Observation of the Peierls distortion in 3d doped Germanium lattice in the vicinity of the insulator-metal phase transition

T.V. Tisnek, A.I. Veinger, A.G. Zabrodskii, S.I. Goloshchapov
Ioffe Physico-Technical Institute, Russian Academy of Sciences, Politekhnicheskaya 26, St. Petersburg, 194021 Russia
Tatjana.Tisnek@mail.ioffe.ru

Abstract. A study of the electron spin resonance in Ge:As revealed that, in uncompensated semiconductors with shallow impurity levels, the insulator state is preserved near the insulator-metal phase transition because of the appearance of lattice distortions caused by interaction of spins localized on impurity atoms and the resulting spin-Peierls transition. In Ge:As, this effect is manifested at carrier concentrations \( n = 3 \times 10^{17} \text{--} 3.7 \times 10^{17} \text{ cm}^{-3} \). Owing to the random distribution of impurities in the Ge lattice, the properties of this transition differ from those of a similar transition in substances in which uncompensated spins are localized on constituent ions of the host lattice.

1. Introduction
It is known that, in some cases, metals can be transformed into insulators because their lattice becomes more complex. Peierls was the first to point to this possibility [1]. He demonstrated for the example of a linear chain of atoms that a regular chain is never stable for a unidimensional metal with a half-filled band (each atom contains a single electron). Distortions of this chain (atomic displacements) lead to formation of atomic pairs (dimerized state) and give rise to a discontinuity in the energy spectrum of electrons, i.e., to a forbidden gap. In this case, the spins of electrons in a pair are aligned antiparallel, and the uniaxial lattice itself becomes antiferromagnetic. The gap is situated in such a way that all states below are filled, and those above, empty. Thus, there occurs a phase transition from the metallic state to that of an antiferromagnetic insulator. Such a transition is energetically favorable because, in this case, the energy of electrons is lowered to an extent exceeding that to which the energy of atoms increases upon their elastic displacement.

In the 1970s, experimental studies revealed transitions of this kind first in unidimensional organometallic compounds, and then in quasi-2D compounds CuGeO₃ [2] and NaV₂O₅ [3]. Later, similar properties were found in Gd₂Ti₂O₇ [4]. The results obtained made it possible to determine the general properties of substances experiencing a spin-Peierls transformation: (i) a static distortion of the structure appearing as a result of the transition to the dimerized state, (ii) the paramagnetic susceptibility sharply decreasing in an isotropic way, and (iii) a gap opening-up in the energy spectrum. These specific features were briefly formulated in [5].

Our recent studies of the electron spin resonance (ESR) in n-type Ga:As semiconductor near the insulator-metal (IM) phase transition have shown that, in a number of cases, the ESR spectrum becomes anisotropic at low temperatures in this impurity concentration range, which points to a lattice distortion [6, 7]. The present study is devoted to analysis of the specific behavior of Ge in order to...
demonstrate that a spin-Peierls transition occurs at low temperatures and to elucidate the conditions for its occurrence in this system.

2. Experimental results

ESR spectra of a shallow As impurity in Ge were studied. The sample fabrication technique and specific features of the low-temperature transport in samples of this kind were described in [6]. It was found that the spectrum becomes anisotropic in the close vicinity of the critical concentration, with the strongest line recession observed when the magnetic field $H$ is aligned with one of the [110] axes.

The dependence of the position of the spectral lines on the direction of the magnetic field is shown in Fig. 1. It can be seen that the spectrum comprises three lines with the positions of two of these lines dependent of the magnetic field direction and the third line being isotropic. As shown in [8], two lines of such a spectrum correspond at a low spin ($\sim 10^{15}$ cm$^{-3}$) to splitting of the isotropic line under a uniaxial compression of the crystal along one of the [110] axes. Consequently, atoms of the Ge lattice are displaced along this axis. The isotropic line indicates that the uniaxial compression is not observed throughout the crystal. We suggest that this part of the spectrum is due to local regions in the crystal, converted to the metallic state because of fluctuations of the As impurity distribution. Thus, it can be stated that a spontaneous appearance of internal stresses is observed near the IM phase transition in Ge, which is one of general indications of the spin-Peierls phase transition.

Temperature dependences of the splitting of the ESR line are shown in Fig. 2 for three samples with different electron concentrations. It can be seen that, at low temperatures (below 20 - 25 K), the splitting remains constant. At higher temperatures it decreases to disappear at around 100 K. The decrease is described by the relation $\Delta H \propto \log T$ at $T \geq 20$ K. The splitting of the spectrum is strongly affected by electron concentration. This effect disappears at the lower impurity concentration.

3. Discussion

If we consider the properties of a spin-Peierls transition caused by interaction of spins of the main lattice, one of its principal features is that it occurs at a certain temperature. By contrast, the random distribution of impurity atoms in a semiconductor results in that the transition must occur in a temperature range, because the exchange interaction of spins, responsible for this transition, exponentially depends on the distance between impurity atoms. However, the relationship between the exchange interaction and the transition temperature is rather complicated, and, therefore, it is impossible to determine the width of this interval. Figure 2, in which the splitting of ESR lines is shown for three samples with different impurity concentrations demonstrates that the low-temperature
boundary of the temperature range in which the lattice distortion decreases lies at approximately 20 K. As temperature increases, the lattice distortion decreases in proportion to the logarithm of temperature.

Another feature of the spin-Peierls transition in substances with uncompensated spins in the host lattice is the sharp decrease in the magnetic susceptibility $\chi$ because of the dimerization, in which two spins are bound antiparallel and give nearly zero contribution to $\chi$. Because the transition caused by the dimerization of impurities in the semiconductor occurs within a certain temperature interval, it may be not accompanied by a sharp change in this parameter. Experimental data analysis showed that the weak growth was observed in this case.

However, analysis of ESR resonance lines makes it possible to directly trace the temperature-related changes in the density of single spins, which are bound into pairs as temperature decreases, and, thus, cease to be recorded by the ESR technique. A procedure for such an analysis was described in detail in [9].

It can be seen that, as temperature is lowered, the density of single spins exponentially decreases, which means that their dimerization occurs. At $T = 0$, all the spins are bound into pairs. All the dependences in Fig. 5 are described by the relation:

$$n_S = n_{S0} \left[1 - \exp \left(-\frac{T}{T_0}\right)\right],$$

(1)

where $n_{S0}$ and $T_0$ are constants, the first of which has a dimension of concentration, and the second, that of temperature.

It can be readily shown that the density $n_P$ of pairs (dimers) increases in accordance with the following formula as temperature is lowered:

$$n_P = n_{P0} \exp \left(-T/T_0\right),$$

(2)

Here, $n_{P0}$ is the pair density at $T = 0$, and $T_0$ is the characteristic binding energy in a pair; for each studied sample, $T_0$ = 20, 22, and 28 K, respectively.

Figure 3 shows that the pair disintegration starts at the absolute zero temperature, but this does not lead to a decrease in the lattice distortion. Comparison with Fig. 2 shows that, only at temperatures higher than the characteristic temperature, when the pair density substantially decreases (by more than a factor of $e$), the effect of the spin system on the lattice begins to decrease. Thus, as temperature increases and reaches the characteristic temperature, a decrease in the lattice distortion starts to be observed. A return to the undistorted cubic lattice occurs at rather high temperatures, at which dimers constitute a negligible part of the spin subsystem.

The occurrence of the spin-Peierls transition in the subsystem of impurity spins in the semiconductor seems to be surprising because, in this case, a comparatively low impurity concentration controls the lattice symmetry. Indeed, the presence of the impurity in Ge in a concentration on the order of $10^{17}$ cm$^{-3}$ leads to displacement of lattice atoms whose concentration is on the order of $10^{21}$ cm$^{-3}$. This contradiction is eliminated if we take into account the Bohr radius of the shallow impurity. Compared with CuGeO$_3$ ionic crystals, in which the Bohr radius of the uncompensated spin is on the order of the ionic radius of Cu$^{2+}$ (on the order of 1 Å), the same Bohr radius in Ge is about 60 Å and the exchange interaction between spins localized on donors is manifested even at such a low spin density.
The third specific feature of the spin-Peierls transition is that, as a result of the elastic lattice distortion, the full energy of electrons decreases and a forbidden gap appears in their energy spectrum. Let us consider how this occurs in Ge:As. A study of the ESR in lightly doped Ge:As has shown that applying a pressure along one of the [110] axes leads to an increase in the spacing between the ground (singlet) and first excited (triplet) levels of As in Ge [8]. This effect is observed in the insulator state only. After transition into the metallic state, ESR spectrum becomes isotropic.

It follows from the aforesaid that, near the IM phase transition, Ge remains in the insulator state due to the spin-Peierls transition, which consists in that the energy of occupied electron states decreases because of the lattice distortion. However, the range in which this effect exists is not wide: it is only observed at electron concentrations of $3 \times 10^{17}$ cm$^{-3}$ and more (Fig. 3) and occurs in none of the samples with electron concentrations $n < 3 \times 10^{17}$ cm$^{-3}$. Thus, it follows from the experiment that the insulator state is preserved in uncompensated and weakly compensated samples at electron concentrations in the range $3 \times 10^{17} - 3.7 \times 10^{17}$ cm$^{-3}$ because of the lattice distortion.

4. Conclusions
The spin-Peierls transition occurs in nonmagnetic uncompensated and weakly compensated semiconductors at low temperatures and has the following properties:
(1) The cubic lattice of the semiconductor is distorted, with atoms displaced along the diagonals of the cube faces, as this occurs under a uniaxial compression along one of the [110] axes.
(2) The distortion is accompanied by binding of donor electrons into pairs, with the result that the concentration of single spins recorded by ESR decreases. As temperature tends to zero, all the spins are paired, so that the ESR signal amplitude also approaches zero.
(3) As a result of the lattice distortion, a gap appears in the energy spectrum of electrons when the electron concentration reaches $\sim 80\%$ of the critical value, and, in further approach to the critical concentration, the insulator properties of the semiconductor are determined just by this gap.

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