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PECULIARITES OF MAGNETORESISTANCE IN SINGLE CRYSTALS InSe AND GaSe, LASER INTERCALATED BY CHROME

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Abstract. Giant magnetoresistance in the laser intercalated by chrome single crystals of gallium selenide and indium selenide is observed. Specific resistance in $<Cr>_x InSe$ is changed both in its value and sign. In $<Cr>_x GaSe$ the applied magnetic field causes 87% change of the specific resistance. Reason of the anomalous magnetoresistance is analyzed.

Keywords: intercalated, magnetoresistance, single crystals

INTRODUCTION

The unique possibilities of change of the ferromagnetic properties of a hybrid system ferromagnetic-semiconductor by the optical and electrical methods cause today heightened interest [1]. Such changes may be used, in particular, at making of the modern functional units of spintronics. As the effect of the influence of semiconductor on a ferromagnetic is more marked for the thin ferromagnetic film there is actual a problem of reception of the semiconductor structures with minimally possible thickness alternating magnetoactive layers. From this viewpoint the particular interest evokes intercalation as a method of the formation of nanostructures with the matrix isolation [2]. It is exclusively important for the solution of a problem of the stability of nanosystems [3]. In the proposed paper observation of giant magnetoresistance (GMR) in layer semiconductor GaSe with introduced into its van der Waals gap monolayers of atom of chrome is presented, and its practical value for technological realization of a superparamagnetism.

THE EXPERIMENTAL PART

Layer semiconductors gallium selenide (GaSe) and indium selenide (InSe) were basic objects in the experiments. Single crystals of these compounds were grown by Bridgman method in the quartz vacuum-processed ampoules, according to the growth process described in [4].

It is known [5], that layers along crystallographic C-axis in gallium selenide and indium selenide are connected between them by weak van der Waals forces. Penetration into van der Waals gaps of foreign ions, atoms or molecules is known as the phenomenon of intercalation [6.] The investigated structures with Cr as a "guest" were obtained by just intercalation. Cr penetration was reached using a laser, because of restriction of an electrochemical method intercalation of *d*-elements, caused by their low potential of eduction on single crystal GaSe and InSe. For this purpose from the obtained ingots samples in the form of a rectangular parallelepiped of 8 mm x 4 mm x 0,5 mm, in which two faces are perpendicular to crystallographic C-axis, and four another ones are parallel to it. On one of these four faces by thermal spraying in vacuum was superimposed a chrome film of thickness 1 ÷ 3 microns. Then the beam of the neodymium laser working in the free generation regime (a pulse length 2 ms, a wave length λ = 1,06 μm, radiation energy density - 9, 5 ± 0, 5 Jcm^{-2}) was directed on the evaporated film at angle of 90º ± 1º to it.

The impedance was measured in the frequency range from 10^{-3} to 10^6 Hz using a measuring complex "AUTOLAB" (firm ECO CHEMIE, Holland), completed by computer programs FRA-2 and GPES.

In fig. 1 dependence of a perpendicular to layers specific resistance of $<Cr>_nInSe$, $\rho_\perp(x)$, at different number of the intercalation impulses n is presented. Fig. 2 shows analogous dependence in such crystal after the 3-rd intercalation impulse in magnetic field. In fig.3 dependence of magnetoresistance of $<Cr>_nInSe$ in permanent magnetic field 0.5 kOe on number of intercalation impulses is presented. Fig.4 presents analogous to fig.2 dependence for wider gap, than InSe, layer semiconductor GaSe namely $<Cr>_nGaSe$ at n=2, and fig.5 is Nyquist diagram of this system.

Let us analyze the obtained results. The nonmonotonic dependence of the specific resistance change in $<Cr>_nInSe$ on the content of an impurity in contrast to the same dependence in $<Cr>_nGaSe$ can be explained by various change of the electron states, caused by intercalation by chrome of various crystalline matrixes. Such difference can be connected with a different degree of the electron mixing of an impurity with InSe- and GaSe-matrixes. Alike, that mixing Cr with GaSe is much less than mixing Cr with InSe. There is more nonordinary possible reason of such nonordinary behaviour of $\Delta\rho_\perp$ (x) in $<Cr>_nInSe$, namely, the change of the thermodynamic stable positions of intercalated atoms in the van der Waals gap (octahedral and tetrahedral sites) at change of their quantity. Such situation is observed in the layer crystal Na_xTiS_2 [3], which has similar with InSe and GaSe crystal symmetry.

As follows from fig.2, $\Delta\rho_\perp$ in $<Cr>_nInSe$ is changed grossly with increase of the intercalated chrome content at even small applied magnetic field. At that $\Delta\rho_\perp$ (x) is changed both in its value and sign (fig. 2b) (in initial samples $\dfrac{\Delta\rho_\perp}{\rho_\perp}$ is within 2.22 %). It can be the consequence of the electron states modification due to intercalation. Such assumption verifies decrease of specific resistance in Cr_nInSe for n=3 in comparison with n=2.

In fig.3 the 87% change of specific resistance due to the applied magnetic field in GaSe, intercalated by chrome, was observed only after the second laser intercalation impulse.

It should be noted, that we investigated magnetoresistance at various mutual orientations of magnetic and electrical field. The above-mentioned analysis was for different their orientations (the maximum effect is at their perpendicular orientation). At the coincident orientations of the fields the effect of the curvature of the carrier trajectories by magnetic field is absent and normal or anomalous behavior of magnetoresistance (i.e. increase or decrease of resistance at increase of magnetic field, accordingly) will be defined by position of an impurity levels with regard to Fermi level. As a whole, for both GaSe and InSe at the magnetic field, oriented along layers, the specific resistance is higher, than for the magnetic field, orientated along C-axis. It can be the result of the additional scattering carriers of the current due to the Lorentz force that is agreed with the two-arc Nyquist diagrams (fig. 4, a curve 3).

DISCUSSION

In the beginning of interpretation of the anomalous large magnetoresistance in the intercalated layer crystals we use some analogies and make generalizations which can be a basis of the phenomenon.

There is known today objects with large magnetoresistance, in which so-called giant magnetoresistance (GMR) takes place. Despite of the today practical using of GMR in some devices, nevertheless, a precise understanding of the mechanism of the phenomenon is absent.

GMR for the first time was observed in magnetic multilayer [7-8] and in some compounds and systems, such as granulated AgCo, CuCo [9-11]. Recent investigations of the phenomena were done in the layer structures *F1/N/F2/F1 / ….* (*F1, F2* are ferromagnetic layers with a portion of impurity, and *N* are layers of nonmagnetic material) [12]. At that the phenomenological theory with consideration of a various spin dependence of the interface and intraface resistances was used. In these and other investigations of GMR two factors, which accompany it, attract attention:

Geometrical factor - the size of the sample and its dimensionality;

Presence at samples of a transition group element.

These factors take place in investigations of GMR in GaSe, intercalated by chrome. Really, GMR has been observed only at presence Cr in gallium selenide (in pure GaSe GMR is absent);

Geometrical factor in observed case, i.e. low dimensionality of the layer crystal GaSe, its quasi two-dimensionality, is caused by weak interlayer electron mixing. The important factor for display GMR in our case is the intercalated impurity (in our case Cr) in van der Waals gaps of the layer crystal.

It should be noted that the pure layer crystals is nonmagnetic. But the intercalated layer crystal is similar to presented above structure *F1/N/F2/F1 / ….*, namely *F/N/F/N ….*, where *F* are the monolayer layers, formed by the intercalated atoms of the transition metals, and *N* is layers of a crystalline matrix. Because of the weak

electron mixing of intercalated layers both between themselves and with neighbor layer of a crystalline matrix it is possible to consider a intercalated crystal as a set of quasi two-dimensional structures with an impurity (Cr), which conserves atomic identity (zero approach). This fact, in our opinion, can be reason of unique of the magnetic behaviour of the transition metal in van der Waals gap of the layer crystal. It is known, that such metals, having in the free state a magnetic moment, can keep only a part of this moment or entirely lose it in a crystalline matrix. It is natural suppose, that the alloyed ("dissolved") atom in a layer crystal has more chances to lose the individuality (in this case magnetic one) as an atom, than an intercalated atom. In the first case we deal with three-dimensional object, and in other one - with quasi two-dimensional. Importance of the geometrical factor in the magnetic phenomena is noted also in papers [13-14]. In them it is shown, that the magnet moment of the chrome clusters is equal 1.6 μ_B whereas for the bulk chrome it equals only 0.54 μ_B (μ_B is a Bohr magneton). Observation by us GMR allows supposing, that intercalated chrome owns a nonzero magnetic moment.

For a theoretical substantiation of GMR let us consider intercalated by the transition metals layer crystal in the framework of the one-impurity approximation, using Anderson model. Let the dispersion law of electrons in the crystal is described by some $E(\vec{k})$, and the level of an impurity is equal E_0. Applied magnetic field H causes the symmetric, in comparison with a case $H = 0$, opposite displacement of bands in a crystal (see fig.6) and an atom levels with opposite spins (the Zeeman effect). Similar effect takes place not only in an intercalated crystal, but also in any other one. Naturally, there is a question - why the abnormal behavior $\rho(H)$ is observed only in the first case and not observed in other? For the answer to such question we view system a layer crystal + intercalated atom of the transition group, which is described in the framework of the one-particle approximation by the Anderson Hamiltonian:

$$\hat{H} = \sum_{k\sigma} t(k\sigma) c_{k\sigma}^+ c_{k\sigma} + \sum_{\sigma} \varepsilon_0(\omega) a_{0\sigma}^+ a_{0\sigma} + \sum_{k\sigma} \left(V_{k\sigma} c_{k\sigma}^+ a_{0\sigma} + h.c. \right) \tag{1}$$

Here

$$t(k\sigma) = E(k) + \mu_B g\omega H \tag{2}$$

where μB is the Bohr magneton, g is the Lande factor, σ is a spin ($\sigma = \pm 1$); $c_{k\sigma}^+$, $c_{k\sigma}$ are the creation and destruction operators of an electron in a state $(k\sigma)$;

$$\varepsilon_0(\sigma) = E_0 + \mu_B g\sigma H + V < n_{-\sigma} > \tag{3}$$

is position of a level of an intercalated atom ($a_{0\sigma}^+$, $a_{0\sigma}$ are the creation and destruction operators of an electron on an intercalated atom in a state with a spin σ); last term describes the Coulomb interaction of electrons with opposite spins on the impurity atom in the framework of the self-consistent field. Last term in (1) is the electron mixing of the intercalant-intercalate system; V_k is an overlapping integral.

Using a double-time retarded Green function $<< a_{0\sigma} | a_{0\sigma}^+ >>$, from an equation of motion for such Green function and a Green function $<< a_{0\sigma} | a_{0\sigma}^+ >>$, generated by it, we obtain

$$<< a_{0\sigma} | a_{0\sigma}^+ >> = \frac{1}{\omega - \varepsilon_0(\sigma) - \Sigma_\omega}, \tag{4}$$

where

$$\Sigma_\omega = \sum_k \frac{|V_k|^2}{\omega - t(k\sigma)} \tag{5}$$

Introducing double-time retarded Green function $<< c_{k\sigma} | c_{k'\sigma}^+ >>$ after similar transformations, we have

$$<< c_{k\sigma} \left| c_{k'\sigma}^{+} \right. >> = \frac{V_k V_{k'}^{*} \prod\limits_{k_1 \neq k, k'} \left(\omega - t(k_1 \sigma) \right)}{\left(\omega - \varepsilon_0(\sigma) \right) \prod\limits_{k_1} \left(\omega - t(k_1, \sigma) \right) - \sum\limits_{k_2} \left| V_{k_2} \right|^2 \prod\limits_{k_1 \neq k_2} \left(\omega - t(k_2, \sigma) \right)} \qquad (6)$$

It is easy to see, that poles of Green functions (4) and (6) coincide. Such poles determine electron states of the intercalant-intercalate system. Let us analyze behaviour of initial position of an impurity level, using the Green function (4). Electron mixing of the impurity atom with the crystalline matrix, proportional V_k, leads to occurrence of a self-energy part. Its real part defines the energy shift of levels, and the imaginary part defines the damping of such levels. Essentially that in our case the overlapping integral V_k is small; hence, damping of the levels is small.

Minimal change of structure of the intercalated atom levels with regard to the structure of the atomic levels up to the intercalation allows as a zero approximation accept $V_k = 0$ in (5) and analyse effect of magnetic field in the layer crystal as in system of non-interacting impurity atom and crystal matrix.

It is known [15], that depending on potential of the impurity atom in a crystal matrix its behaviour is various. If potential is sufficiently large the atomic orbitales are bound states. If the potential is not so large to create the bound states its levels move into a conduction band. Thus electrons become delocalized, capable to take part in the kinetic phenomena.

Prolong our analysis from the viewpoint of change of the carrier concentration, which to a great extent defines the kinetic phenomena. It is known, that magnetic field in a crystal matrix leads to growth of carrier concentration. Really, in the case T=0 in a crystal with Fermi level ε_F in a conduction band described by the isotropic dispersion law in magnetic field H the total carrier concentration equals [16]

$$n = n_{+} + n_{-},$$

where

$$n_{\pm} = \frac{4\pi}{3h^3} 2m \left(\varepsilon_F \pm \mu_B gH \right)^{3/2}$$

At the limit of small fields, $\mu_B gh << \varepsilon_F$,

$$n = 2 \frac{8\pi m}{3h^3} \left[\varepsilon_F^{3/2} + \frac{3}{4\sqrt{\varepsilon_F}} \left(\mu_B gH \right)^2 \right],$$

i.e. the carrier concentration grows with growth of H.

As to a layer crystal, the dispersion law of carriers in it is sharp anisotropic. It is a constant except of area order of the allowed band width along a normal to the layers. If to neglect such fact, i.e. a layer crystal to view as a set of the noninteracting layers, a density of states in it $\rho(\omega) = const$. Hence,

$$n = n_{+} + n_{-} = \int_0^{\varepsilon_F + \mu_B gH} const \rho(\omega) d\omega + \int_0^{\varepsilon_F - \mu_B gH} const \rho(\omega) d\omega = 2 const \varepsilon_F,$$

i.e. n is independent at all on the field H. It follows that in a real layer crystal will be the nonzero change of carrier concentration, caused by magnetic field, but such change will more less than in the case of an isotropic crystal.

Consider an impurity (foreign atom), intercalated into a crystal matrix. If at absence of a magnetic field it is characterized by the localized states at some value of a magnetic field the upper splitted by the magnetic field level will cross the lower spitted band with an opposite spin In future this level becomes resonance. It is accompanied by growth of carrier concentration. At further increase of H the resonant level will move to ε_F. It should be noted importance of the resonance level localization in the band. The level closed to ε_F gives greater contribution to the kinetic phenomena, than the same level at near bottom of the band.

In case of the intercalant-intercalate system such increase will be more pronounced than in the case of a

usual doping of a crystal by impurities because of small overlapping integral V_k and, as consequence, its greater density of states. Therefore in this case the factor of increase of carrier concentration in GMR can be prevailed over the factor of opposite effect related with curvature of the trajectories of carriers in the magnetic field. In case of a usual doping the increase of carrier concentration also takes place. But caused by it the decrease of the resistance yields to increase of the resistance caused by the curvature of trajectories of carriers in a magnetic field, normal oriented to a current.

The unique confirmation of the above mentioned description of GMR demands of the additional investigations of electron states of the intercalated impurities (in particular, Cr) in layer crystals (in particular, in GaSe). Such information will allow predicting the presence or absence GMR for the concrete impurities of atoms of the transition metals in concrete layer crystals.

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