observed near the fundamental absorption edge is related to the basic lattice of the α-Ga$_2$S$_3$ crystal rather than to its defects or deviations from stoichiometric composition, and is of an excitonic character. The influence of temperature on the electrical conductivity and the Hall effect was investigated in the temperature range 418~733 K [13]. We found the energy gap and the ionization energy to be 2.38 eV and 0.71 eV, respectively. The thermoelectric phenomenon for single crystals of Ga$_2$S$_3$ was investigated in the temperature range from 180 to 500 K [14]. The thermoelectric power decrease with increasing temperature up to 300 K and then increase slightly above 340 K. The sign of α remained positive throughout the whole temperature range investigated, indicating the p- type nature of the crystal. The green photoemission of the Ga$_2$S$_3$ crystals was reported in Ref. 15 based on data from infrared absorption and photoexcitation measurements. It was concluded that the emission center for the green emission band existed at about 0.4 eV above the valence band.

The effect of doping with transition-metal and rare-earth impurities on the physical properties of Ga$_2$S$_3$ and Ga$_2$Se$_3$ has been studied [16–21]. However, no study exists on the electronic structure of rare-earth impurity atoms in Ga$_2$S$_3$ single crystals. It would be of interest

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to investigate the state of the centres formed by Eu impurity nuclei in Ga$_2$S$_3$ defect crystals. Resonance techniques [NGR, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR)] 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 charged atoms under study and their electronic structure. An obvious approach would be to study magnetically disordered materials, in which only the electric hyperfine interactions related to charge densities and electric-field gradients at the probed nuclei are detected (*i.e.*, the isomer shift and the quadrupole splitting of a Mössbauer line). In this paper, we present the results of measurements of the Mössbauer effect in Ga$_2$S$_3$:Eu and Ga$_2$S$_3$:EuS single crystals in the temperature range 77∼300 K.

II. EXPERIMENTAL PROCEDURES

High-quality α-Ga$_2$S$_3$ single crystals were grown from the melt by using the Bridgman methods. The purity of the material used was as follows: Ga-99.9999 %, and S-99.9999 %. ^{151}Eu-doped Ga$_2$S$_3$ was obtained by using vacuum-technique methods in quartz tubes at 1400 K for 8 hours with regular stirring. The impurity ^{151}Eu concentration was determined by atomic absorption analysis and X-ray fluorescence analysis (XRFA). From the atomic absorption analysis, it was found that within the batch produced in the same synthesis, the ^{151}Eu impurity ranged from 0.37 % to 2 %.

Figure 1 shows the XRFA spectra of Ga$_2$S$_3$:^{151}Eu at 1 %, 3 %, and 5 % ^{151}Eu impurity concentrations. The intensity of the spectra were correlated with the ^{151}Eu concentration in the samples. The lattice constants are a=6.4081 Å and 6.3909 Å and c=17.985 Å and 18.0118 Å for pure α-Ga$_2$S$_3$ (p6$_1$) and Ga$_2$S$_3$:Eu, respectively.

Mössbauer spectra from the Ga$_2$S$_3$:Eu and the Ga$_2$S$_3$:EuS samples were recorded at the MS-700 M set up at temperatures of 77 and 300 K with Sm$_2$O$_3$ as the source and isomer shift values were determined relative to EuF$_3$. The absorber sample thicknesses were 100∼150 Mg/cm^2.

III. RESULTS AND DISCUSSION

Figure 2 shows typical NGR spectra for Ga$_2$S$_3$:5 % Eu at 77 K and 300 K. The Mössbauer spectra of the Ga$_2$S$_3$:Eu samples consisted of a single line with a Lorentzian profile and showing a weak dependence on the temperature and the amount of doping. We will not go into the details of the theory of the Mössbauer effect. However, it is worthwhile to consider briefly one other aspect of the resonance; its depth, which is determined
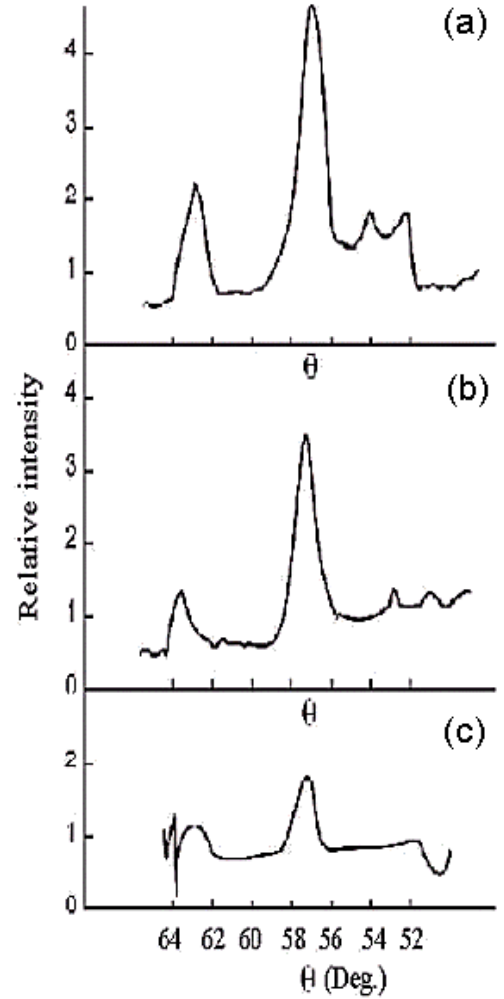

Fig. 1. X-ray fluorescence analysis (XRFA) spectra of Ga$_2$S$_3$:Eu single crystals at various impurity concentrations: (a) for Ga$_2$S$_3$:5 %Eu, (b) for Ga$_2$S$_3$:3 %Eu, and (c) for Ga$_2$S$_3$:1 %Eu.

by the fraction of Eu nuclei in the Ga$_2$S$_3$ single crystals that absorb with no recoil. An analysis of the relative line intensities can be used to quantify the fraction of atoms, provided that thickness effects play no role [22]. If no thickness effects are present, the resonance area is directly proportional to the Debye-Waller factor, f_A, of a Mössbauer absorber. Thus, the absolute values of the resonance areas are required to determine f_A. In contrast, the relative Debye-Waller factors of different Eu sites in a spectrum can be derived from the temperature dependence of the relative areas of their subspectra. The calculation of the recoil-free fraction, f_A, depends on the properties of the crystals. However, it is more complicated than the simple question of whether or not the recoil energy exceeds the lattice binding energy. Crystals can absorb energy in many ways other than by removing atoms from their lattice sites. At low energies and temperatures, the primary way is through lattice vibra-
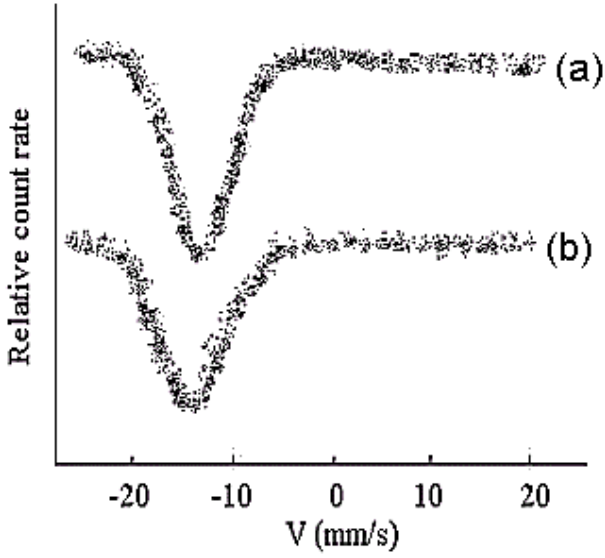
Fig. 2. NGR spectra of Ga_2S_3:5 %Eu single crystals at (a) 77 K and (b) 300 K.

tions. These vibrations occur for a spectrum of frequencies from zero up to a maximum, ω_{max}. The temperature corresponding to the energy, called the Debye temperature, θ_D, is defined so that $h\omega_{max} = k\theta_D$ where k is the Boltzmann constant. For typical crystals, $h\omega_{max} \cong 0.01$ eV, and $\theta_D \cong 1000$ K. The recoilless fraction is given as [23]

$$f_A = \exp\left[-\frac{<x^2>}{(\lambda/2\pi)^2}\right] , \qquad (1)$$

where $<x^2>$ is the mean-square vibrational amplitude of the absorber nucleus and λ is the wavelength of the γ ray. Using the Bose-Einstein distribution function for the vibrational phonon spectrum permits the calculation of the mean-square amplitude, and the recoilless fraction can be written as

$$f_A = \exp\left\{-\frac{6E_R}{k\Theta_D}\left[\frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x dx}{e^x - 1}\right]\right\} , (2)$$

where E_R is the recoil energy given as $E_R = E_\gamma^2/2Mc^2$ with E_γ being the gamma-ray energy to excite the nucleus.

At low temperature, $T \ll \theta_D$, the last term in the exponent is negligible. Values of θ_D do not vary greatly among metals (θ_D is 400 K for Fe and 300 K for Ir), so the recoil energy E_R is essential in determining the recoilless fraction. For the 14.4-keV transition of Fe^{57}, E_R=0.002 eV and f_A=0.92 while for Ir, f_A=0.1. The second term in the exponent of Eq. (2) is always negative; thus, this term will work to make f_A smaller than the low-temperature estimates.

To test the assumption of Ref. 24 about an impurity solution without bond formation, we measured the ratio of the spectral intensities (I) at 77 and 300 K and
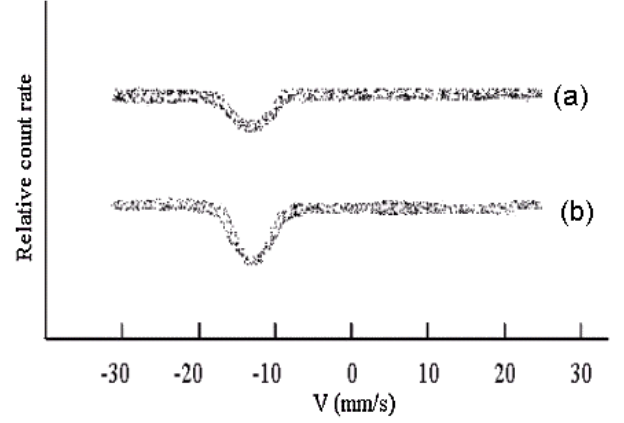

Fig. 3. NGR spectra of Ga_2S_3:3 %EuS single crystals at (a) 300 K and (b) 77 K.

calculated the effective Debye temperature, θ_D, for the impurity ^{151}Eu atoms from the relationship

$$\frac{I(77K)}{I(300K)} = \exp\left\{\frac{6E_R}{k\theta_D}\left[f_A\left(\frac{300}{\theta_D}\right) - f_A\left(\frac{77}{\theta_D}\right)\right]\right\} . \qquad (3)$$

From the above formulas, the following values were calculated for Ga_2S_3:Eu (Fig. 2) and Ga_2S_3:EuS (Fig. 3), respectively:

$$\frac{I(77K)}{I(300K)} = 1.24 \pm 0.05 , \quad \theta_D = 260 \pm 5K \qquad (4)$$

and

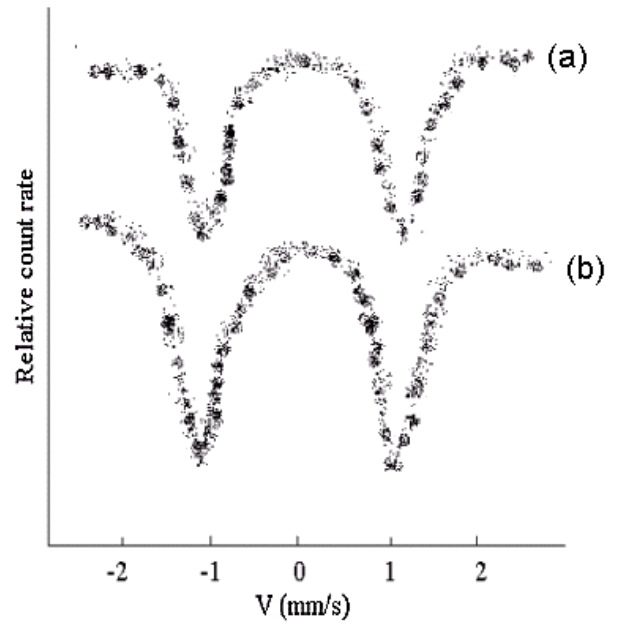$$\frac{I(77K)}{I(300K)} = 1.12 \pm 0.05 , \quad \theta_D = 292 \pm 5K . \qquad (5)$$

Fig. 4. NGR spectra of Ga_2S_3:3 %Fe single crystals at (a) 300 K and (b) 77 K [7].

Table 1. Parameters for NGR spectra of Ga_2S_3:Eu_x, $Ga_{2-x}Eu_xS_3$, Ga_2S_3:$Fe_{0.03}$, and $Ga_{1.97}Fe_{0.03}S_3$.

Compounds	Isomer Shift δ (mm/s)	Quadrupole splitting, Δ (mm/s)	Observed effect value, ϵ	DebbyTemp. θ_D (D)
Ga_2S_3:$Eu_{0.01}$	-14.0 ± 0.6	–	1.2	254 ± 5
$Ga_{1.99}Eu_{0.01}S_3$	-14.0 ± 0.4	–	1.2	254 ± 5
Ga_2S_3:$Eu_{0.03}$	-14.2 ± 0.1	–	1.6	256 ± 5
$Ga_{1.97}Eu_{0.03}S_3$	-14.1 ± 0.3	–	1.8	258 ± 5
Ga_2S_3:$Eu_{0.05}$	-14.3 ± 0.6	–	2.1	260 ± 5
$Ga_{1.95}Eu_{0.05}S_3$	-14.2 ± 0.5	–	2.2	260 ± 5
Ga_2S_3:$Fe_{0.03}$ [7]	0.62 ± 0.02	3.02 ± 0.03	6.9	270 ± 5
$Ga_{1.97}Fe_{0.03}S_3$ [7]	0.62 ± 0.02	3.1 ± 0.03	6.3	270 ± 5

In an earlier study [7], the Debye temperature, θ_D, of Ga_2S_3:Fe single crystals was calculated from NGR spectra (Fig. 4). The spectra depended only slightly on the measurement temperature and the iron concentration. The Ga_2S_3:Fe spectrum was comprised of a superposition of two quadrupole doublets:

$$\frac{I(77K)}{I(300K)} = 1.54 \pm 0.05 , \quad \theta_D = 270 \pm 5K . \qquad (6)$$

The NGR spectral parameters are listed in Table 1. The results obtained are in agreement with those of the other studies [25]. The resulting θ_D values are characteristic for Fe compounds (*e.g.*, θ_D=250 K for Fe in NiS_2) and can hardly be achieved without chemical bond formation.

In this research, moreover, we recorded NGR spectra for $Ga_{2-x}Eu_xS_3$-type samples. For such compositions, gallium substitution for iron should take place, even in the framework of the model [24], to yield common chemical compounds. The spectral parameters of the $Ga_{2-x}Eu_xS_3$ samples coincide with those of $Ga_2S_3Eu_x$. This provides additional evidence of bond formation by Eu upon superstoichiometric doping. The results obtained for those two different compounds are also given in Table 1.

The ability to observe the electron spin resonance (ESR) spectrum of Eu right up to room temperature indicated that the Eu centers were in the S state. On the other hand, the complex nature of the spectra was typical of paramagnetic Eu centers experiencing a strong crystal field of non-cubic symmetry and resembled the spectra of Eu in glassy semiconductors. Since the Mössbauer spectrum consisted of a single line, we concluded that one type of center predominated. Our results, thus, indicated that, in spite of the different crystal structures of Ga_2S_3 and Ga_2Se_3, Eu created identical low-symmetry centers in the both of them. This could be explained by the fact that both crystal structures were of a defect nature with a disordered distribution of vacancies and were in this sense similar to glasses. Obviously, Eu atoms were most likely to occupy vacancies. However, since they were larger than the vacancies, they were shifted relative to the center of the vacancy, thus creating asymmetric double Eu-V_{Ga} centers. We determined the charge state

of the Eu. The S state could be realized in two ways: a neutral Eu^0 ($4f^76s^2$) atom or an Eu^{2+} ($4f^7$) ion; in both cases the spin was S=7/2. The magnitude of the isomeric shift, δ, of the Mössbauer line gave a clear indicated which of these was the way. In the case of a neutral Eu^0 ($4f^76s^2$) atom, the isomeric shift was $\delta \cong 5$ mm/s [26]. However, in our study, we found a value of $\cong -14$ mm/s for the isomeric shift, as shown in Table 1. We, therefore, concluded that the Eu impurity in Ga_2S_3 was in the Eu^{2+} state. Since doping with Eu did not alter the type of conduction in Ga_2S_3, we also concluded that an atom of Eu in this compound did not create electrically active levels in the band gap of the crystal. This provided additional support for the conclusion that Eu is not a substitutional impurity in the investigated compounds.

We, therefore, reached the following conclusion: In contrast to semiconductors with a defect-free structure, Eu in Ga_2S_3 compounds does not replace a host lattice atom, but interacts with the vacancy, forming a double center of an $(Eu^{2+}$-$V_{Ga}^{2-})^\circ$ type. This, in turn, can give rise to the energy levels in the band gap of Ga_2S_3:Eu single crystals responsible for the luminescence line at 0.54 μm [20, 27]. Obviously, the state in the band gap is formed from band states; *i.e.*, it splits off from the allowed bands because of lifting of the degeneracy by strong local stresses.

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