ELECTRON PARAMAGNETIC RESONANCE OF Gd^{3+} IONS IN THE CHALCOGENIDE GLASS $\mathrm{Tl_2SeAs_2Se_3}$

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Fig. 1

Figure 1: Fig. 1

Abstract

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ELECTRON PARAMAGNETIC RESONANCE OF Gd^{3+} IONS IN THE CHALCOGENIDE GLASS $Tl_2SeAs_2Se_3$

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Electron paramagnetic resonance (EPR) was investigated in glassy samples of $Tl_2SeAs_2Se_3$ containing 0.2–0.5 wt.% gadolinium as an impurity. The samples were synthesized according to the procedure described in [1]. The rate of temperature increase was 150 deg/hour, with holding for one hour at 600 and 900°C. Cooling was carried out either by allowing the switched-off furnace to cool or by quenching in cold water. Gadolinium was introduced as $Tl_2SeAs_2Se_3$ in excess of 100%. X-ray phase analysis showed that the samples obtained are glass-forming.* Recording of the EPR spectra was carried out on a standard RE-1301 spectrometer at room and liquid-nitrogen temperatures. Observation of EPR for a sample with 0.5% Gd at 4.2°K was carried out on a superheterodyne spectrometer in the three-centimeter range. EPR was studied on two samples with 0.5% Gd and three samples with 0.2% Gd.

Fig. 1. *a* –EPR spectrum of Gd^{3+} in $Tl_2SeAs_2Se_3 + 0.2\%$ Gd, synthesized under the usual conditions [1], at a temperature of 77°K; *b* –EPR spectrum of Gd^{3+} in a transparent sample of $Tl_2SeAs_2Se_3 + 0.2\%$ Gd at room temperature.

As can be seen from Fig. 1, where the spectral curves of samples $Tl_2SeAs_2Se_3 +$ 0.2% Gd at room and liquid-nitrogen temperatures are presented, the observed spectra are very complex and constitute a superposition of lines of different widths and intensities.

In high fields the change in the derivative occurs monotonically and, apparently, corresponds to an intense asymmetric line at $g \approx 1.98$ (left half-width $\delta H \sim 140$ Oe), on the right, less intense extremum of which a weak, poorly resolved structure and an intense peak at $g \sim 2.7$ are superposed. At $g \sim 5.9$ a narrow ($\delta H = 110 \pm 5$ Oe) asymmetric line is observed.

Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility of a $Tl_2SeAs_2Se_3 + 0.5\%$ Gd sample

Figure 2: Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility of a $Tl_2SeAs_2Se_3 + 0.5\%$ Gd sample

The intensity of the spectrum, when the temperature is lowered from room temperature to liquid-nitrogen temperature, increases by approximately a factor of 4, which agrees with the temperature variation of the inverse susceptibility,** close to the Curie law (Fig. 2), in the range 273–87°K. With increasing concentration gadolinium concentration the intensity of the spectrum increases (especially in the region $g \sim 2$), and the structure becomes less resolved. The method of cooling the samples has no substantial effect on the structure of the spectrum.

Changing the synthesis regime (maximum temperature 750°C, holding at this temperature for 16 h, cooling with the furnace switched off) also caused practically no change in the EPR spectrum. A sample with 0.2% Gd obtained under this regime proved transparent when examined in an MIK-1 infrared microscope. No crystalline inclusions were found, but small dark spots of indeterminate shape, ~ 1–$5\,\mu$ in size, uniformly distributed throughout the ingot, were observed. The EPR spectrum of this more homogeneous sample is characterized by somewhat greater intensity and resolution than the spectrum of a $Tl_2SeAs_2Se_3 + 0.2\%$ Gd sample obtained in the usual way and not transparent, but the positions of the spectral lines in the magnetic field remain practically unchanged. Thus, the spectrum has very good reproducibility from sample to sample and, within the indicated regimes, does not depend substantially on the regime or method of cooling.

Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility of a $Tl_2SeAs_2Se_3 + 0.5\%$ Gd sample.

The positions of the spectral lines also do not depend on temperature in the range 300–77°K. Apparently this is also the case at liquid-helium temperature. Thus, the spectrum of a $Tl_2SeAs_2Se_3 + 0.5\%$ Gd sample at 4.2°K (the spectrum was recorded by observation on an oscilloscope) had approximately the same structure as at 77°K. The stable complex spectrum observed in glassy

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* X-ray phase analysis of one of the samples $Tl_2SeAs_2Se_3 + 0.2\%$ Gd was carried out in the X-ray laboratory of Leningrad University on a URS-50I apparatus using copper radiation, whose sensitivity ($\sim$ 0.5–1%) is higher than that in ordinary X-ray phase analysis. The presence of a crystalline phase was likewise not detected.

** Measurements of the magnetic susceptibility were performed by V. N. Prudnikov.

Fig. 3. EPR spectrum of Gd^{3+} in $As_2Se_3 + 0.5\%$ Gd at room temperature

Figure 3: Fig. 3. EPR spectrum of Gd^{3+} in $As_2Se_3 + 0.5\%$ Gd at room temperature

$Tl_2SeAs_2Se_3$ is apparently associated with Gd^{3+} ions located in the glass network in different positions, characterized by different magnitudes and symmetries of the crystal field. Thus, the line with $g \approx 1.98$ is probably due to Gd^{3+} ions located at sites giving a weak crystal field of high symmetry. The intense narrow line with g-factor ~ 5.9, as well as the peak in the region $g \sim 2.7$, are possibly due to Gd^{3+} ions located in the glass network in positions producing a strong crystal field of low symmetry.

Fig. 3. EPR spectrum of Gd^{3+} in $As_2Se_3 + 0.5\%$ Gd at room temperature.

For Gd^{3+}, lines with a g-factor considerably greater than 2 have been observed in deoxyribonucleic acid ($g = 5.90$) (^{2}) and in sulfuric-acid and borate glasses ($g = 5.3$ and $g = 4.7$, respectively) (^{3}). The appearance of the last two lines was explained in terms of a strong crystal field with a predominant rhombic component (^{3},^{4}). It is possible that the intense lines observed in $Tl_2SeAs_2Se_3 +$ Gd with a g-factor considerably greater than 2 are also connected with effects of a strong crystal field.

The possibility of the occurrence of a strong crystal field for Gd^{3+} ions in samples of stoichiometric composition of the glassy As—Se—Tl system may be connected with the presence in it of ionic complexes Tl^+Se^- (^{5},^{6}), distributed over the covalently bonded network of the glass. Thus, the EPR spectrum of Gd^{3+} in the binary As—Se system (spectra were studied for glasses of stoichiometric composition As_2Se_3 with an admixture of 0.5 and 1 wt.% Gd),

which contains no ionic complexes and consists of covalently bonded trigonal structural units $[AsSe_{3/2}]$, is a single broad ($\delta H \sim 1800$ Oe), intense line with a g-factor of ~ 2.1 (Fig. 3). The spectrum is distinguished by a significantly larger scatter of its parameters than in the case of $Tl_2SeAs_2Se_3$.

The greater stability of the EPR spectrum in $Tl_2SeAs_2Se_3$ indicates that here, in the glass network, unlike in As_2Se_3, there exist positions with a stable environment in which the introduced gadolinium atoms are located, forming Gd^{3+} ions. At the same time, some of the Gd^{3+} ions may be situated in an environment with a strong crystalline field of low symmetry. The fact that the position of the spectral line does not depend on temperature or on the synthesis regime shows that the coordination of the Gd^{3+} ions is sufficiently stable.

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1. N. A. Goryunova, B. T. Kolomiets, V. P. Shilo, ZhTF, **28**, 981 (1958).
2. W. H. Walsh, L. W. Rupp, B. J. Wyluda, Proc. First Intern. Conf., Jerusalem, July (1962), p. 836.
3. H. C. Tarczy-Hornoch, M. M. Zaring, FTT, **6**, no. 5, 1545 (1964).
4. J. S. Griffith, Molec. Phys., **8**, no. 3, 213 (1964).
5. L. A. V. Kokorina, Optical-Mechanical Industry, no. 6, 48 (1961).
6. R. L. Muller, T. P. Markova, Vestn. LGU, no. 4, 75 (1962).

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