Determining from this the Green's functions, and with their aid the mean values of interest to us, we get the following expressions which enable us, when account is taken of (13), to express $\lambda_{01}^{(4)}, \bar{\lambda}_{01}^{(5)}$ in terms of $\lambda^{(2)}, \lambda^{(3)}$:

$$f_{01}^{(4)} = K^{-1}N^{-1}f_0^{(2)}\bar{f}_1^{(3)},$$

$$\bar{f}_{01}^{(5)} = (NK)^{-1}[f_1^{(3)} - \langle Z_m^{22}\rangle]f_0^{(2)}.$$

[1]V. P. Zinov'ev, P. V. Gel'd, and A. L. Sokolov, Fiz. Tverd. Tela (Leningrad) **18**, 1329 (1976) [Sov. Phys. Solid State **18**, 764 (1976)].
[2]H. Katzman and J. A. Myodosh, Phys. Rev. Lett. **29**, 998 (1972).
[3]G. Oomi and T. Mitsui, J. Phys. Soc. Jpn. **41**, 705 (1976).
[4]A. J. Arko, M. B. Brodsky, and W. J. Nellis, Phys. Rev. B **5**, 4564 (1972).
[5]E. E. Havinga, K. N. J. Buschow, and H. J. Van Daal, Solid State Commun. **13**, 621 (1973).
[6]I. Peschel and P. Fulde, Z. Phys. **238**, 99 (1970).
[7]M. B. Brodsky, Phys. Rev. B **9**, 1381 (1974).
[8]M. Kamimoto, Y. Takahashi, and T. Mukaibo, J. Phys. Chem. Solids **37**, 719 (1976).
[9]R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Lett. **19**, 840 (1967).
[10]B. Cournut and B. Coqblin, Phys. Rev. B **5**, 4541 (1972).
[11]R. Jullien, M. T. Beal-Monod, and B. Coqblin, Phys. Rev. B **9**, 1441 (1974).
[12]A. F. Barabanov, K. A. Kikoin, and L. A. Maksimov, Solid State Commun. **18**, 1527 (1976).
[13]D. Wohlleben J. Phys. (Paris) **37**, C4-232 (1976).
[14]C. M. Varma, Rev. Mod. Phys. **48**, 219 (1976).
[15]J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).
[16]E. V. Kuz'min, G. A. Petrakovskiĭ, and E. A. Zavadskiĭ, Fizika magnitouporyadochennykh veshchestv (Physics of Magnetically Ordered Substances), Nauka, Novosibirsk, 1976.
[17]A. F. Barabanov, K. A. Kikoin, and L. A. Maksimov, Teor. Mat. Fiz. **20**, 364 (1974).
[18]E. S. Alekseev and A. F. Barabanov, Fiz. Tverd. Tela (Leningrad) **18**, 1686 (1976) [Sov. Phys. Solid State **18**, 979 (1976)].
[19]J. Hubbard, Proc. R. Soc. London Ser. A **285**, 542 (1965).
[20]R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[21]D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [Sov. Phys. Usp. **3**, 320 (1960)].
[22]M. Darby and K. N. Taylor, Physics of Rare-Earth Solids, Halsted, 1972.
[23]Yu. N. Smirnov and I. A. Prokhorov, Zh. Eksp. Teor. Fiz. **67**, 1017 (1974) [Sov. Phys. JETP **40**, 504 (1975)].
[24]V. M. Polovov, Zh. Eksp. Teor. Fiz. **65**, 1557 (1973) [Sov. Phys. JETP **38**, 775 (1974)].
[25]V. M. Polovov and L. G. Maĭstrenko, Zh. Eksp. Teor. Fiz. **68**, 1418 (1975) [Sov. Phys. JETP **41**, 707 (1975)].
[26]S. Doniach, Proc. of Seventeenth Conf. on Magnetism and Magnetic Materials, Chicago, 1971, AIP, New York, 1972.

Translated by J. G. Adashko

Many-particle impurity complexes in silicon doped with boron, phosphorus, and antimony

A. S. Kaminskiĭ, V. A. Karasyuk, and Ya. E. Pokrovskiĭ

Institute of Radio Engineering and Electronics, Academy of Sciences of the USSR, Moscow

(Submitted 28 December 1977)
Zh. Eksp. Teor. Fiz. **74**, 2234–2243 (June 1978)

Recombination radiation emitted at helium temperatures from silicon doped with boron, phosphorus, and antimony was investigated experimentally as a function of the photoexcitation conditions and uniaxial compression. The results obtained confirmed the formation of many-particle impurity complexes and were interpreted using the shell model of these complexes.

PACS numbers: 78.60.–b, 78.20.Hp

1. INTRODUCTION

The recombination radiation spectra of silicon doped with group III and V elements exhibit, at helium temperatures, a series of narrow lines[1-3] located on the low-energy side directly beyond the bound-exciton peak.[4,5] The spectral positions of these lines in the series are characteristic for each of the dopants and the lines themselves appear in decreasing order of their energy as the excitation rate is increased. On this basis, it has been concluded[1-3] that the new lines are due to the radiative decay of many-particle complexes formed as a result of the consecutive capture of one, two, or more excitons by an impurity atom. We shall denote these complexes by $B_1, B_2, \ldots$ and the corresponding recombination radiation lines by $\alpha_1, \alpha_2, \ldots$, and so on.[6] Thus, a complex B_m consists of a singly charged impurity atom, m carriers of the same sign, and $m+1$ carriers of the opposite sign. A system of this kind is basically different from an ordinary atomic or molecular system because the latter contains light particles of just one sign.

The proposed explanation[1-3] of the origin of these α lines has been confirmed in a number of investigations[7-9] of the kinetics of formation and decay of many-particle complexes. Later investigations[10,11] have been concerned with the splitting of the α lines in a magnetic field and as a result of uniaxial deformation of silicon. According to these authors, the results obtained cannot be explained by any model of many-particle impurity complexes. It is suggested[10,11] that the

0038-5646/78/061162-06$02.40

α lines are due to the decay of a bound exciton B_1 accompanied by the creation of a neutral impurity center in the ground or excited state and a photon of energy which depends on the initial state of B_1 and the final state of the impurity center. The superlinear dependence of the intensities of the α lines on the excitation rate is explained assuming additionally the participation of some elementary excitations of a crystal in the decay process.

We shall report experimental results which contradict this attribution of the α lines to the decay of a bound exciton alone. Our results confirm the existence of many-particle impurity complexes[1-3] and can be explained using the recently proposed[6,12] shell model of complexes.

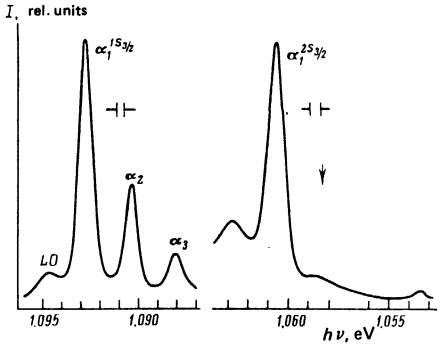

FIG. 1. Luminescence spectra of many-particle complexes in silicon doped with boron (6×10^{14}cm^{-3}), recorded at 4.2°K. The $LO-TO$ components are shown and, of these, the $1S_{3/2}$ and $2S_{3/2}$ components are recorded under identical conditions.

2. EXPERIMENTAL METHOD

We investigated silicon samples doped with boron, phosphorus, and antimony in concentrations of $10^{14}-10^{15}$ cm^{-3}. A more homogeneous excitation was ensured by using thin ($10\times4\times0.15$ mm) plates. In a study of the influence of uniaxial compression, use was made of $17\times1.8\times1.8$ mm samples cut along the [111] or [100] directions. Compression was applied in a device similar to that described earlier.[13] Before measurements, a sample was polished chemically in a $5HNO_3+3HF$ mixture. Excitation was provided by modulated radiation of an argon laser, focused by a cylindrical lens on the surface of a sample to form an illuminated 7×0.2 mm strip. Some of the measurements were carried out in the presence of intense background illumination. This illumination was provided by a second argon laser whose radiation was focused by the same cylindrical lens in such a way that the strips illuminated by modulated and unmodulated radiation coincided on the surface of the sample. The resultant recombination radiation was analyzed with an MDR-2 monochromator and recorded with a liquid-nitrogen-cooled photomultiplier. The modulated part of the photoresponse was amplified resonantly, passed through a lock-in detector, and plotted on the chart of an automatic potentiometer. The apparatus made it possible to record reliably the luminescence spectra of many-particle complexes with a resolution of 0.1-0.5 meV.

3. ANALYSIS OF VARIOUS RADIATIVE TRANSITIONS ASSOCIATED WITH DECAY OF MANY-PARTICLE COMPLEXES

Figure 1 shows the $LO-TO$ components of the recombination radiation (luminescence) spectrum of boron-doped silicon. It is clear from this figure that the spectrum includes the luminescence line α_1^{1S}, corresponding to the decay of a bound exciton B_1 from the ground state resulting in the creation of an acceptor in the ground state $1S_{3/2}$; the spectrum also includes α_2 and α_3 lines. Moreover, at lower energies, there is an α_1^{2S} line corresponding to the decay of B_1 accompanied by the creation of an acceptor in the excited state $2S_{3/2}$. Had the lines α_2 and α_3 been due to the decay of the bound exciton B_1 from its ground state, involving elementary excitation of a crystal, there would have been corresponding lines also in the part of the spectrum representing the creation of an acceptor in an excited state and the amplitude of the α_2 line would have had the amplitude identified by an arrow in Fig. 1. Since there is no such line, it follows that the α lines cannot be due to the decay of the bound exciton B_1 from the ground state. On the other hand, the absence of the α_2 and α_3 lines from this part of the spectrum is natural in the case of many-particle complexes because the decay of the B_2 and B_3 complexes is not accompanied by the creation of a neutral acceptor and their luminescence spectra should reflect the structure of the excited states of an acceptor. The absence of correlation between the α-line spectrum and the α_1 lines corresponding to the decay of a bound exciton accompanied by the creation of a donor in the excited states $2S$, $3S$, $4S$, and $5S$ is clearly demonstrated in Fig. 2 by the no-phonon (NP) component of the luminescence of the com-

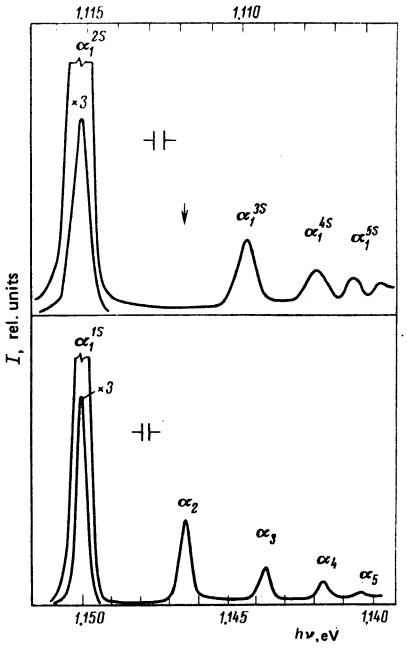

FIG. 2. No-phonon (NP) components of the luminescence of many-particle complexes in silicon doped with phosphorus (3×10^{14}cm^{-3}), recorded at 4.2°K under identical conditions.

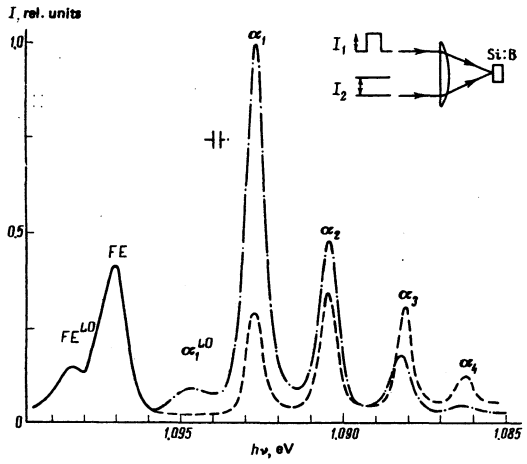

FIG. 3. Modulated parts of the *LO–TO* components in the luminescence spectrum of many-particle complexes in silicon doped with boron (2×10^{13}cm^{-3}), recorded at 4.2°K: the chain curve represents the results of excitation with the modulated radiation I_1 alone; the dashed curve gives the spectrum obtained on excitation with the modulated radiation I_1 of the same power in the presence of steady background illumination I_2; the continuous curve is the modulated part of the free-exciton luminescence, which is identical in both cases.

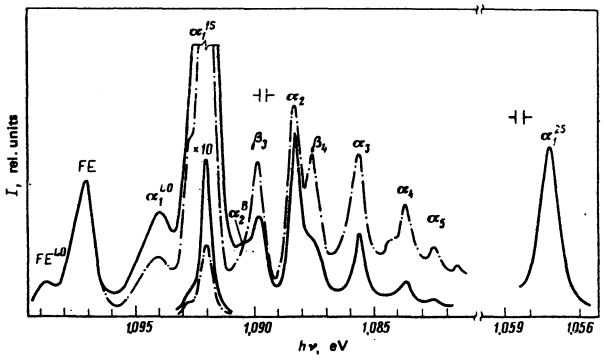

FIG. 4. Modulated part of the *LO–TO* components of the luminescence of many-particle complexes in silicon doped with phosphorus (3×10^{14}cm^{-3}), recorded at 4.2°K: the chain curve represents the results obtained by excitation with modulated radiation and steady background; the continuous curve gives the results of excitation with just the modulated radiation of the same power.

plexes in phosphorus-doped silicon.

Figure 3 demonstrates the influence of steady background illumination on the spectrum of the *LO–TO* components of the luminescence emitted from boron-doped silicon. It is clear from this figure that the steady background illumination greatly alters the ratio of the amplitudes of the α lines, whereas the amplitude of the modulated part of the free-exciton luminescence is not affected. It is clear from Fig. 3 that the background illumination largely saturates the concentration of the B_1 and B_2 complexes and, therefore, the modulated parts of the α_1 and α_2 lines decrease in intensity. On the other hand, the background illumination saturating the concentration of the B_2 complexes facilitates the formation of B_3 and B_4 under the action of the modulated exciting radiation and this increases the amplitude of the α_3 and α_4 lines in the spectrum shown dashed in Fig. 3. The changes in the amplitudes of the α lines under the action of the steady background illumination, shown in Fig. 3, are in conflict with the hypothesis[10,11] that this series is due to the decay of the bound B_1 exciton from an excited state. In fact, the background illumination can only increase the concentration of the bound B_1 excitons and elementary excitations and, therefore, the modulated part of the intensity of the α_2 line should have increased as a result of the steady illumination.

The use of intense steady background illumination has made it possible to identify much more clearly some components of many-particle impurity complexes with large values of m. These components are usually poorly resolved in the spectra recorded in the ordinary way because they lie near intense α-series lines. According to the shell model of many-particle impurity complexes,[6,12] the $\alpha_2, \alpha_3 \ldots$ lines appear as a result of the creation of the B_1 and B_2 complexes in excited states. The creation of the $B_1, B_2, \ldots$ complexes in the ground state produces β lines, observed only in the phonon components of the luminescence, and have low intensities.[14] Figure 4 shows the luminescence spectra of the complexes bound to phosphorus atoms. It is clear from this figure that the β lines, visible in the absence of the background illumination in the form of relatively small features against the stronger α_1 and α_2 lines, are well resolved in the presence of the background illumination and appear as easily identifiable peaks. The identification of the β_3 and β_4 peaks is reliable because their intensity in the presence of the background illumination varies in the same way as the intensity of the α_3 and α_4 lines. Hence, it follows that the β_3 and β_4 lines do indeed appear as a result of the decay of the B_3 and B_4 complexes responsible for the α_3 and α_4 lines.

Figure 5 shows the no-phonon (*NP*) and *LO–TO* components of the luminescence emitted by complexes in antimony-doped silicon. It is clear from this figure that there are no β lines in the *NP* component but they are well resolved in the *TO* case. It is appropriate to mention here that the α-series spectra are almost identical for silicon doped with phosphorus and antimony. Only the ratio of the amplitudes of the *TO* and *NP* components is different: it is 3 for phosphorus and ≈40 for antimony. The spectral positions of the β_3 and β_4 lines of these impurities differ much more strongly. This can

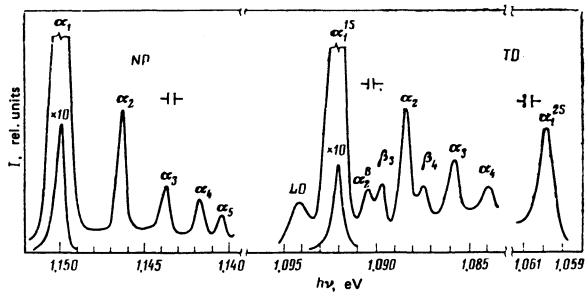

FIG. 5. Various (*NP*, *LO*, and *TO*) components of the luminescence spectrum of many-particle complexes in silicon doped with antimony (1.7×10^{15}cm^{-3}), recorded at 4.2°K. The *NP* and α_1^{2S} lines represent the results obtained using only modulated radiation; *TO* is the part of the spectrum recorded in the presence of a steady background.

be used in more reliable identification of the phosphorus and antimony impurities in silicon. An even greater difference is observed for the α_1^{2S} lines corresponding to the excited states of the donors. In the case of antimony, the line in question is shifted by 2.8 meV toward higher energies, compared with the corresponding line of phosphorus.

4. INFLUENCE OF UNIAXIAL COMPRESSION ON LUMINESCENCE SPECTRA OF COMPLEXES

Uniaxial deformation of silicon crystals splits the valence and conduction band branches and reduces the degree of band degeneracy. Since many-particle impurity complexes contain both electrons and holes, the features of the splitting of the valence and conduction bands should be manifested in the luminescence spectra of complexes in deformed silicon.

Figure 6a shows the luminescence spectrum of boron-doped silicon recorded under compression along the [111] direction. This direction is equivalent for all six conduction-band valleys and the luminescence spectra only show the valence-band splitting. It is clear from this figure that, at 4.2°K, the α_1, α_2, and α_3 lines split into two components each and these components are separated by approximately the same amount as the valence band branches (3×10^{-6} eV·kg^{-1}·cm^2). Cooling or increase in splitting greatly enhances the relative amplitude of the α_1' line. The amplitudes of the α_1' and α_1'' become comparable at temperatures above 4.2°K if the splitting is slight. The amplitude ratios $\alpha_2''/\alpha_2'\approx2$ and $\alpha_3''/\alpha_3'\approx1$ are practically independent of temperature and applied pressure. This behavior of the α lines is in good agreement with the shell model.[6,12] In fact, according to this model, holes fill a quadruply degenerate shell with the wave-function symmetry Γ^8 corresponding to the symmetry at the top of the valence band. Uniaxial compression splits the state corresponding to this shell into two doubly degenerate levels. The bound exciton B_1 contains two holes which may be located at the upper (lower-energy) level and the lower level may be populated only by thermal excitation. Therefore, the spectrum is dominated by the α_1'' line and the α_1' line is weak because of the small thermal population of the lower level, which decreases strongly as the temperature is lowered. The complex B_2 contains three holes, of which two are at the upper level and one at the lower level. The ratio of the populations of the levels should not change greatly with temperature and pressure, and should remain close to 2:1. It is indeed found that the ratio of the amplitudes of the α_2'' and α_2' lines is close to this value. The complex B_3 has two levels with two holes in each and, therefore, the intensities of the α_3'' and α_3' lines should be approximately the same, in agreement with Fig. 6a, and their ratio should be independent of temperature.

Similar splitting of the luminescence lines of the investigated complexes as a result of compression along the [111] direction is exhibited by phosphorus-doped silicon (Fig. 6b). However, in the case of donors, the hole population of the upper level is complete for $m=2$ and that of the lower level for $m=4$. Consequently, the amplitudes of the α_1' and α_2' lines decrease as a result of cooling or of increase in splitting, whereas the amplitude ratios $\alpha_3''/\alpha_3'\approx2$ and $\alpha_4''/\alpha_4'\approx1$ are practically independent of temperature and pressure.

The changes in the luminescence spectra of the complexes bound to boron atoms are more complex when silicon is compressed along the [100] direction (Fig. 7). Low pressures split the α lines into two peaks. For minimal deformations, the amplitudes of the α' and α'' lines are comparable but an increase in splitting reduces strongly the amplitudes of the α' lines and, for $\Delta_1\approx1.5$ meV, these lines are not observed even at

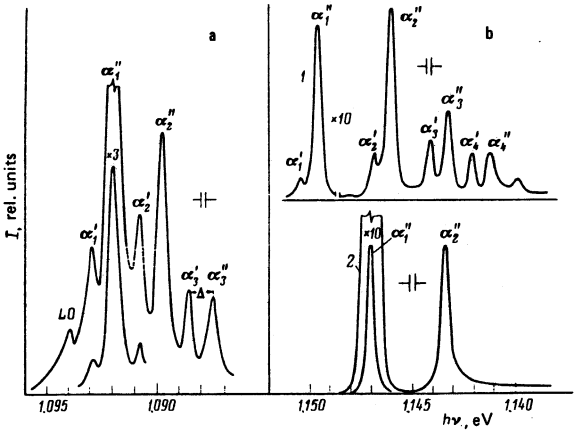

FIG. 6. Spectra of many-particle complexes in silicon recorded at 4.2°K under compression along the [111] direction: a) silicon doped with boron (6×10^{14}cm^{-3}) subjected to $P=332$ kg/cm^2 (the $LO-TO$ components are shown; the rate of splitting of the α lines is $\Delta/P\approx3\times10^{-6}$ eV·kg^{-1}·cm^2); b) silicon doped with phosphorus (7×10^{14}cm^{-3}) subjected to pressures $P=275$ kg/cm^2 (1) and $P=1400$ kg/cm^2 (2); the NP component is shown.

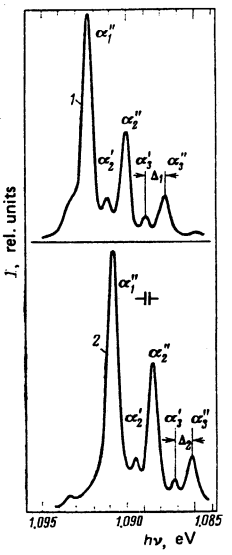

FIG. 7. Spectrum of the $LO-TO$ components in the luminescence of many-particle complexes in silicon doped with boron (6×10^{14}cm^{-3}), recorded at 4.2°K under compression along the [100] direction: 1) $P=80$ kg/cm^2; 2) $P=220$ kg/cm^2. The rate of splitting of the α lines is $\Delta_2/P\approx4.5\times10^{-6}$ eV·kg^{-1}·cm^2.

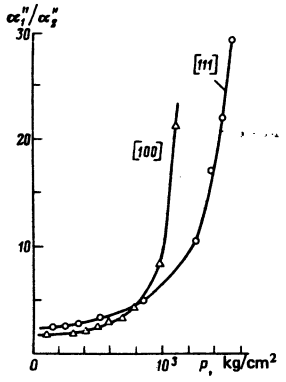

FIG. 8. Dependence of the amplitude ratio α_1''/α_2'' of silicon doped with boron (6×10^{14}cm^{-3}), recorded at 4.2°K under a pressure P applied along the [100] and [111] directions.

4.2 °K. Cooling also reduces the amplitudes of the α' lines. The dependence of the splitting Δ_1 on the applied pressure P is much stronger than that expected for the valence band and, therefore, we shall assume that at low deformations the important effect is the splitting of strongly degenerate electron levels of complexes with the wave-function symmetry $\Gamma^{3,5}$.[12,15] The fairly strong degeneracy of the lower level shows that all the electrons from the complexes can be accommodated and, therefore, the upper level becomes filled only as a result of thermal excitation and this results in a strong dependence of the amplitude of the α' lines on temperature and splitting Δ_1.

A further increase in pressure results in additional splitting of the α_2 and α_3 lines. However, in this case, the splitting depends much less on pressure and corresponds to the valence band splitting along the direction (4.5×10^{-6} eV·kg^{-1}·cm^2). The amplitude ratios α_2''/α_2' and α_3''/α_3' are now independent of temperature and pressure. As in the case of compression along the [111] direction, both holes of the B_1 complex may be located at the upper level and the population of the lower level, representing an excited state of B_1, should depend strongly on the splitting and temperature. In the case of the B_2 and B_3 complexes, the populations of the lower level are 1/2 and 1. This makes the amplitude ratios α_2''/α_2' and α_3''/α_3' independent of temperature and splitting, in agreement with the experimental results. Unfortunately, the small amplitudes of the α_2' and α_3' lines do not make it possible to carry out a more detailed quantitative analysis of the experimental results.

The luminescence spectra obtained at 2 °K for complexes in phosphorus-doped silicon compressed along the [100] direction are reported by Alkeev *et al.*[17] In this case, the α_3 and α_4 lines become split into α_3', α_3'' and α_4', α_4''. A study of the spectral positions and splitting of these lines as a function of the applied pressure shows that the effect is due to the splitting of the hole levels of the complexes (and not to the splitting of the electron states, as suggested by Alkeev *et al.*[17]).

We shall conclude by considering the dependence of the amplitude ratio α_1''/α_2'' of boron-doped silicon on the pressure P applied along the [111] and [100] directions (Fig. 8). This amplitude ratio depends weakly on the applied pressure as long as the valence-band splitting is less than ≈4.4 meV; when this splitting is exceeded, the ratio rises steeply because of the reduction in the intensity of the α_2'' line, whereas the intensity of the α_1'' line changes slightly, in agreement with the results reported by Kulakovskiĭ.[16] Both lines, α_2' and α_2'', disappear at approximately the same pressure. A similar dependence is exhibited also by the B_3 complex. The disappearance of the B_2 and B_3 complexes can be explained because an increase in pressure increases the energy of the holes at the lower level of these complexes and this reduces the binding energy per particle. When the splitting is sufficiently large, the existence of the B_2 and B_3 complexes may not be favored by the energy considerations. Strong compression of phosphorus-doped silicon along the [111] and [100] directions suppresses the luminescence lines of the B_3 and B_4 complexes (Fig. 6b) containing three and four holes, respectively. Thus, the disappearance of the luminescence lines of the complexes containing more than two holes as a result of large splitting of their levels caused by the uniaxial deformation of silicon also confirms the basic assumptions of the shell model.[6,12]

5. CONCLUSIONS

A quantitative model of many-particle impurity complexes is far from complete. This is due to the unusual nature of such systems and the consequent circumstance that the highly developed methods for the calculations of many-electron atomic systems cannot be applied. Nevertheless, although the shell model of many-particle complexes[6,12] does not make it possible to find directly the energy spectrum of the levels of these complexes, it does explain qualitatively and, sometimes, quantitatively the experimental results. Our data confirm the existence of many-particle complexes in silicon and can be explained within the shell model framework.

The authors are grateful to G. I. Voronkova for her help in the selection of doped silicon samples with the required properties, and to K. I. Svistunova for discussing the results.

[1]A. S. Kaminskiĭ and Ya. E. Pokrovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 381 (1970) [JETP Lett. **11**, 255 (1970)].
[2]A. S. Kaminskiĭ, Ya. E. Pokrovskiĭ, and N. V. Alkeev, Zh. Eksp. Teor. Fiz. **59**, 1937 (1970) [Sov. Phys. JETP **32**, 1048 (1971)].
[3]Ya. E. Pokrovskii (Pokrovsky), A. S. Kaminskii (Kaminsky), and K. Svistunova, Proc. Tenth Intern. Conf. on Physics of Semiconductors, Cambridge, Mass., 1970, publ. by US Atomic Energy Commission, Washington, D.C. (1970), p. 504.
[4]J. R. Haynes, Phys. Rev. Lett. **4**, 361 (1960).
[5]P. J. Dean, J. R. Haynes, and W. F. Flood, Phys. Rev. **161**, 711 (1967).
[6]G. Kirczenow, Solid State Commun. **21**, 713 (1977).
[7]R. Sauer, Phys. Rev. Lett. **31**, 376 (1973).
[8]K. Kosai and M. Gershenzon, Phys. Rev. B **9**, 723 (1974).
[9]R. Sauer, Proc. Twelfth Intern. Conf. on Physics of Semiconductors, Stuttgart, 1974, publ. by Teubner, Stuttgart (1974), p. 42.

[10]R. Sauer and J. Weber, Phys. Rev. Lett. 36, 48 (1976).
[11]R. Sauer and J. Weber, Phys. Rev. Lett. 39, 770 (1977).
[12]G. Kirczenow, Can. J. Phys. 55, 1787 (1977).
[13]Ya. E. Pokrovskiĭ and K. I. Svistunova, Zh. Eksp. Teor. Fiz. 68, 2323 (1975) [Sov. Phys. JETP 41, 1161 (1975)].
[14]M. L. W. Thewalt, Can. J. Phys. 55, 1463 (1977).
[15]G. L. Bir and G. E. Pikus, Simmetriya i deformatsionnye effekty v poluprovodnikakh (Symmetry and Deformation Effects in Semiconductors), Nauka, M., 1972.
[16]V. D. Kulakovskii, Eksitony v poluprovodnikakh, Tezisy Vsesoyuznogo soveshchaniya (Abstracts of Papers presented at All-Union Conf. on Excitons in Semiconductors), Leningrad (1977), p. 28.
[17]N. V. Alkeev, A. S. Kaminskiĭ, and Ya. E. Pokrovskiĭ, Fiz. Tverd. Tela (Leningrad) 17, 843 (1975) [Sov. Phys. Solid State 17, 535 (1975)].

Translated by A. Tybulewicz

Electrical properties of copper-doped $CdCr_2Se_4$

K. P. Belov, L. I. Koroleva, and M. A. Shalimova

M. V. Lomonosov Moscow State University
(Submitted 2 January 1978)
Zh. Eksp. Teor. Fiz. **74**, 2244–2249 (June 1978)

The temperature dependence of the Hall emf and the electrical resistance of single crystals of $Cd_{1-x}Cu_xCr_2Se_4$ ($x = 0.04$; 0.07; 0.14) is studied. It is found tht the Normal Hall coefficient is maximal in the vicinity of 150 K, while the anomalous coefficient is maximal in the vicinity of 130 K (the Curie point of this compound). The carrier concentration passes through a minimum in the vicinity of 150 K, whereas the mobility is maximal in this temperature region. The mobility decreases, while the carrier-number concentration increases, with increase of the copper admixture in $CdCr_2Se_4$. The character of the dependence of the electrical resistivity ρ on temperature T varies from the semiconductor type for $x = 0.04$ to the semimetallic type for $x = 0.14$, the ρ(T) curve for the compound with $x = 0.07$ being nonmonotonic with a maximum in the vicinity of the Curie point.

PACS numbers: 72.20.My, 72.20.Jv, 72.80.Jc, 72.60.+g

In the present paper we study the temperature dependence of the Hall emf and the resistivity, ρ, of single crystals of $Cd_{1-x}Cu_xCr_2Se_4$ ($x = 0.04$; 0.07; 0.14). Measurements with direct current were performed by a null method on rectangular plates cut from the crystals; the Hall-effect and ρ measurements were carried out simultaneously on one and the same sample. The preparation of the samples and the ohmic contacts with them, as well as the magnetic properties of these compounds are described in our earlier paper.[1] According to our measurements, the transverse magnetoresistance in this material is small (not more than 2%). It was positive in the paramagnetic region and negative in the ferromagnetic region.

The magnetization curves of the $Cd_{1-x}Cu_xCr_2Se_4$ system have a complex character because of the complexity of the properties of the magnetic impurity state. This is manifested especially clearly in the region of temperatures above the Curie point (130 K). In this temperature interval the magnetization in high fields cannot be represented as consisting of two simple contributions: spontaneous magnetization and the magnetization of the para-process, since the effects connected with the presence of magnetic impurity states (ferrons) are stronger than the effects of the para-process by not less than an order of magnitude.[2] Therefore, for the computation of the normal Hall coefficient R_0 and the anomalous Hall coefficient R_1 we used the standard formula for the Hall emf, U_x, in ferromagnets without allowance for the para-process:

$$U_x = (R_0 H + R_1 M) I/d, \qquad (1)$$

where M is the magnetization at the given temperature T and field intensity H, I is the current flowing through the sample, and d is the sample dimension in the direction of the magnetic field.

It should be emphasized that, because of the complexity of the processes occurring in the vicinity of the Curie point, the formula (1) is only a crude approximation and the constants R_0 and R_1 are some effective parameters. The normal Hall coefficient was determined from the slope of the $U_x(H)$ curve for fields higher than the saturation field, when the second term in Eq. (1) is a constant. The anomalous component of the Hall emf was determined by extrapolating the $U_x(H)$ curve to the ordinate axis from the high-field region. The saturation magnetization (M_s) data necessary for the computation of R_1 were taken from Ref. 1.

In Figs. 1 and 2 we show the temperature dependence of the quantities R_0, R_1, for ρ for all the compositions studied. As can be seen from Figs. 1 and 2, the anom-

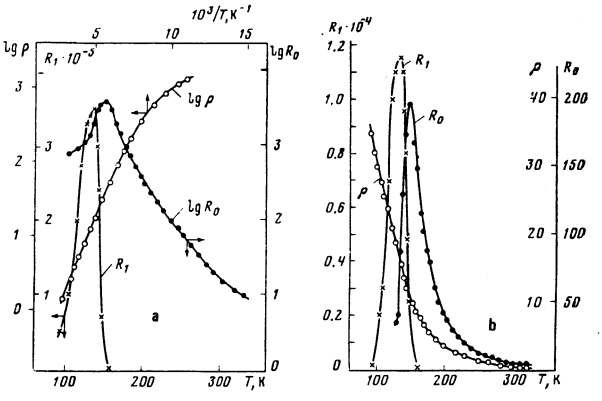

FIG. 1. Dependence of the anomalous Hall coefficient, R_1, the normal Hall coefficient, R_0, and the resistivity, ρ, on temperature for the compounds: a) $Cd_{0.96}Cu_{0.04}Cr_2Se_4$; b) $Cd_{0.93}Cu_{0.07}Cr_2Se_4$; R_1 and R_0 are given in cm^3/C; ρ, in Ω-cm.

 0038-5646/78/061167-03$02.40