Comparative Study of the Magnetic Susceptibility of n-Ge near the Insulator–Metal Phase Transition by Means of ESR and SQUID

A.I. Veinger, A.G. Zabrodskii, T.L. Makarova, T.V. Tisnek, S.I. Goloshchapov and P.V. Semenikhin

Ioffe Physico-Technical Institute of the Russian Academy of Sciences, Politekhnicheskaya 26, St.Petersburg, 194021, Russia

Impurity paramagnetic susceptibility of n-Ge has been measured in the vicinity of the insulator–metal phase transition by two techniques: ESR and SQUID. A comparison of these methods demonstrated that their results qualitatively coincide at low temperatures, but differ at high temperatures. The advantage of the ESR technique is in its substantially higher relative precision, but SQUID makes it possible to obtain on principle absolute values of the magnetic susceptibility. It was found that, in the present-day state of development, the SQUID method has a substantially poorer precision, compared with ESR

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INTRODUCTION

It is well known that an increase in the impurity concentration in a semiconductor gives rise to interaction between separate impurity centers, as a result of which the semiconductor passes from the insulator to the metallic state. This problem, a part of the general problem of the insulator–metal (IM) phase transition in a solid, is widely discussed in the scientific literature and, in particular, in a number of monographs (see, e.g., [1, 2]). It is known, the magnetic properties of a substance change in the vicinity of the transition: the insulator state is characterized by Curie paramagnetism or antiferromagnetism, whereas in the metallic state, the magnetic properties of the substance are described by the Pauli paramagnetism or ferromagnetism.

In nonmagnetic semiconductors (e.g., in Ge and Si), the paramagnetism is determined by impurities. Each atom of a shallow impurity has an unpaired spin, and the ensemble of these spins is manifested as a paramagnetic contribution to the magnetic susceptibility $\chi$. The temperature dependence of $\chi$ in the absence of a spin–spin interaction and at temperatures above 1 K is described by the Curie law:

$$\chi = n_S \mu_B^2 p_{ef}^2 / 3kT,$$ (1)
where $n_S$ - is the spin concentration; $\mu_B$ - Bohr magneton; $p_{\text{eff}}$ - effective magnetic moment per atom ($p_{\text{eff}}=1$ for the $s$-state); $k$ - Boltzmann constant; and $T$ - temperature.

The interaction of shallow impurities near the IM phase transition gives rise to cooperative phenomena: spins may be oriented in parallel to each other (ferromagnetic interaction) or be antiparallel (antiferromagnetic interaction). Analysis of interactions of this kind furnishes information about specific features of these phase transitions. If there are spin interactions, the temperature dependences $\chi(T)$ above the Curie point (for ferromagnetics) or Neel point (for aniferromagnetics) obey the Curie–Weiss law:

$$\chi = n_S \mu_B^2 p_{\text{eff}}^2 / 3k(T+\Theta),$$

where the parameters have the same meanings as those in (1), but a temperature constant $\Theta$ is added. This constant is positive for a ferromagnetic and negative for an antiferromagnetic.

It follows from (2) that, if the dependence $1/\chi = f(T)$ is plotted, it crosses the abscissa axis, making an intercept $\Theta$, with the interaction being ferromagnetic at low temperatures at $\Theta > 0$ and antiferromagnetic at $\Theta < 0$.

The most effective way to study the magnetic properties of shallow impurities in a semiconductor is by the ESR technique [3]. In this case, a model material is silicon. All stages of variation of ESR spectra with increasing spin density, caused by the spin–spin interaction, have been observed for this semiconductor doped with phosphorus [4].

However, these measurements were insufficiently detailed because of the small number of samples in the set under study and insufficiently gradual change in the spin density. A more detailed study could be performed for this range of spin concentrations in Ge:As samples [5, 6].

A study of the ESR in n-Ge:As in the vicinity of the IM phase transition makes it possible to obtain an abundant information about changes in the magnetic properties of the impurity subsystem in this range of concentrations. However, this technique has an important disadvantage which consists in that it is by no means applicable for all paramagnetic impurities. The most interesting impurities in this regard are acceptors in Ge. They are also paramagnetic, but commonly do not appear in ESR because of the another type of the hole wave function [3].

The magnetic properties of p-Ge in the vicinity of the IM phase transition can be studied by measuring the static magnetic susceptibility. But it is necessary to find out how the results are precise that can be obtained from measurements of this kind. We made an attempt to solve this problem by comparing the results of measurements of the static magnetic susceptibility ($\chi_{\text{stat}}$) of n-Ge:As on a SQUID installation and the dynamic magnetic susceptibility ($\chi_{\text{dyn}}$) by means of ESR. An analysis of results obtained using both techniques for n-Ge:As is the goal of the present study.

**COMPARISON OF THE RESULTS OF THE PARAMAGNETIC SUSCEPTIBILITY MEASUREMENTS IN N-GE:AS**

The magnetic susceptibility was measured on the samples previously used to study ESR spectra [5, 6]. It was found from the resonance ESR absorption signal (dynamic
magnetic susceptibility $\chi$ as $\chi \approx \int P dH$, with the existence of a skin layer, changes in the Q-factor of the resonator, and the Dysonian shape of the absorption line taken into account. The static magnetic susceptibility was measured with a SQUID MPMS-XL-1 instrument operating in the temperature range 1.7–400 K in magnetic fields of up to 10 kOe. The "reciprocal sample option" function improved the measurement accuracy to $10^{-9}$ cm$^3$/g.

Figure 1 shows temperature dependences of the dynamic magnetic susceptibility for a set of samples with spin concentrations close to the critical concentration for the IM phase transition ($n_C = 3.7 \times 10^{17}$ cm$^{-3}$). The same figure presents, for comparison, the dependence corresponding to the Curie law. It follows from (1) that the slope ratio of the curve obeys this law when the number of paramagnetic species is preserved as the temperature is varied; a faster decrease with increasing temperature occurs if the number of paramagnetic species becomes smaller, and a slower decrease, if this number grows.

All the temperature dependences show three regions of departure from the Curie law: low-temperature ($T \leq 5$ K), in which $\chi$ rapidly decreases with increasing temperature; intermediate ($5$ K $\leq T \leq 20$ K), in which $\chi$ is nearly invariable; and high-temperature ($T \geq 20$ K), in which $\chi$ gradually decreases.

Plotting the dependence $1/\chi(T)$ makes it possible to determine the nature of interaction between spins at their different densities near the IM phase transition. These dependences are shown in Fig. 2 for several samples for the low-temperature range ($T < 15$ K). The intersection of the dependences in the figure with the abscissa axis can be used to judge, in accordance with (2), about the nature of the carrier interaction. At high temperatures ($T > 6$ K), $1/\chi(T)$ gradually decreases as the temperature becomes lower. This temperature range was analyzed in our previous studies [7, 8]. The behavior of the magnetic susceptibility at these temperatures was attributed to the appearance of antiferromagnetically coupled pairs of spins. However,
using now the digital signal recording and a cryostat working at temperatures down to 2 K, we could reveal additional low-temperature region.

In this range χ rapidly grows with the temperature falls and, consequently, the function 1/χ(T) rapidly decreases. As can be seen from these curves, the decrease of the function 1/χ(T) below 3.5 K can be represented by a straight line crossing the abscissa axis at T > 0. In this case, it should be admitted that, in accordance with the Curie–Weiss law, a ferromagnetic coupling of spins is observed in this temperature range. With approach to the critical point, this effect becomes less pronounced and sample 1, the closest to the transition, is a paramagnetic and the dependence 1/χ(T) for this samples has Θ = 0.

**FIGURE 3.** Temperature dependences of the static magnetic susceptibility for the same samples after subtracting the lattice susceptibility.

**FIGURE 4.** Superimposed temperature dependences of χ, determined from EPR and SQUID: (1) EPR, right-hand scale; and (2) SQUID, left-hand scale (sample 2).

Our experiments demonstrated that all the samples under study are diamagnetic. This is natural because the lattice diamagnetic susceptibility substantially exceeds the impurity paramagnetic susceptibility. After its diamagnetic part is subtracted from the full susceptibility, the temperature dependences χ(T) take the form shown in Fig.3. It can be seen that the temperature-dependent part of χ has two characteristic portions: an increase in temperature at low temperatures (T ≤ 10 K) leads to a decrease in χ, and that at high temperatures (T ≥ 10 K), to an increase in this parameter. Comparison with Fig.1 shows that the behavior of the temperature-dependent part of the curves at low temperatures qualitatively coincides with the results of EPR measurements, i.e., it is determined by the presence of impurity spins in a sample. However, an increase in temperature in ESR measurements leads to a substantial decrease in χ, whereas in SQUID measurements, this decrease is less than 20%. This difference is indicative of a large contribution to the magnetic susceptibility from other materials present in the measuring volume and characterized by a magnetic moment proportional to the field and a temperature-independent χ.

To combine the dependences χ(T) obtained by using both techniques, we transformed the static susceptibility so that these dependences coincided in the low-temperature range. The result of such transformation for one of our samples is presented in Fig. 4.
FIGURE 5. Temperature dependences of the static (black symbols) and dynamic (white symbols) magnetic susceptibility $\chi$ for the same n-Ge:As samples upon fitting; 5 – Curie law.

FIGURE 6. Temperature dependences of the inverse static magnetic susceptibility for the same samples upon fitting.

Comparison of the temperature dependences of the dynamic and static magnetic susceptibilities shows that the most noticeable difference between the dependences $\chi(T)$ appears at high temperatures: $\chi_{\text{dyn}}(T)$ decreases and $\chi_{\text{stat}}(T)$ increases. Presumably, this occurs because the concentration of single spins in the samples grows, but these spins do not appear in the EPR. Such properties are characteristic of electrons in the conduction band. For these electrons, the spin relaxation time is short, so that there is no resonance absorption by these carriers. We cannot compare values of $\chi_{\text{stat}}(T)$ and $\chi_{\text{dyn}}(T)$ for this temperature range because of the difference between the spin concentrations manifested in each measurement technique.

In the liquid-helium and sub-liquid-helium temperatures range, both the static and dynamic magnetic susceptibilities increase as the temperature becomes lower. However, this increase occurs in different ways relative to the Curie law. The dynamic susceptibility increases more rapidly than according to this law, and the farther the spin concentration from the critical point, the faster this increase. At the same time, a wide scatter is observed in the growth rates of the static susceptibility. There are samples of three kinds: with faster rise, the same as that for the dynamic susceptibility; with a rise obeying the Curie law; and with a slower rise. In addition, a wide scatter of experimental values is observed in this temperature range. This is natural because the uncertainty in measurement results substantially grows when one large value is subtracted from another.

The numerical value of $\chi_{\text{stat}}$ at a temperature of 2 K fluctuates from $10^{-8}$ to $3 \times 10^{-9}$ cm$^3$/g, but there is only any trend in the dependence of these values on the carrier concentration. Therefore, we can estimate the absolute value of $\chi_{\text{dyn}}$ with the small accuracy. Its variation at T = 2 K from 200 to 1400 relative units approximately corresponds to the scatter in $\chi_{\text{stat}}$, but with a certain dependence on the carrier concentration observed for $\chi_{\text{dyn}}$.

Comparison of Figs. 2 and 6 shows that the EPR technique can sufficiently precisely determine specific features of the interaction of spins at low temperatures, but the dependences for the static susceptibility, $\chi_{\text{stat}}(T)$, proved to be much less accurate. The large scatter of points, observed for the static susceptibility, masks true
dependences. If these dependences are extrapolated with straight lines, they cross the abscissa axis in the vicinity of zero. This means that, to within the accuracy with which \( \chi_{\text{stat}} \) could be measured, the samples are paramagnetic and no spin–spin interaction can be observed. At the same time, ESR measurements demonstrate that these interactions exist, but the accuracy with which the static susceptibility is measured is insufficient for their detection.

On the whole, comparison of the results obtained in measuring the paramagnetic susceptibility of semiconductors in the vicinity of the IM phase transition shows that the SQUID technique can also be used for this purpose, but it needs modification to improve its accuracy and sensitivity.

**CONCLUSIONS**

1. Comparison of the results obtained by measuring the magnetic susceptibility by different methods shows that each of these has its own advantages and disadvantages: ESR gives the accurate temperature dependence of \( \chi \), but cannot determine its absolute value; SQUID gives the absolute value of \( \chi \) but has an insufficient accuracy for determining its temperature dependence.

2. The temperature dependences of \( \chi \) behave at low temperatures in qualitatively the same way, irrespective of the measurement technique. A decrease in temperature in the high-temperature range leads to a decrease in \( \chi \) in SQUID measurements and to a weak increase in \( \chi \) in ESR measurements.

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