the theoretical estimates and experimental results confirmed once again the correctness of the selected models.

It can be shown that the general relationships governing the formation of the domain structure in {111} iron garnet plates apply also to other multiaxial ferromagnets with a similar magnetic anisotropy and comparable dimensions and crystallographic orientations of the samples. The domain structure can then be described by the theoretical representations put forward in the present paper.

It should be mentioned specially that the observation of colored domain structure patterns in which the color of a domain identifies the magnetic phase to which it belongs, opens up new possibilities for correct interpretation of the domain structure and identification of magnetic phases in magnetically multiaxial polydomain crystals. Clearly, a more careful analysis of the color patterns, carried out using special optical methods, may in future give much more extensive information on the distribution of the magnetization in domains and on the mechanism of changes in the domain structure than that obtained in the present study.

The authors are grateful to A. V. Andreev for an x-ray diffraction study of the crystals and to V. V. Zverev for his help in the investigation.

1)A macrodomain structure with a stripe substructure has been observed earlier in {100} single-crystal Mg–Mn ferrite films[3,6,7] and in {100} nickel plates.[11]

2)The hysteresis loop was recorded using a Faraday hysteresis plotter when the angle between the transmission axes of the analyzer and polarizer was 45°.

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Phase transition in a nonequilibrium plasma and its effect on exciton condensation in germanium

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Results are presented of an experimental investigation of recombination emission, absorption, and dispersion of microwaves in thin and bulky samples of pure germanium subjected to surface optical excitation. The results may be explained by means of an hypothesis that assumes the formation near the illuminated surface of the sample, of metastable dense plasma clusters that relax into electron-hole condensate drops.

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After L. V. Keldysh suggested in 1968 the possibility of the onset of electron-hole drops in semiconductors,[1] a large number of experimental studies were made of this phenomenon (see, e.g., [2–6]). The results obtained to date allow us to conclude that at sufficiently low temperature the non-equilibrium excitons in germanium can condense into drops; the particle concentration in the drops is $(2-3)\times 10^{17}$ cm^{-3}, and the temperature dependence of the dew point is extremely steep and corresponds to an activation energy ≈ 1.5 meV.[4] Owing to the strong degeneracy ($E_F/kT \gg 1$), the electrons and holes in the drop have a high mobility corresponding to a relaxation time $\tau_r \sim 10^{-10}$ sec. The theoretical estimates of the particle concentration in the drop[5] agree

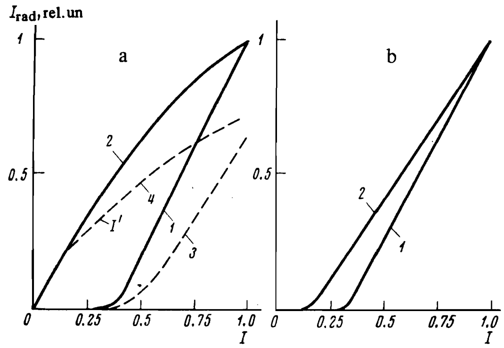

FIG. 1. Dependence of the exciton-condensate radiation intensity on the excitation power for: a—a sample 325 μ thick (1, 3—$T = 4.2$ °K; 2, 4—$T = 1.45$ °K; curves 1 and 2 were obtained at a microwave field intensity ≈ 0.1 V/cm, curves 3 and 4—at 5 V/cm); b—of a sample 28 μ thick (1—$T = 4.2$ °K; 2—$T = 1.45$ °K. Here and in the other figures the excitation intensity I is indicated in units of $I_{max} \approx 10$ W/cm^2. The maximum emission signals at low microwave power have been reduced to a single scale.

with the experimentally observed values.

An important methodological feature of most cited experiments is that bulky ($\gtrsim 1$ mm thick) germanium samples were used for the experiments; the thin layer of the sample near the surface, in which the non-equilibrium electrons and holes are bound into excitons, does not seem to play an essential role in the investigated phenomena. Investigations of the condensation in thin ($\lesssim 50$ μ) germanium samples, however, has revealed that both the particle density in the drops and the dew point are significantly different than in bulky samples.[2,7,8] As shown in[2], in an investigation of the differential transmitted-radiation spectrum, the particle density in the drop is $(2-4)\times 10^{16}$ cm^{-3}, and the dew point, first, depends little on the temperature, and second, corresponds to a very high average density of the particles over the sample ($\bar{n} > 10^{15}$ cm^{-3}). In investigations[7,8] of the absorption of microwave radiation in optically-excited thin samples of germanium we observed absorption that fluctuates strongly in time after the termination of the pump pulse. The absorption set in at an average density $\bar{n} > 10^{15}$ cm^{-3} and depended little on the temperature in the range up to 10 °K. The magnitude of the absorption, its behavior in a magnetic field, and the fluctuating character of the absorption have made it possible to conclude that this absorption is due to the appearance of drops in which the momentum relaxation time is $\tau_r \sim 10^{-12}$ sec, corresponding to a particle density in the drop 3×10^{16} cm^{-3}.

The facts noted above allow us to assume that in the layer near the surface (and consequently in a thin sample) the condensation mechanism may turn out to be significantly different than in a thick sample. We have therefore investigated the absorption and dispersion of an 8-mm band wave in optically excited thin ($\lesssim 50$ μ) and thick ($\gtrsim 300$ μ) samples of germanium, and registered simultaneously the recombination radiation of the samples.

EXPERIMENTAL PROCEDURE

Samples of pure germanium with residual-impurity concentration $N \lesssim 10^{12}$ cm^{-3} and with thickness from 10 to 350 μ were mechanically polished and bright-dipped in H_2O_2 + KOH, and then placed in a stub of an 8-mm band waveguide through a slit in the middle of the broad wall. The samples were excited with an LG-126 helium-neon laser at 1.15 μ wavelength. The maximum radiation power was ≈ 20 mW. The laser beam was focused into a spot of ≈ 300 μ diameter and was incident on the target through a hole of 1 mm diameter in the narrow wall of the waveguide. The recombination radiation was observed from the opposite side of the sample through an opening, covered with a metallic grid, in the narrow wall and was analyzed with an MDR-2 monochromator. The receiver was a Ge:Cu sample cooled to $T \approx 120$ °K.

The microwave absorption and dispersion were registered by the procedure described in[8], using a homodyne microwave spectrometer. The phase was set for "absorption" or "dispersion" by a phase shifter in the reference arm of the microwave channel. For measurements in a magnetic field, the waveguide could be placed in a superconducting solenoid with maximum magnetic field 35 kOe.

The laser radiation was modulated by a rotating disk at a frequency 800 or 120 Hz, and the microwave and recombination-radiation signals were registered with narrow-band amplifiers and synchronous detectors. For automatic recording of the signals as functions of the excitation energy, the laser beam passed through a slowly rotating polaroid filter; part of the light power was diverted to a "reference" photodiode, and the corresponding signal was fed to the X coordinate of an $X-Y$ recorder.

Besides experiments in which continuous excitation was used, in same cases the samples were pumped with pulses of ≈ 50 nsec duration from a ruby laser.

EXPERIMENTAL RESULTS

1. *Recombination radiation.* In the investigation of the recombination radiation, attention was paid first to the position and shape of the "condensate" and exciton emission lines (0.709 and 0.714 eV, respectively), and second to the dependence of the intensities of these lines on the excitation intensity.

The emission spectra in both thick and thin samples turned out to be identical with the previously obtained spectra,[3,4] but the dependence of the emission line of the "condensate" (0.709 eV) on the excitation intensity turned out to be significantly different for different samples (Fig. 1). As seen from the figure, the dependence of the radiation intensity on the pump for a thick sample at 4.2 °K has a threshold, the pumping threshold decreasing sharply with decreasing temperature, so that at $T \lesssim 1.8$ °K this dependence is practically linear when plotted in the scale of the figure (we note, however, the presence of a weak sublinearity starting with the intensity I' on Fig. 1). Our results agree with

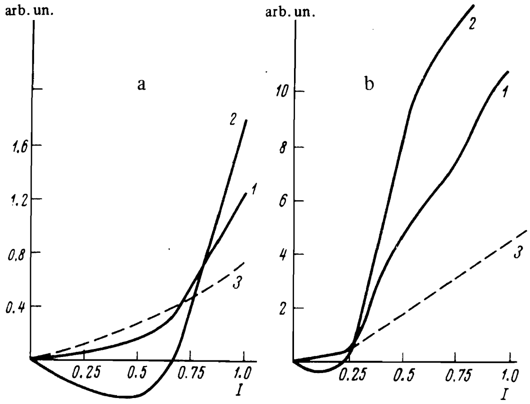

FIG. 2. Absorption and dispersion signals in a zero magnetic field at $T=4.2\,°K$ (a) and $1.45\,°K$ (b). Curve 1—absorption, 2—dispersion, 3—absorption in a strong microwave field at a microwave power $P_{max} \approx 10$ mW. Sample 35 μ thick.

those of[4], where thick germanium samples were also investigated.

The radiation from a thin sample has an entirely different character: when the temperature is lowered from 4.2 to 1.45 °K the threshold for the appearance of this line changes very little (by a factor 2–4), i.e., the "dew point" of the condensed phase, first, remains quite high and, second, depends little on the temperature.

The character of the indicated dependences is stable and does not vary from sample to sample; in particular, it is practically independent of the surface quality of the samples, of their polishing, and of the method of etching. We note that at $T < 2\,°K$ the radiation threshold shifts to lower pump values with increasing sample thickness. If, following[4], we connect the threshold excitation intensity with the dew point, then we can conclude that the temperature dependence of the dew point in a thin sample is significantly different from that in a thick one.

2. *Absorption and dispersion of microwaves in the absence of a magnetic field.* We shall show below how the absorption and dispersion signals depend on the excitation intensity. It is to be expected that at a low excitation level (up to the threshold of the onset of the condensed phase) the absorption and dispersion are due mainly to the presence of a low electron and hole density; when limited metallized regions of sufficiently high density ($\omega_p = (4\pi ne^2/\varepsilon_0 m^*)^{1/2} \gg \omega$, where ω is the microwave frequency), both the absorption and the dispersion should exhibit a strong dependence on the excitation intensity. Regardless of the particle concentration in the metallized region (4×10^{16} or 3×10^{17} cm^{-3}), the dispersion signal should reverse sign, from negative to positive, and should increase in proportion to the volume of the condensed phase,[9] whereas the absorption can either increase strongly if $\omega\tau_r \sim 1$,[8] or remain practically unchanged if $\omega\tau_r \gg 1$.

Figure 2 shows plots of the absorption and dispersion signals against the pump at $T=4.2$ and $T=1.8\,°K$. The plots for the thin and thick samples, in contrast to the situation in recombination radiation, were analogous. Moreover, the absolute magnitudes of the signals turned out to be of the same order. When the pump is increased to a certain value I_{thr}, the absorption and the dispersion increased monotonically with the pump and were due to the free electrons and holes. These signals decreased appreciably with decreasing temperature.

At $I = I_{thr}$, a steep increase of the absorption signal took place, and the dispersion signal changed abruptly from negative to positive, thus indicating an abrupt appearance, in both thick and thin samples, of a dense plasma ($\omega_p \gg \omega$) having considerable absorption.

When the temperature was decreased from 4.2 °K to ≈ 1.5 °K, the character of the indicated dependences remained the same, but the threshold dropped to an excitation intensity lower by a factor 2–4, and was more distinctly pronounced. It must be indicated that the threshold values of the excitation intensity depended on the sample surface quality and on the etching method; in particular, etching in CP-4, which should increase the role of surface recombination, increased the absorption and dispersion thresholds by approximately two times, and this led, owing to the nonlinear dependence of the signals on the pump, to an abrupt decrease of their absolute values.

3. *Investigation of the absorption and dispersion of microwaves in a magnetic field.* These investigations yielded certain important parameters of a dense plasma, and in particular estimates of its density. The corresponding results are shown in Fig. 3. As seen from Fig. 3a, at $I > I_{thr}$ the absorption receives a contribution that depends little on the magnetic field, so that it can be concluded that this contribution is due to a dense plasma with $\omega\tau_r \lesssim 1$. However, in addition to the dense plasma, there are also regions where the carrier density is low. In fact, against the background of the absorption with $\omega\tau_r \lesssim 1$ cyclotron resonance lines appear (similar results were obtained in[8] following excitation with light pulses). The width of these lines increases

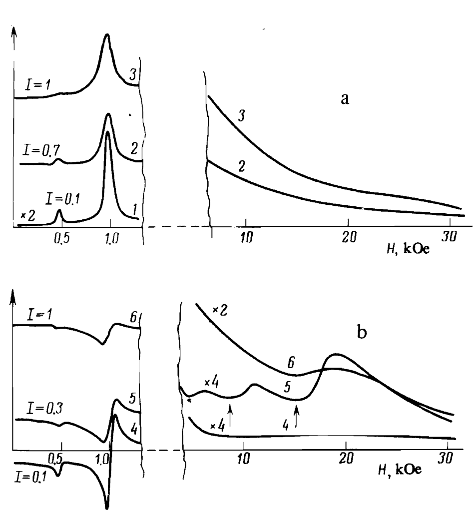

FIG. 3. Absorption (a) and dispersion (b) spectra in a magnetic field. Sample 325 μ thick. $T=1.8\,°K$. The magnetic-field direction coincides with the ⟨111⟩ axis.

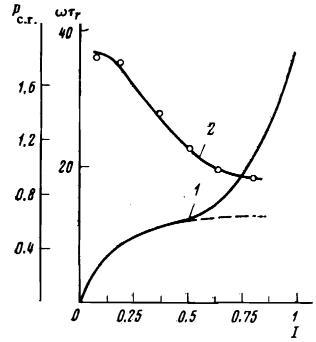

FIG. 4. Electron cyclotron resonance signal ($M^* = 0.08\ m_0$) vs the excitation intensity—curve 1. The abrupt growth of the signal at $I \gtrsim 0.6 I_{max}$ is due to suppression of the absorption, which depends little on the magnetic field. Plot of $\omega\tau_r = 2H_c/\Delta H$ against the excitation intensity—curve 2. Sample 325 μ thick, $T = 4.2\,^\circ$K.

with the pump at $I < I_{thr}$, and stabilizes at $I > I_{thr}$ at a value $2H_c/\Delta H = \omega\tau_r \approx 18$–$20$ at 4.2 °K and ≈ 30 at 1.8 °K. The cyclotron resonance signal with the contribution independent of the magnetic field subtracted, just as the line width, saturates at $I > I_{thr}$.

The dependence of the cyclotron-resonance signal and of $\omega\tau_r$ on the pump is shown in Fig. 4. It indicates that when the pump is increased the density of the free electrons and holes first increases and then ceases to vary. Assuming that the value of τ_r under the experimental conditions is determined by the mechanism of the electron-hole scattering,[10] we can estimate the concentration of the particles in the rarefied plasma: $(n, p) \approx 5 \times 10^{12}$ cm^{-3}.

The dispersion signals are shown in Fig. 3b. In weak magnetic fields at $I \gtrsim I_{thr}$ the dispersion signal reverses sign, thus indicating the appearance of a plasma with $\omega_p \gg \omega$ in the sample. In the region of strong magnetic field, the dispersion signal oscillates. Such oscillations set in at $I \approx I_{thr}$ and retained their position when the pump increased from threshold to the maximum value (the ratio of the oscillating and monotonic components of the dispersion signal, however, changed in this case, the contribution of the monotonic component being larger than that of the oscillating component at the maximum pump). The position of the oscillations changed with changing sample orientation relative to the magnetic field.

In our opinion, the observed oscillations of the dispersion signal can be interpreted as a manifestation of the Shubnikov–de Haas effect. A similar behavior of the dispersion signal was observed in an investigation[11] of n-InSb with $n \approx 10^{16}$ cm^{-3}; it was shown that it sets in at low values of $\omega\tau_r$ and is due to the Shubnikov–de Haas oscillations in the sample conductivity. Since the position of the oscillations observed by us did not vary with the pump, it can be concluded that the Fermi level in this plasma remained unchanged. The Fermi energy of the electron subsystem turned out to be $E_F \approx 0.9$ meV,[12] corresponding to a density $\approx 5 \times 10^{16}$ cm^{-3}. Thus, an investigation of the absorption and dispersion in a magnetic field shows that at $I > I_{thr}$ the density of an electron-hole plasma does not increase monotonically; a stratification of the plasma into dense and tenuous phases seems to take place in the excitation region.

4. *Microwave diagnostics in a strong* HF *field.* An additional proof of the stratification of the plasma into two phases is, in our opinion, the behavior of the absorption signal when the microwave power incident on the sample is increased to ~ 10 mW.

As shown in Fig. 2 (curves 3), at $I < I_{thr}$ the absorption signal increases slightly in a strong microwave field, apparently as a result of the increase of the number of carriers by impact ionization of the excitons,[13] but at $I > I_{thr}$ the absorption and dispersion signal decrease significantly, possibly because of the decreased volume of the dense plasma. We note that in a dense plasma the carrier heating should be stronger than in a tenuous one, owing to the small value of $\omega\tau$. It is impossible to identify at present the mechanism that decreases the plasma volume: the decay of the plasma clusters can be due either to heating of the carriers inside the plasma clusters, or to the slowing down of the dense-phase formation because of the temperature rise of the unbound carriers. However, the assumption that the dense-plasma volume is decreased in a microwave field is well-founded, since the absorption (and positive dispersion) of a uniform plasma should increase with increasing microwave power.

5. Let us dwell finally on the agreement between the threshold values in microwave diagnostics and in recombination radiation. It has turned out that in thin samples the threshold for the appearance of recombination radiation, as the temperature changes from 1.45 °K to 4.2 °K, coincides exactly with the threshold of the microwave absorption and dispersion, as well as with the appearance of an oscillatory structure in the dispersion signal in a strong magnetic field.

As to thick samples, the thresholds are likewise equal at 4.2 °K, but with decreasing temperature, when the radiation threshold shifts abruptly to lower pumps, the thresholds in the microwave phenomena are only negligibly lowered. Thus, the threshold of exciton condensation and the threshold for the appearance of a dense plasma are significantly different. With increasing microwave field strength, a quenching of the luminescence was observed simultaneously with the change of the signals in microwave phenomena. The behavior of the emission signals of the excitons and of the condensate in weak and strong microwave fields, and the increase of the number of free electrons and holes (Fig. 2a, curve 3), shift the threshold for exciton condensation into drops (the 0.709 eV line) towards larger pumps and decreases the number of particles in the condensed phase of the excitons.

6. In concluding this section, we note that the appearance of "ordinary" electron-hole drops with density $\approx 2 \times 10^{17}$ cm^{-3} and $\tau_r \sim 10^{-10}$ sec is quite difficult to record by a microwave procedure, since the absorption by such drops is quite small and the contribution from the nonequilibrium free carriers predominates in the absorption and dispersion signals in the case of stationary pumping. With pulsed excitation, however, it is

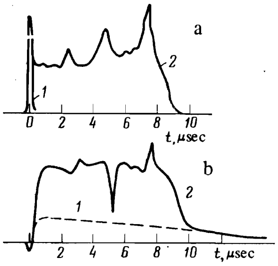

FIG. 5. Oscillograms of absorption and dispersion pulses at $T = 1.6\,^\circ$K: a—absorption, b—dispersion. Excitation intensity in relative units: 1—10, 2—20.

possible to separate after the termination of the pulse a positive signal in the dispersion, similar to that observed in[9]. It was observed in the case of strong pumping ($I > I_{thr}$) that irregular fluctuating bursts, corresponding to formation of plasmoids, are superimposed on this slowly decreasing (in time) signal. At the same time, irregular bursts (Fig. 5) appear also in the absorption threshold above the threshold, indicating that absorption takes place after the termination of the light pulse.[7] The duration of these signals did not exceed $\sim 10\ \mu$sec, whereas the recombination radiation was attenuated with a time constant $\gtrsim 30\ \mu$sec.

DISCUSSION OF RESULTS

1. The possibility of plasma stratification into a "plasma vapor" and a "plasma liquid" with a strong Coulomb interaction between the charged particles was analyzed theoretically in a number of papers.[14,15] In view of the absence of a theory of a strongly nonideal plasma, no final conclusion concerning the existence of such a transition was drawn. There is likewise no experimental proof of a phase transition in a plasma at present.

In our opinion, the results obtained in this study can be explained most plausibly by assuming that in a thin layer of a surface-excited sample a phase transition takes place in the plasma of the nonequilibrium electrons and holes. When the sample is illuminated, electron-hole pairs are produced near the surface and, diffusing into the volume, become bound into excitons. However, the depth of the region where the density of the carriers that did not mange to be bound into excitons is quite appreciable, on the order of $L = \sqrt{Dt_b}$. Assuming that the ambipolar diffusion coefficient D is equal to $\sim 10^3$ cm^3/sec and the time t_b of binding into excitons is $\sim 10^{-8}$ sec, we obtain $L \sim 30\ \mu$. In this region of the crystal, where the pumping rate exceeds the binding rate, there exists a free-carrier plasma with a density estimated to exceed $\sim 5\times 10^{13}$ cm^{-3} at an incident light intensity $\sim 5\times 10^{19}$ quanta/cm^{2}sec. The presence of a plasma of appreciable density in a region $\sim 50\ \mu$ near the sample surface can produce in the plasma a phase transition that leads to a stratification of the system into a "plasma vapor" and a "plasma liquid." The results described above, in our opinion, point to the existence of such a phase transition, namely: when a certain pump threshold is reached, plasma regions of high density are produced in the sample, with parameters $n \approx 5\times 10^{16}$ cm^{-3} and $\tau_r \sim 10^{-12}$ sec, while the density of the free carriers in the remainder of the sample ceases to increase.[1)]

2. The difference between the properties of the dense-plasma clusters and the properties of the condensed exciton phase, the weak temperature dependence of the threshold at which the plasma phase appears and the strong temperature dependence of the exciton condensate, and the difference between the thresholds of these phenomena in thick samples at $T < 2.5\,^\circ$K all indicate that the exciton condensate differs physically from the observed plasma formations. On the other hand, the equality of the thresholds in the radiation and in the microwave measurements in thin samples indicate that these two phenomena are closely related.

The lack of a consistent theory of a dense plasma,[14] as well as the fact that the appearance and disappearance of "plasma liquid" clusters in a semiconductor are in principle nonequilibrium processes, do not make it possible at present to understand fully the nature of the investigated phenomenon. However, from the results of pulse measurements of the absorption and dispersion signals, which reveal abrupt and irregular variations of the dense-plasma volume, it can be assumed that the condensed "plasma-liquid" state is metastable and that these plasma clusters are transformed quite rapidly (within $\lesssim 10\ \mu$sec) into "ordinary" exciton-condensate drops with density $n \approx (2-3)\times 10^{17}$ cm^{-3}. This assumption is confirmed by the fact that in thin samples the threshold for the onset of exciton condensate coincides with the threshold for the plasma transition, and also by the simple consideration that when the plasma clusters are converted into exciton-condensate drops they minimize their energy.

3. The mutual relation between these plasma clusters and the exciton condensate can be visualized in the following manner: in thin samples ($\lesssim 50\ \mu$), besides the excitons, there is an appreciable condensation of the free electrons and holes in the entire volume of the sample. The presence of the free carriers possibly shifts the dw point of the exciton condensation towards larger pumps. With increasing pump, if the sample were uniformly filled with plasma, condensation of the excitons into drops could not occur at all in the sample. If, however, the plasma becomes stratified at $I = T_{thr}$ into a low-density plasma and clusters of "plasma liquid," then these clusters relax rapidly into drops and lead to a threshold-dependent appearance of recombination radiation at the 709-meV line. Thus, in thin samples the gas–liquid phase transition for the exciton system is controlled by the phase transition in the plasma. It is obvious that in thick samples, where an appreciable fraction of the volume is filled with exciton gas, that is in equilibrium with an electron-hole plasma of low density ($p \lesssim 10^{10}$ cm^{-3} at $T \lesssim 2\,^\circ$K), the electron-exciton interaction can be neglected, and the excitons condense into drops in accordance with the usual model of a gas-to-liquid transition.

Our investigations thus allow us to assume that at low temperature and at a sufficiently rapid generation rate, metastable plasmoids of high density are produced in germanium and relax rapidly into exciton-condensate drops. This hypothesis explains satisfactorily a number of effects observed at microwave frequencies, and to understand the specifics of the phenomenon of exciton condensation in thin and thick germanium samples.

The authors are quite grateful to S. M. Ryvkin and I. D. Yaroshetskiĭ for support and interest during the performance of this work.

[1)]The observed phenomena cannot be attributed to overheating of the sample by the laser light, since the exciton line present at 4.2 °K was not observed at 1.8 °K, and the width of the cyclotron resonance lines at $I \approx I_{\text{thr}}$ was much less at 1.8 °K than at 4.2 °K.

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Effect of impurity oscillations on the superconducting transition point in dilute U or Be solutions in V

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The specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ was measured in the temperature range 1.2–40°K without a field and in fields of 18 and 40 kOe at 1.2–6°K. An anomalous behavior was observed in the phonon specific heat, related to the appearance of quasilocal and local oscillations in the phonon spectrum upon the introduction in the V of heavy impurity atoms of U and light atoms Be. The effect of modification of the phonon spectrum on T_c is studied. Estimate of the scale of change of T_c from deformation of the phonon spectrum showed that softening of the phonon spectrum in the alloy $V_{97.2}U_{2.8}$ leads to a decrease in T_c; on the other hand, hardening of the spectrum of $V_{96.9}Be_{3.1}$ gives a positive contribution to δT_c.

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1. INTRODUCTION

As follows from a theoretical analysis,[1] the transition temperature T_c of superconductors with tight binding depends essentially on the details of the phonon spectrum. For the study of the connection between the deformations of the phonon spectrum and T_c, the weak solid substitution solutions are of interest, in which the mass of the impurity atoms differs markedly from the mass of the matrix atoms. It is well known that in such impurity systems, quasilocal and local modes can exist and the phonon spectrum turns out to be anomalously restructured. The possibility of the existence of specific impurity modes was predicted by I. Lifshitz[2] and Yu. Kagan.[3] These modes were discovered experimentally in a number of metals in the measurement of inelastic neutron scattering,[4,5] low-temperature specific heat,[5,6] electric conductivity,[7] and tunnel characteristics.[8]

The problem of the change in T_c in metals due to direct deformation of the phonon spectrum by impurity modes has been studied theoretically in a number of researches. The analysis was carried out on the basis of the Éliashberg equations.[9] Appel[10] carried out an analysis using a model description of the kernel of the integral of the Éliashberg equation. The form of the characteristic function α of the electron-phonon interaction was not specified. Actually, however, the value of α depends on the relation between the characteristic phonon frequency of the regular lattice and that of the alloy. The results of Appel were criticized by Maksimov[11] who, analyzing the behavior of T_c in impurity systems, obtained a formula for T_c similar to the for-

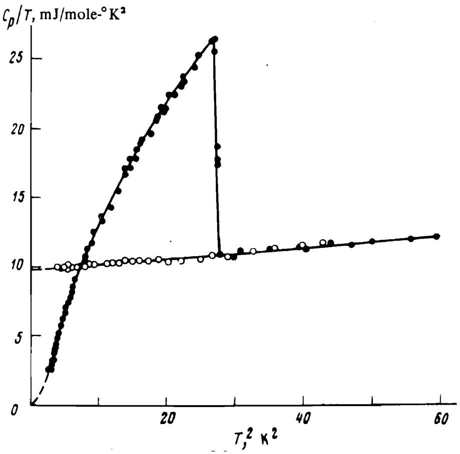

FIG. 1. Specific heat of pure V: ●—without field and ○—in a field of 18 kOe.

mula of McMillan.[1] In particular, he showed that if the impurity atom is an isotopic defect, then the electron-phonon interaction constant does not change.

The character of the change of T_c in superconductors with impurity atoms was analyzed in detail in[12] and the dependence of T_c on parameters describing the phonon spectrum of the impurity system was investigated. An expression for T_c was obtained with account of the frequency dependence of the parameter of the energy gap Δ. We turn our attention to the fact that McMillan,[1] in the derivation of his well-known expression for T_c, neglected the frequency dependence of Δ. We note that Δ as a function of frequency generally has the same singularities as the function of the density of phonon states of the non-regular lattice. When account is taken in the expression for T_c of the singularities of $\Delta(\omega)$ that are due to the presence of impurity atoms, of the factor preceding the exponential is re-determined. (In most superconductors, the effective electron-phonon coupling constant is not small, and the value of T_c is determined to an equal degree by the values of the exponential and pre-exponential factors.) The indicated change turns out to be especially important in the presence of specific impurity modes in the vibrational spectrum. It was shown in[12] that if the effective force constants change simultaneously when quasilocal and local modes appear, then this causes a perceptible renormalization of λ, too.

We have undertaken a systematic study of the connection between the restructuring of the phonon spectrum and the temperature of the T_c transition to the superconducting state. The effect of deformation of the phonon spectrum on T_c upon introduction of Ta, W and Hf impurity atoms into V was studied in[13,14]. According to[14], quasilocal oscillations in the phonon spectrum of the alloy $V_{94.3}Ta_{5.7}$ were revealed by the inelastic scattering of cold neutrons. The anomalous behavior of the phonon specific heat in the range of low temperatures of alloys of V with Ta also indicates a restructuring of the phonon spectrum in the region of low frequencies. Similar anomalies in the phonon specific heat were observed in alloys of V with Hf and W. In these systems, the softening of the phonon spectrum led to a decrease in T_c.

In the present work, the results are given of the measurement of the specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ in the range 1.2–40°K. We note that, from estimates in the alloy of V with U, the characteristic frequency of the quasilocal mode should be considerably lower on the frequency scale than in alloys of V with Ta, W and Hf. Therefore, all the anomalies in the behavior of thermodynamic characteristics in the V–U system because of the quasilocal modes should be especially clearly pronounced.

In the V–Be system, the local modes were observed directly in the study of inelastic neutron scattering.[15] Consequently, it was interesting to see how the hardening of the phonon spectrum because of the light impurities affects the value of T_c.

2. CHARACTERISTICS OF SAMPLES, RESULTS OF MEASUREMENTS AND THEIR DISCUSSION

The measurements of the low-temperature specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ were carried out in a vacuum adiabatic calorimeter with a superconducting solenoid[13] in the temperature range 1.2–40°K in the absence of a field and at fields of 18 and 40 kOe in the temperature range 1.2–6°K.

The samples of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ were prepared from vanadium of type VEL-2, subjected to additional zone purification in a vacuum of 10^{-6} mm Hg in an electron-beam furnace. The alloy of V with U was smelted in the electron-beam furnace on a water-cooled copper pan in an argon atmosphere. For a uniform distribution of the U, the sample was turned over several times and remelted, after which it was quenched. The alloy $V_{96.9}Be_{3.1}$ was prepared in an induction oven in a vacuum of 10^{-5} mm Hg. For homogenization, the sample was subjected to annealing at a temperature of 1650° for a period of 10 hr with subsequent rapid cooling.

Data of x-ray and metallographic analyses showed that the investigated samples are single-phase and represent solid solutions. The content of U, Be, and foreign impurities in the vanadium was determined by chemical and spectral analyses. According to these analyses, the total content of foreign impurities did not exceed 0.03%.

The results of measurements of the temperature dependence of the specific heat of the pure vanadium and its alloys with U and Be, without field and in fields of 18 and 40 kOe, in the temperature range 1.2–8°K, are shown in Figs. 1–3 in the coordinates C/T and T^2. The temperature of the superconducting transition T_c, the width of the transition ΔT_c, and the value of the jump $\Delta C/\gamma T_c$ were determined from the jump in the specific heat in measurements in the absence of field. To calculate the coefficient of the electronic specific heat γ and the Debye temperature Θ, it was necessary to destroy the superconductivity of the samples and carry out measurements of the specific heat in the normal state down to 1.2°K. It turned out here that the fields

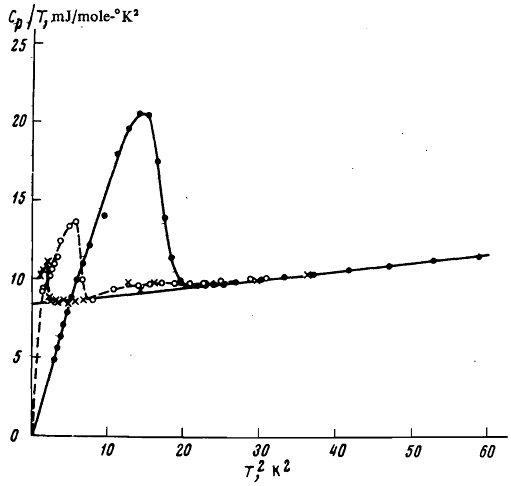

FIG. 2. Specific heat of the alloy $V_{97.2}U_{2.8}$: ●—$H=0$, ○—$H=18$ kOe. —$H=40$ kOe.

of 18 and 40 kOe were insufficient to destroy the superconductivity of the alloy of V with U. The alloy of V with U remained a hard superconductor.

From the location of the jumps in the specific heat without field and in fields of 18 and 40 kOe, the critical field of this alloy was calculated. It turned out that $H_{c2} \sim 50$ kOe. The dependence $H_{c2}(T)$ for the alloy of V with U is shown in Fig. 4.

Figure 5 shows the results of measurements of the specific heat of pure V and its alloys with U in the range 1.2–30°K and with Be in the range 1.2–40°K in the normal state. As is seen from this drawing, the introduction of 2.8 at.% U into the V lattice leads to a sharp increase in the specific heat in all temperature ranges studied, with the exception of the low-temperature region. In the region of low temperatures, the specific heat of the V–U system is substantially smaller than the specific heat of V because of the decrease in the electron specific heat. In the case of V–Be, the picture turns out to be qualitatively different. The introduction of 3.1 at.% Be into the lattice of vanadium leads to a decrease in the total specific heat over the entire range of temperatures studied.

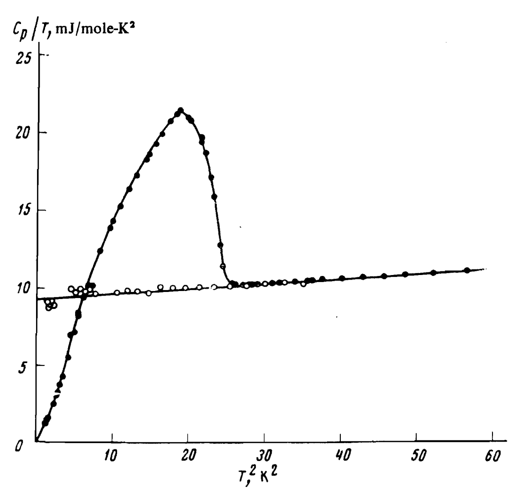

FIG. 3. Specific heat of the alloy $V_{96.9}Be_{3.1}$: ●—$H=0$, ○—$H=18$ kOe.

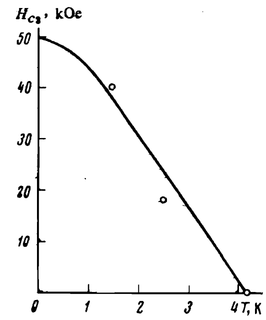

FIG. 4. Dependence of H_{c2} on T for the alloy $V_{97.2}U_{2.8}$.

The effect of the impurity atoms on the restructuring of the phonon spectrum appears most graphically in the temperature dependence of the relative change of the phonon specific heat

$$\Delta C_{ph}(T)/\eta C_{ph}^{(0)}(T), \quad \Delta C_{ph}=C_{ph}(\eta)-C_{ph}^{(0)}(0)$$

(where $C_{ph}^{(0)}$ is the phonon component of the specific heat of the lattice, and η the concentration of the impurity). As is well known (see, for example,[16]) if specific impurity modes develop in the phonon spectrum, then this leads to singularities of the low-temperature behavior of the specific heat ΔC_{ph}. The presence of a sharp maximum in the curve $\Delta C_{ph}(T)/\eta C_{ph}^{0}(T)$ for $T\sim 12$°K for the alloy of V with U indicates the appearance of a quasilocal mode in the phonon spectrum of this system.[16,17] In the case of the V–Be system, the observed behavior of ΔC_{ph} is connected with the decrease in the density of phonon states in the long-wavelength portion of the spectrum; these data enable us to assume the presence of local modes in the V–Be spectrum in agreement with the results of the work of Mozer.[15]

Theoretical calculations, carried out for the systems V–U and V–Be show that the restructuring of the phonon spectrum is connected not only with the difference in

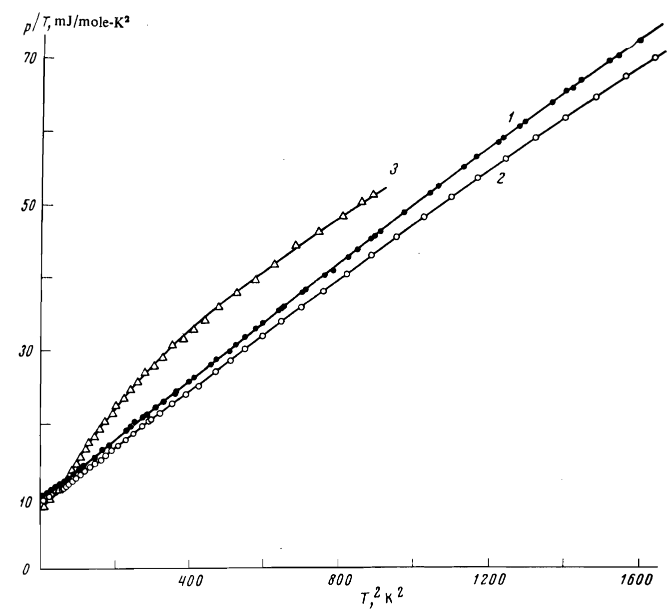

FIG. 5. V and its alloys with U and Be in the normal state in the region of 1.2–40°K: 1—V, 2—$V_{96.9}Be_{3.1}$; 3—$V_{97.2}U_{2.8}$.

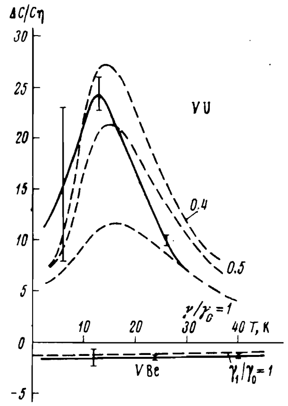

FIG. 6. Temperature dependence of the relative change in the phonon specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$, normalized to the concentration: continuous curves—experimental; dashed curves—theory with account of the change in the effective force constants.

the masses of the impurity atoms and the atoms of the matrix, but also with the change in the effective force constants. The results of the calculations are given in Fig. 6 by the dashed lines. The anomalously large increase in the phonon specific heat for the alloy of V with U is connected with the difference in the masses of the atoms and with the sharp decrease in the force constants ($\gamma_1/\gamma_0 \sim 0.45$). In the alloy of V with Be, the force constants change comparatively little ($\gamma_1/\gamma_0 \approx 0.8$). (By γ_1 and γ_0, we mean the effective force constants for the impurity atom and the atom of the matrix.)

We now proceed directly to the discussion of the effect on the value of T_c of vanadium atoms for the impurity atoms U and Be. The experimental results are given in Table 1. In this table we also show the values of T_c obtained from measurements of the electrical conductivity. As is seen, the introduction of the impurity atoms of U and Be in V leads to a decrease in T_c that is significant for the V–U system and insignificant for V–Be. The coefficient of the electron specific heat γ falls off, the Debye temperature Θ falls off significantly for V–U and insignificantly for V–Be.

In order to represent the scale of the change of T_c due to the appearance of quasilocal modes in the phonon spectrum of V–U and of local modes in V–Be, we have estimated this contribution on the basis of the results

TABLE 1.

	V	$V_{97.2}U_{2.8}$	$V_{96.9}Be_{3.1}$
$\rho(300\,K)/\rho(T_c)$	24	2.2	9.7
T_c, K* I	5.24	4.16	4.86
T_c, K* II	5.21	4.30	4.89
ΔT_c, K**	0.2	0.6	0.5
γ, mJ/mole-K^2	9.80	8.30	9.10
Θ, K	373	323	378
$\Delta C/\gamma T_c$	1.40	1.04	0.95
$(C_{es}/C_{en})_{T_c}$	2.52	2.25	2.22

*Here I—T_c obtained from measurements of the specific heat; II—from measurements of the electrical conductivity.
**ΔT_c is the width of the superconducting transition.

TABLE 2.

	$V_{97.2}U_{2.8}$	$V_{96.9}Be_{3.1}$
γ_1/γ_0	0.45	0.80
$N(\varepsilon_F)$, $(eV \cdot at)^{-1}$	1.76	1.93
M_0/M_1 *	0.21	5.66
$\gamma_1 M_0/\gamma_0 M_1$	0.10	4.53
$\langle\langle a_1^2\rangle\rangle/\langle\langle a_0^2\rangle\rangle$	2.10	1.44
A_1	0.35	0.08
A_2	−0.40	−0.19
A_3	−0.22	0.02
$(\delta T)_{calc}$	−0.27	−0.09
$(\delta T)_{exp}$	−0.21	−0.07

*M_0 and M_1 are the mass of the matrix atom and the impurity atom, respectively.

of the earlier work.[12] Since the ratio $\rho\,(300°\,K)/\rho(T_c) \approx 24$ for the initial samples of V, the contribution to T_c from the impurity isotropization of the energy gap was not taken into account. Then, in account with[12,8] the relative change is determined by the contribution of three terms:

$$\delta T_c = \frac{T_c(\eta) - T_c(\eta=0)}{T_c(\eta=0)} = A_1 + A_2 + A_3.$$

A few words are necessary on the coefficients A_i. The quantity A_1 is determined by the ratio of the effective scattering amplitudes of the electrons and the force constants of the atoms of the impurity and of the initial matrix, and A_2 reflects the role of the renormalized electron states on the Fermi surface. The coefficient A_3 describes the effect on T_c of the impurity modes. The analytic expressions for A_1, A_2 and A_3 are given in[18] (Eqs. P. 3–P. 5).

The value of the parameters entering into the expressions for A_i in[18] and also the coefficients A_i for the investigated alloys are given in Table 2. We note that the values of γ_1/γ_0 and $N(\varepsilon_F)$ are obtained from data on the measurement of the specific heat and the ratio $\langle\langle a_1^2\rangle\rangle/\langle\langle a_0^2\rangle\rangle$, where a_1 and a_2 are the scattering amplitudes of electrons on the impurity atom and the matrix atom, as estimated from results on the measurement of the electrical conductivity. As is seen from Table 2, excellent agreement is observed between the experimental and theoretical values of the relative change of T_c, both in sign and in order of magnitude.

In the V–U system, the contribution to T_c due to the difference in the scattering amplitudes and the force constants is positive ($A_1 > 0$) since $a_1 > a_0$ and $\gamma_1 < \gamma_0$. Decrease in the density of normal electron states on the Fermi surface $N(\varepsilon_F)$ leads to the result that the coefficient A_2 becomes negative. Because of the radical restructuring of the frequency dependence of the parameter of the energy gap $\Delta\,(\omega)$ in the range of low frequencies, brought about by the presence of quasilocal modes, the coefficient A_3 is large in magnitude and negative in sign. In other words, the softening of the phonon spectrum leads to a decrease in T_c. We note that the coefficients A_1, A_2, and A_3 are similar in value. As a result of the above, it follows that the falling off of T_c in the V–U system can be explained if we take simultaneously into account the deformations of the phonon and electron spectra.

In the V–Be system, the picture is as follows. Since $a_1 > a_0$ and $\gamma_1 < \gamma_0$, the coefficient A_4 is positive. The correction to T_c due to the restructuring of the electron spectrum (A_2) is negative. The presence of a local mode in the phonon spectrum is responsible for the substantial change in the form of the frequency dependence of the parameter of the energy gap in the high frequency region. The hardening of the phonon spectrum brought about by this leads to a positive contribution A_3 to δT_c. The coefficients A_1 and A_2 are close in value. It follows from the consideration given that the negative sign of δT_c in the V–Be system is connected with the decrease in the density of the normal electron states on the Fermi surface. Renormalization of the value of the effective scattering amplitudes and hardening of the phonon spectrum essentially cancel the contribution to δT_c from the renormalization of $N(\varepsilon_F)$.

3. CONCLUSION

As a result of the study of the low-temperature specific heat of alloys of V with U and Be in this work, and alloys of V with Hf, Ta and W in[13,14], we can draw the following conclusions.

1. The softening of the phonon spectrum because of the heavy impurity atoms leads to a significant drop in T_c. On the other hand, upon the introduction of light impurities, i.e., in a situation in which the spectrum is hardened, the corresponding contribution to T_c turns out to be positive.

2. In the considered systems, as it turns out, the effective force constants are considerably reduced. This change has a significant effect on the value of the effective electron-phonon interaction constant. The great weakening of the force constants, which is observed in the systems V–Hf and V–U, promote an increase in T_c. The increase in the force constants, as, for example, in the case of V–W, decreases T_c.

3. In alloys based on vanadium, the changes of T_c because of the appearance of specific impurity modes in the phonon spectrum and the redistribution of the density of normal electron states on the Fermi surface have the same order of magnitude.

4. As follows from the given analysis, in weak solutions, where the atoms of the second component are light and simultaneously the effective force constants are significantly weakened, the resultant deformation of the phonon spectrum leads to an increase in T_c.

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