

The thermodynamics of the melting of the alkali metals

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The densities of lithium, potassium, and rubidium have been measured near the fusion curves at pressures of up to 15 kbar with the aid of a piston piezometer. The volume and entropy changes accompanying the melting of the indicated substances are computed. The obtained results are analyzed with the use of the previously published data on the melting of sodium and cesium. It is shown that the inhomogeneity of the electron gas has a significant effect on the shape of the fusion curves of the alkali metals at low pressures. The relative volume jump accompanying the melting of the alkali metals tends, in contrast to the case of the inert gases, to zero as the metals are subjected to ever increasing compression, whereas the entropy jump has a finite limit. Evidence is presented which supports the hypothesis that the anomalies on the melting curves of potassium, rubidium, and cesium are connected with the *s-d*-electron transition. An independent estimate is obtained for the crystallization coordinates of a classical one-component plasma on the basis of the experimental data.

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INTRODUCTION

In spite of the absence of a general theory of melting, the physical picture of this phenomenon for such simple substances as argon is sufficiently clear. Real and "computer" experiments indicate that the short-range repulsive interaction plays the dominant role in the crystallization of the inert gases,^[1, 2] and this allows us to draw important conclusions about the thermodynamics of melting at very high pressures. In particular, it can be asserted that the melting of substances like argon remains a transition of the first order at all pressures and temperatures, and that the melting point of these substances increases without restriction as they are compressed.

Unfortunately, these results cannot be extended to the case, of interest to us, of the alkali metals, because of the more complex character of the interparticle interaction. Furthermore, the shape of the fusion curves of the alkali metals at high pressures differs from the shape of the corresponding curves in the case of the inert gases. As follows from the experimental data, the fusion curve of cesium exhibits two maxima, while the slopes of the fusion curves of potassium and rubidium become very small at high pressures.^[3, 4]

The present paper is devoted mainly to the experimental study of the melting of the alkali metals at high pressures, but we shall preface the exposition of the experimental material with some remarks elucidating this problem.

If we regard melting as an order-disorder transition, then it is natural to assume that the structure-sensitive part of the total energy is the characteristic energy responsible for the melting-crystallization transition. In second-order pseudopotential theory,^[5] in terms of which we shall carry out the discussion, the structure-sensitive part of the total energy is given by the ionic energy E_i and the second-order term, $E_e^{(2)}$, in the expansion of the electronic energy in powers of the pseudopotential. The value of $E_e^{(2)}$ in the alkali metals is small compared to the ionic energy^[6]; nevertheless, it can play an important role in the melting process, since the difference between the $E_e^{(2)}$ values in the co-

existing phases can be comparable in magnitude to the corresponding difference between the ionic energies.^[7]

Let us consider the question of the shape of the fusion curves of the alkali metals in the V - T plane. It is clear that if the ionic energy E_i were the only structure-sensitive component of the energy of an alkali metal, then the fusion curves of the alkali metals in the V - T coordinates would have the form $T \sim 1/V^{1/3}$, while the dimensionless parameter $\Gamma_m = Z^2 e^2 / r_a kT$, where r_a is the radius of the ionic sphere, would be equal on the fusion curve to ~ 150 for all the alkali metals (the numerical estimate $\Gamma_m \approx 150$ follows from the results of computer experiments on the crystallization of a classical one-component plasma^[8-10]).

In reality, however, at normal pressure the value of the parameter Γ_m at the melting point varies from alkali metal to alkali metal and lies within the limits from 110 (Li) to 180 (Cs), varying in accordance with the atomic number of the metal.

In order to explain these results, it is clearly necessary to take into account the other structure-sensitive component of the total energy that is due to the inhomogeneity of the electron gas and is described by the second-order term $E_e^{(2)}$. As is well known, the second-order correction to the total electron energy is always negative,^[11] and has a larger, i.e., a less negative, value for a solid than for a liquid.^[7] The latter gives the key to the explanation of the observed deviations of the values of Γ_m on the fusion curves of the alkali metals from the corresponding values for the classical one-component plasma. Indeed, Fig. 1 shows that, when allowance is made for the energy $E_e^{(2)}$, the volume value corresponding to the phase transition shifts in the direction of smaller values, which in its turn leads to an increase in the value of Γ_m .

As can be seen from Fig. 1, under conditions of strong compression this change can be expressed approximately by the relation

$$V_m^0 - V_m \approx \Delta E_e^{(2)} / P_m, \quad (1)$$

where V_m^0 is the volume coordinate of the point of intersection of the two branches of the free energy in a pure-

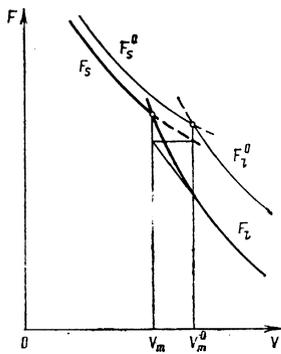


FIG. 1. Diagram illustrating the influence of the energy of the indirect pair interaction of the ions on the volume coordinate of fusion; $F = F^0 - E_e^{(2)}$; F_s is the free energy of the solid; F_l , the free energy of the liquid.

ly Coulomb system, V_m is the corresponding coordinate when allowance is made for the second-order term $E_e^{(2)}$, $\Delta E_e^{(2)}$ is the difference between the $E_e^{(2)}$ values in the coexisting phases, and P_m is the phase-transition pressure.

In the case when $E_e^{(2)} \ll PV$, it is not difficult to rewrite (1) in the form

$$\Gamma_m \approx \Gamma_0 + \Gamma_0 \Delta E_e^{(2)} / 3P_m V_m, \quad (2)$$

where Γ_m is the running value of the parameter Γ along the fusion curve and Γ_0 is the value of the parameter Γ for a purely Coulomb system. Since the thermodynamic parameters are not independent along the fusion curve, the expression (2) can, keeping in mind that its right-hand side should be dimensionless, be transformed as follows:

$$\Gamma_m = \Gamma_0 + f(V_m/V_c), \quad (3)$$

$$\Gamma_m = \Gamma_0 + \varphi(T_c/T_m), \quad (4)$$

where the parameters V_c and T_c should be related to the corresponding parameters characterizing the electron-ion interaction.

To elucidate the question of the tendency of the parameter Γ_m to vary along the fusion curve, it is necessary to make certain assumptions about the form of $\Delta E_e^{(2)}$ and P_m . Let us assume that the $E_e^{(2)}$ term can be roughly approximated by a dependence of the form α/V , where the constant α has different values for the liquid and solid phases. An approximation of this sort implies that we are using a pseudopotential of a special form, and are neglecting the change in the properties of the electron gas when compressed. This assumption is, apparently, sufficiently reasonable in a finite density range.

Further, approximating the function $P_m = f(V_m)$ by a dependence of the form $P \sim V^{-n}$, we find from (1) that

$$\Gamma_m = \Gamma_0 + cV_m^{n-2}. \quad (5)$$

From the expression (5) we can conclude that, for $n > 2$ (a condition which is satisfied in the case of the alkali metals), the parameter Γ_m will decrease along the fusion curve, tending to a constant value Γ_0 in the limit of infinite compressions.

Let us now turn to the question of the behavior of the relative volume jump, $\Delta V/V_s$, that occurs when an al-

kali metal is melted. Considering the system at a high density, we shall assume that the entropy of fusion is a constant quantity and neglect the contribution of $E_e^{(2)}$ to the thermodynamic properties. Let us recall further that, in accordance with the form of the ionic energy $E_i \sim -1/V^{1/3}$, a system of point charges in a homogeneous compensating background possesses negative pressure and compressibility. Consequently, the stability of an alkali metal is secured by the purely volume terms of the ionic energy, to wit, by the mean value of the non-Coulomb part of the electron-ion interaction energy $E_e^{(1)} \sim 1/V$ and the energy of the interaction electron gas $E_e^{(0)}$.^[6] The magnitude of the latter depends weakly on the volume at moderate densities, but at high compressions the energy of the interacting electron gas has the form $E_e \sim 1/V^{2/3}$.

Thus, at infinite compression the free energy and the pressure of the alkali metals are mainly determined by the term $E_e^{(1)}$, whereas the existence of the fusion-crystallization phenomenon and the shape of the fusion curve in the V - T coordinates are ensured by the ionic energy E_i . The latter assertion is easy to understand if we remember that the purely volume components of the energy cannot alter the volume coordinate of the point of intersection of the two branches of the free energy. Using the thermodynamic relation $\Delta U + P\Delta V = T\Delta S$, we obtain that

$$\Delta V/V_s = T\Delta S/V_s P - \Delta U/V_s P. \quad (6)$$

Taking into consideration the fact that

$$T \sim 1/V^{1/3}, \quad \Delta U \sim 1/V^{1/3}, \quad P \sim 1/V^2,$$

we find from (6) that

$$\Delta V/V_s \approx cV^{2/3}. \quad (7)$$

Thus, in contrast to the case of the inert gases, it is to be expected that the relative volume change that occurs upon the melting of the alkali metals tends to zero as the metals are subject to ever increasing compression. It is clear that this result will not change if we use for the pressure a dependence of the more general form $P \sim V^{-n}$ for $n > \frac{4}{3}$.

It should be emphasized that there is no room for maxima on the fusion curves in our simple picture of the melting of the alkali metals, and an explanation of this interesting phenomenon should be sought probably in changes in the form of the electron-ion interaction, changes which can occur at high pressures.

EXPERIMENTAL PROCEDURE AND RESULTS

Experimental data characterizing the thermodynamics of fusion of the alkali metals were obtained by measuring the P - V - T relations along the fusion curves of the metals under study. The measurements were carried out with the aid of a piston piezometer fitted with a rheostatic displacement detector.^[12, 13] In the course of the measurements the piezometer was located inside a thick-walled gas cylinder, the pressure inside which was produced with the aid of an external device. The details of the experiment are given in the cited literature. The error in the volume measurements was

TABLE I. The thermodynamics of fusion of lithium, potassium, and rubidium (experimental data).

Metal	T, K	P, kbar	$\Delta V, \text{cm}^3/\text{mole}$	$V_s, \text{cm}^3/\text{mole}$	$\Delta S/R$	$\Delta U, \text{cal/mole}$
Li	453.76*	0.001	0.213*	13.353*	0.794	715.6
	454.25	0.149	0.211	13.335	0.791	713.0
	457.62	1.211	0.199	13.212	0.782	705.5
	462.90	3.005	0.182	13.013	0.776	700.7
	467.82	4.826	0.167	12.824	0.774	699.9
	472.80	6.836	0.151	12.630	0.766	694.6
	477.95	9.105	0.137	12.427	0.764	695.6
	483.05	11.581	0.124	12.216	0.760	695.2
	485.95	13.122	0.117	12.092	0.762	699.3
	336.96	0.001	1.173	45.982	0.844	565.2
343.74	0.417	1.095	45.410	0.830	555.6	
359.70	1.488	0.945	44.075	0.811	546.1	
375.50	2.691	0.819	42.758	0.800	543.7	
394.20	4.334	0.695	41.190	0.794	550.2	
412.78	6.253	0.584	39.660	0.787	558.5	
442.79	10.135	0.438	31.160	0.783	583.0	
452.76	11.693	0.396	36.338	0.782	592.9	
K	312.12*	0.001	1.450*	56.380*	0.828	513.5
	313.65	0.074	1.435	56.225	0.831	515.3
	332.78	1.077	1.190	54.250	0.815	507.9
	352.67	2.310	1.000	52.210	0.809	511.7
	372.65	3.773	0.840	50.200	0.803	518.6
	392.80	5.518	0.705	48.175	0.799	530.5
	412.70	7.566	0.584	46.203	0.788	540.4
	432.61	10.016	0.482	44.225	0.781	556.0
	452.64	12.995	0.395	42.250	0.778	576.7
	Rb	312.12*	0.001	1.450*	56.380*	0.828
313.65		0.074	1.435	56.225	0.831	515.3
332.78		1.077	1.190	54.250	0.815	507.9
352.67		2.310	1.000	52.210	0.809	511.7
372.65		3.773	0.840	50.200	0.803	518.6
392.80		5.518	0.705	48.175	0.799	530.5
412.70		7.566	0.584	46.203	0.788	540.4
432.61		10.016	0.482	44.225	0.781	556.0
452.64		12.995	0.395	42.250	0.778	576.7

*Extrapolated values.

not greater than $\pm 0.01\%$. The temperature and pressure were determined to within $\pm 0.01^\circ\text{C}$ and ± 5 bar for pressures of up to 15 kbar; at higher pressures the corresponding errors were $\pm 0.1^\circ\text{C}$ and ± 25 bar. The quantity of impurities in the investigated metals did not exceed 0.01% for Na, K, Rb, and Cs and 0.05% for Li. The Li sample was enriched with the ^7Li isotope (99.66%). The piezometers were filled with the metals to be investigated in $\sim 10^{-6}$ -Torr vacuum.

On the basis of the obtained data we computed the variation of the volume with pressure. Then with the aid of the Clausius-Clapeyron equation we determined the enthalpy, internal-energy, and entropy jumps. The experimental data and the results of the thermodynamic computations for lithium, potassium, and rubidium are given in Table I. The corresponding results for sodium and cesium have been published elsewhere.^[14, 15] Figures 2-6 illustrate the behavior of the thermodynamic characteristics of fusion along the fusion curves of the investigated metals.

DISCUSSION OF THE RESULTS

In the Introduction we arrived at the conclusion that, in general outline, the shape of the fusion curves of the alkali metals is similar to the shape of the fusion

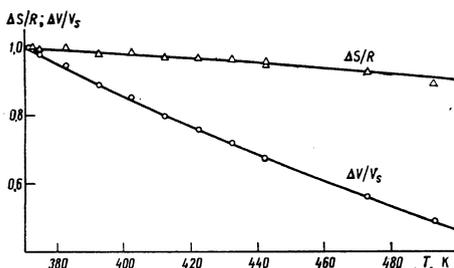


FIG. 2. The relative volume jump, $\Delta V/V_s$, and the entropy change, $\Delta S/R$, that occur upon the melting of sodium as functions of the melting temperature. The quantities $\Delta V/V_s$ and $\Delta S/R$ have been normalized to the corresponding values at atmospheric pressure.

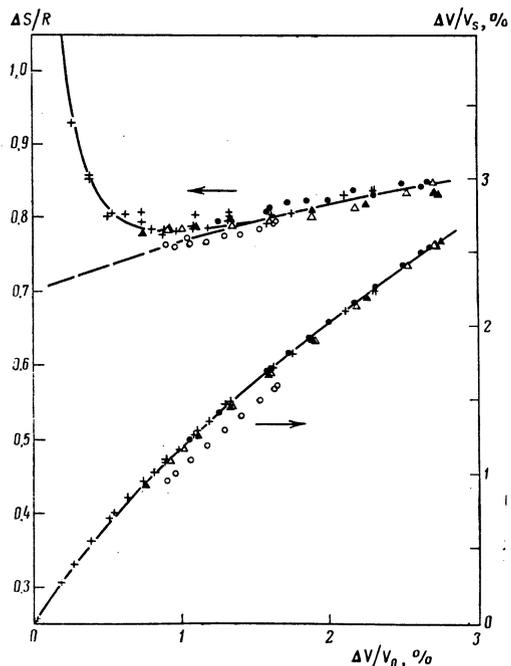


FIG. 3. The relative volume jump, $\Delta V/V_s$, and the entropy change, $\Delta S/R$, that occur upon the melting of the alkali metals as functions of the reduced volume jump $\Delta V/V_0$ (V_0 is the volume of the metal at $T=0$ K and atmospheric pressure): (○) Li; (●) Na; (△) K; (▲) Rb; (+) Cs.

curves of the inert gases. If the correction to the total energy taking the inhomogeneity of the electron gas into account is a monotonic function of the volume, then the only distinctive feature of the melting of the alkali metals, as compared with the case of the inert gases, is that the asymptotic value of $\Delta V/V_s$ will be equal to zero. Indeed, as can be seen from Fig. 2, which illustrates the characteristic behavior—as obtained in sodium—of $\Delta V/V_s$ and $\Delta S/R$ as functions of temperature, there is no basis for assuming that $\Delta V/V_s$ tends to a finite value as $T \rightarrow \infty$. The behavior of $\Delta S/R$ also does not exhibit any tendencies different from the corresponding tendencies exhibited in the melting of the inert gases.

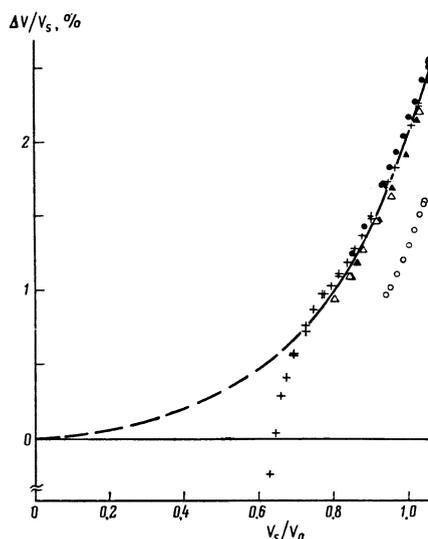


FIG. 4. The relative volume jump, $\Delta V/V_s$, as a function of the reduced volume V_s/V_0 . The symbols have the same meaning as in Fig. 3.

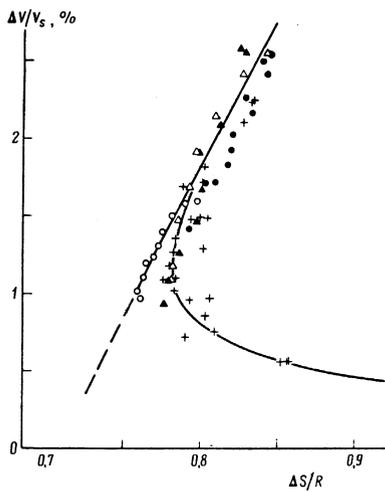


FIG. 5. Relation between the relative volume jump $\Delta V/V_s$ and the entropy jump $\Delta S/R$ that occur upon the melting of the alkali metals. The symbols have the same meaning as in Fig. 3.

More informative from the point of view of the establishment of the asymptotic values of $\Delta V/V_s$ and $\Delta S/R$ is Fig. 3, where these quantities are represented as functions of the volume jump ΔV . It follows from Fig. 3 that as ΔV tends to zero, $\Delta V/V_s$ also tends to zero for all the alkali metals. However, Fig. 3 does not allow us to find the differences between the cases when $\Delta V/V_s$ goes to zero at infinite compression and when this occurs at some finite pressure.

In this connection, it is useful to examine Fig. 4, in which the quantity $\Delta V/V_s$ is depicted as a function of the molar volume V_s . From Fig. 4 it can be seen that the behavior of the initial sections of the corresponding curves for all the alkali metals is not at variance with our conclusion that $\Delta V/V_s$ tends to zero as $V_s \rightarrow 0$ (see Eq. (7)). However, at high pressures the function $\Delta V/V_s = f(V_s)$ for cesium changes its form quite sharply, and $\Delta V/V_s$ becomes equal to zero at the finite volume corresponding to the temperature maximum on the fusion curve of cesium.

It is interesting to find out whether such behavior is general for all the alkali metals, or it is a specific property of cesium. To seek an answer to this question let us turn our attention to Figs. 2, 3, and 5, which illustrate the behavior of the entropy jumps along the fusion curves of the alkali metals. It can be seen from Fig. 3 that the entropy of fusion of cesium increases quite rapidly in the vicinity of the maximum on the fusion curve. At high temperatures the entropy of fusion of potassium and rubidium has a tendency to increase as compared with the behavior of the corresponding function for lithium and sodium. This tendency is manifested more sharply in Fig. 5, which exhibits the relation between the entropy of fusion and the relative volume jump. As can be seen from Fig. 5, at small values of $\Delta V/V_s$ the dependence $\Delta S/R = f(\Delta V/V_s)$ splits up into two branches: one branch covers the data for lithium and sodium; the other, the data for potassium, rubidium, and cesium.

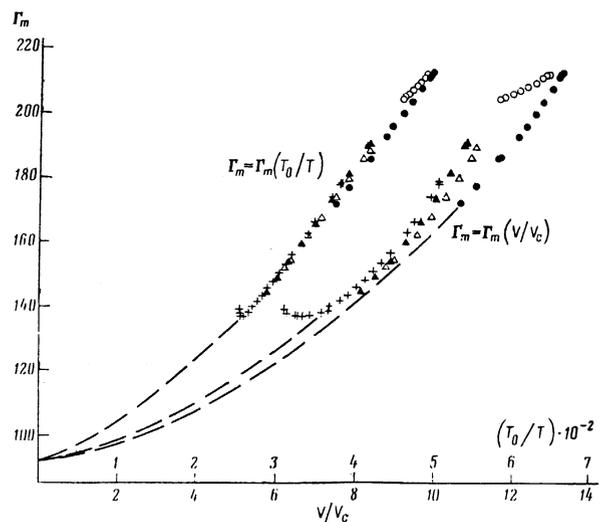


FIG. 6. The parameter Γ_m as a function of the reduced melting temperature T_0/T and of the reduced volume V/V_c ; $T_0 = 1/r_c$; $V_c = \frac{4}{3}\pi r_c^3$; r_c is the Ashcroft core radius. The numerical values of r_c were taken from the paper by Price *et al.* (Ref. 16). The symbols have the same meaning as in Fig. 3.

In connection with the above-noted difference in the behavior of the entropy jumps occurring upon the melting of the alkali metals, let us recall that, in contrast to lithium and sodium, potassium and rubidium have, as does cesium, vacant d states at low pressures. It is clear that this fact can be used to explain the significant decrease in the slope of the fusion curves of potassium and rubidium at high pressures^[4] and, thus, the existence of anomalies on the fusion curves of the alkali metals can be connected with the electron s - d transition.

Now let us turn to the question of the shape of the fusion curve of the alkali metals in the V - T plane. Let us examine Fig. 6, which shows the dependence of the parameter $\Gamma_m = Z^2 e^2 / r_a kT$ on temperature and volume. As follows from this figure, the experimental data confirm our result that the parameter Γ_m decreases along the fusion curve and tends to a constant value. It can be seen that the extrapolation of the corresponding dependences leads to a Γ_m value that does not exceed 100. This result disagrees somewhat with the latest estimates for the classical one-component plasma^[9, 10] and requires further analysis.

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Influence of a microwave field on the critical current of superconducting contacts

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An investigation is reported of the influence of nonequilibrium electrons on the critical current of a superconducting contact subjected to an external hf field. It is shown that the effective cooling of electrons trapped in the region of the contact which has a lower value of the gap may result in a considerable increase of the critical current. The maximum critical current is found and a study is made of the dependence of this current on the power at various temperatures. On approach of the critical temperature there should be a transition from stimulation to suppression of superconductivity in the contact, which agrees with the experimental results. The frequency limits of the existence of the effect are estimated.

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1. INTRODUCTION

Experiments carried out on superconducting contacts (bridges, point contacts, etc.) demonstrate the possibility of increasing the critical current by irradiation with a microwave field (Dayem–Watt effect).^[1–3] The influence of a microwave field on the critical current of a spatially homogeneous superconductor was considered by Éliashberg,^[9] who showed that stimulation of superconductivity occurs because of a change in the electron energy distribution function under the influence of the electric field. We shall find the critical current of a contact between superconductors in a microwave field.

When a superconducting current flows through a contact, the order parameter in the region of the contact Δ becomes smaller than its value Δ_0 outside the contact. Electrons of energy $\epsilon < \Delta_0$ cannot escape outside the contact and execute finite motion in a potential well, being reflected by the contact edges. In an hf field the superconducting contact and the order parameter become alternating quantities. This “jitter” of the potential well results in energy diffusion of electrons, and their distribution function becomes of nonequilibrium type. This mechanism at the contacts is stronger than the direct influence of the electric field.

A considerable change in the electron distribution function occurs near the bottom of the potential well where the energy diffusion process results in an electron deficiency compared with the equilibrium distribution. This corresponds to effective cooling of the contact. On the other hand, diffusion may result in the

accumulation of electrons at higher energies. The resultant effect on the critical current depends on the power and frequency of the incident radiation.

When this power is sufficiently high, the energy diffusion is a strong effect and all the electrons of energy $\epsilon < \Delta_0$ are cooled, whereas electrons of energy $\epsilon > \Delta_0$ do not accumulate in the contact region because of spatial diffusion and their distribution function remains of the equilibrium type. This stimulates superconductivity and the critical current of the contact rises.

At low radiation powers only the electrons of energies in a narrow region near the bottom of the well are cooled. These electrons are localized near the middle of the contact and the order parameter increases there. Elsewhere in the contact the electrons are heated and the order parameter decreases. It follows that the critical current of the contact decreases for a sufficiently low power.

When the frequency of the radiation field is increased, the range of energies where there are significant changes in the electron distribution begins to depend on the frequency and becomes wider. Electron cooling occurs in a wider region and, beginning from a certain frequency, the rise of the critical current occurs even at low radiation powers.

2. ENERGY DIFFUSION OF ELECTRONS IN A CONTACT

The distribution function of electrons in a contact subjected to an external alternating electromagnetic field