

# Paramagnetic effect of the magnetic field on superconductors with charge-density waves

T. Ekino<sup>1</sup>, A.M. Gabovich<sup>2</sup>, and A.I. Voitenko<sup>2</sup>

<sup>1</sup>*Hiroshima University, Faculty of Integrated Arts and Sciences, 1-7-1 Kagamiyama Higashi-Hiroshima 739-8521, Japan*

<sup>2</sup>*Crystal Physics Department, Institute of Physics of the National Academy of Sciences  
46 Nauki Ave., Kiev 03028, Ukraine  
E-mail: gabovich@iop.kiev.ua*

Received May 17, 2004

The limiting field  $H_p$  for spin-singlet superconductors with charge-density waves (CDWs), which paramagnetically destroys the ordered phase, possessing coexisting superconducting and CDW order parameters, is calculated self-consistently. It is shown that  $H_p$  always exceeds the Pauli limits both for pure superconducting and pure CDW phases. Relevant experimental data for inorganic and organic superconductors with high upper critical magnetic fields are analyzed and are shown to be in qualitative agreement with the proposed theory.

PACS: 71.45.Lr, 74.20.Fg, **75.20.-g**

## 1. Introduction

Clogston [1] and Chandrasekhar [2] discovered theoretically the Pauli paramagnetic suppression of the spin-singlet Cooper pairing. In the framework of the original Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity [3] they obtained a limit

$$H_p^{BCS} = \frac{\Delta_{BCS}(T=0)}{\mu_B^* \sqrt{2}} \quad (1)$$

from above on the upper critical magnetic field  $H_{c2}$  at zero temperature  $T$ . Here  $\Delta_{BCS}(T)$  is the superconducting energy gap,  $\mu_B^* = e\hbar/2m^*c$  is the effective Bohr magneton,  $e$  is the elementary charge,  $\hbar$  is Planck's constant,  $m^*$  is the effective electron mass, and  $c$  is the velocity of light.

This conclusion may be violated in the dirty case, when a large concentration of strong spin–orbit scattering sites exist and the spins of the electrons constituting the Cooper pairs are flipped [4]. A corresponding enhancement of  $H_{c2}$  has been indeed observed in Al films coated by monolayers of Pt [5]. The Pt atoms served there as strong spin–orbit scatterers due to their large nuclear charge  $Z$ . On the other hand, a similar contamination of another superconductor, the A15 compound  $V_3Ga$ , exhibiting Pauli paramagnetic effect

in the absence of impurities, altered neither  $H_{c2}$  nor the Zeeman splitting of the tunnel conductance [6]. Therefore, the spin–orbit mechanism of overcoming the Clogston–Chandrasekhar limit remains open to investigation.

There exists another collective state revealing a paramagnetic effect similar to the Clogston–Chandrasekhar one [1,2] inherent to the BCS  $s$ -wave superconductivity. It is a charge-density wave (CDW) low- $T$  insulator or a CDW metal (CDWM), where only certain sections of the Fermi surface (FS) are gapped below the critical structural transition temperature  $T_d$  [7,8]. The same description is applicable at a phenomenological level to both a Peierls insulator emerging due to the electron–phonon interaction [9] and an excitonic insulator caused by the Coulomb electron–hole attraction [10,11]. The dielectric CDW instability is a consequence of the nesting condition

$$\xi_1(\mathbf{p}) = -\xi_2(\mathbf{p} + \mathbf{Q}), \quad (2)$$

characterizing the electron spectrum at the FS sections labeled by  $i = 1, 2$ , where  $\mathbf{Q}$  is the CDW vector. So, here, the electron spectra are degenerate ( $d$ ) and a CDW-related order parameter  $\tilde{\Sigma}$  appears on those nested sections. The rest of the FS ( $i = 3$ ) remains undistorted, and its spectrum branch  $\xi_3(\mathbf{p})$  is nondegenerate ( $n$ ).

In the weak-coupling approximation, the superconducting  $\Delta$  and dielectric  $\tilde{\Sigma} = \Sigma e^{i\varphi}$  order parameters obey self-consistency equations of the same form [3,11]. Here  $\varphi$  is the phase of the CDW, usually pinned by defects or the background crystal lattice in subthreshold electrostatic fields [9,12]. Those properties of the low- $T$  phases, which are not dependent on the peculiar differences between the so-called diagonal and off-diagonal long-range orders [10,11,13,14], should be quite close to one another. That was indeed proved true for the Peierls insulator [15] (see also Refs. 16–18). A physical reason for the similarity consists in the fact that the electron–hole pairing couples the bands (in the excitonic insulator) or the different parts of the one-dimensional self-congruent band (in the Peierls insulator) with the same spin direction, contrary to the SDW case, where current carriers with the opposite spin directions are paired. When  $H$  is switched on, both congruent FS sections having the chosen spin projection ( $\pm$ ) shift either up or down in energy. Therefore, the corresponding nesting CDW vectors  $\mathbf{Q}_+$  and  $\mathbf{Q}_-$  do not coincide any more, and the initial CDW state is gradually destroyed [19].

In normal CDWMs, the highest possible magnetic field  $H_p^{CDWM}$  (taking into account the paramagnetic effect only!) can be easily found from the same simple considerations as in the superconducting case [3], so that

$$H_p^{CDWM} = \frac{\Sigma^*}{\mu_B^*} \sqrt{\frac{\mu}{2}}. \quad (3)$$

Here,  $0 \leq \mu \leq 1$  is the relative portion of the FS sections gapped by CDWs,  $\Sigma^* = \pi T_d / \gamma$  is the bare CDW gap at  $T = 0$  in the absence of superconductivity, and  $\gamma = 1.7810\dots$  is the Euler constant. The parameter  $\mu$  is defined by the relation

$$\mu = N_d(0) / N(0), \quad (4)$$

where  $N(0) = N_n(0) + N_d(0)$  is the total initial (above  $T_d$ ) electronic DOS on the FS, and  $N_d(0)$  and  $N_0(0)$  are the relevant DOSs on the  $d$  and  $n$  FS sections, respectively.

At the same time, the diamagnetic reaction of substances gapped by CDWs is much weaker [20] than that in superconductors with their complete Meissner diamagnetism below the first critical magnetic field [3]. Nevertheless, it always manifests itself in CDW metals or insulators and can even modify the very CDW wave vector [21–25]. Therefore, in calculating the total response both the paramagnetic (spin) and diamagnetic contributions should be taken into account [18,26–33].

In this connection, Eq. (3), similar to the case of BCS superconductors, gives a limiting upper value for

$H$  that does not destroy the CDW state. One should note, however, that CDW-triggered persistent currents were claimed to be observed far above the Pauli limit (3) in the ac susceptibility measurements for the compound  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> [22]. The authors of Refs. 22,34 suggested the existence of the Fröhlich ideal conductivity [35] in this substance. These intriguing conclusions have not yet been confirmed by other groups.

It is well known that there are plenty of materials in which CDWs and superconductivity coexist at  $T < T_c < T_d$  [7,8]. Here  $T_c$  is the critical temperature of the superconducting state. It is important to stress that the assumed superconductivity is possible only if the CDW gapping of the electron spectrum is partial [7,8,36], i.e., the distorted phase remains metallic. From the aforesaid, it is natural to expect that in the mixed phase, possessing two spin-singlet order parameters  $\Delta$  and  $\tilde{\Sigma}$ , the paramagnetic limit  $H_p$  exceeds both expressions (1) and (3) inherent to the states with either of two orderings.

Indeed, some time ago [37] the inequality  $H_p > H_p^{BCS}$  was demonstrated to be valid for all possible values of the parameters inherent to the Bilbro–McMillan model [36]. That result, as is shown below, remains correct in a more accurate approach. Nevertheless, our previous considerations [37–39] had a significant limitation. Specifically, the treatment of the superconducting phase with CDWs was not self-consistent, which quite unexpectedly made the whole problem *more* rather than less involved. In our current calculations we use the results of the self-consistent calculations of the thermodynamic properties [40] applied to a metal with two order parameters: a dielectric one  $\tilde{\Sigma}(T)$ , existing on the nested FS sections, and a superconducting one  $\Delta(T)$ , unique for both the  $d$  and  $n$  sections [36]. The ratio  $H_p / H_p^{BCS}$ , contrary to its counterpart in the non-self-consistent approach [37], turns out to be described by a simple analytical formula.

On the other hand, the relationship between  $H_p$  and  $H_p^{CDWM}$  is examined for the first time and an additional inequality  $H_p > H_p^{CDWM}$  is proved below to be valid for any set of the input parameters. We obtain several phase diagrams in the parameter space for  $T = 0$  and carry out their analysis in terms of the observed variables. Relevant experimental data are discussed.

## 2. Calculation of phase diagrams

To calculate the paramagnetic limit, one should consider free energies  $F$  per unit volume for all possible ground state phases in an external magnetic field  $H$ . The parent non-reconstructed phase (actually existing only

above  $T_d$ !), with both superconducting and electron–hole pairings switched off and in the absence of  $H$ , serves as a reference point. At  $T < T_d$ , we deal with relatively small differences  $\delta F$  reckoned from this hypothetical «doubly-normal» state [3].

Since we assume the Meissner diamagnetic response to be negligibly small, the external magnetic field  $H$  should coincide with that inside the specimen and be almost uniform. Therefore, the additional energy of the paramagnetic phase in the magnetic field, when both  $\Delta$  and  $\tilde{\Sigma}$  are equal to zero, takes the form [41]

$$\delta F_p = -N(0)(\mu_B^* H)^2. \quad (5)$$

The reconstructed superconducting state with the FS gapped both by superconductivity and CDWs constitutes another thermodynamic phase at  $T < T_c$ . Its free energy can be obtained from the following simple arguments. In the adopted Bilbro–McMillan model [36], the order parameters  $\Delta(T)$  and  $\tilde{\Sigma}(T)$  satisfy the self-consistent equation system [40]. This system has a solution, which determines two different  $T$ -dependent energy gaps on  $n$  and  $d$  sections of the FS. Specifically, there is the superconducting energy gap  $\Delta(T) = \Delta_{BCS}(\Delta_0, T)$  below  $T_c$  on the  $n$  sections, whereas the  $d$  sections are influenced by the effective gap  $D(T) = \Delta_{BCS}(D_0, T)$ . Here  $\Delta_{BCS}(G, T)$  is the Mühlischlegel gap function of the BCS theory with  $G = \Delta_{BCS}(T = 0)$ , so  $\Delta_0$  and  $D_0$  are the values of the relevant gaps at  $T = 0$ . The effective quantity  $D(T)$  is a combination of both constituent gaps

$$D(T) = \sqrt{\Delta^2(T) + \Sigma^2(T)}. \quad (6)$$

The value  $D_0$  is equal to the parameter  $\Sigma_*$ , defined in the Introduction. The assumed equality of the superconducting gaps  $\Delta_n$  and  $\Delta_d$  on the  $n$  and  $d$  FS sections, respectively, is a consequence of the strong mixing of the electron spectrum branches by the matrix elements of the effective four-fermion interaction Hamiltonian.

Thus, on both parts of the FS, BCS-like (but different!) gap functions are developed. The change of the free energy  $\delta F_s$  at  $T = 0$  is determined by their zero- $T$  values in the conventional manner [3]:

$$\delta F_s = -N_n(0) \frac{\Delta_0^2}{2} - N_d(0) \frac{\Sigma_*^2}{2}. \quad (7)$$

Finally, a paramagnetic superconducting CDW phase should be considered. The free energy of this phase, characterized by two order parameters  $\Delta(T)$  and  $\tilde{\Sigma}(T)$ , depends on  $H$  explicitly. Moreover, both gaps depend on  $H$  in a strange way, increasing with  $H$ . Such a phase is a generalization of the metastable one, found theoretically by Sarma for BCS superconduc-

tors (see, e.g., Refs. 3 and 42). The free energy of the paramagnetic superconducting CDW phase is higher than that given by Eq. (7) for all values of  $H$  up to the limiting value, when superconductivity ceases to exist, i.e.  $H_p$  [37], so that it can not be realized in the system. Of course, the same is true for the Sarma phase in BCS superconductors.

It is worth noting that any orbital magnetic field effects favorable for the CDW state are not taken into account, because the values of  $H$  relevant to the problem concerned are considerably smaller than those which reduce the dimensionality of the electron spectrum [21,27,33]. We also do not take into account the possibility of the Larkin–Ovchinnikov–Fulde–Ferrel (LOFF) nonhomogeneous superconducting state [3], although there are some hints that it might have been observed in low-dimensional organic compounds [43].

Thus, with the assumption of the order parameter homogeneity, the procedure of the paramagnetic limit determination is formally the same as that used by Clogston [1] and Chandrasekhar [2]. Namely, one should equate  $\delta F_p$  and  $\delta F_s$ . This leads to a basic relationship for the actual paramagnetic limit  $H_p$  of the mixed phase with two superconducting gaps  $\Delta$  and  $\Sigma$ :

$$(\mu_B^* H_p)^2 = \frac{1}{2} [(1 - \mu)\Delta_0^2 + \mu\Sigma_*^2] = \frac{1}{2} [\Delta_0^2 + \mu(\Sigma_*^2 - \Delta_0^2)]. \quad (8)$$

Since  $\Sigma_* = D_0 > \Delta_0$ , which is a consequence of equation (6), the limiting magnetic field  $H_p$  in a CDW superconductor *always exceeds* the Clogston–Chandrasekhar value  $H_p^{BCS}$  (1). At the same time,  $H_p$  is *always larger* than the paramagnetic upper limit  $H_p^{CDWM}$  (3) in the normal CDWMs.

The quantity  $D_0 = \Sigma_*$ , as has been indicated in the Introduction, is linked to the structural (excitonic) transition temperature  $T_d$  by the BCS relationship. The same is true for the pair  $\Delta_0$  and  $T_c$  [40]. Hence, it comes about that

$$\left( \frac{H_p}{H_p^{BCS}} \right)^2 = 1 + \mu \left[ \left( \frac{D_0}{\Delta_0} \right)^2 - 1 \right] = (1 - \mu) + \mu \left( \frac{T_d}{T_c} \right)^2 \quad (9)$$

and

$$\left( \frac{H_p}{H_p^{CDW}} \right)^2 = 1 + \frac{(1 - \mu) \Delta_0^2}{\mu D_0^2} = 1 + \frac{(1 - \mu)}{\mu} \left( \frac{T_c}{T_d} \right)^2. \quad (10)$$

All quantities in Eqs. (9) and (10) can be easily measured or inferred from the experimental data. The corresponding contour curves are displayed in Fig. 1. One can readily see that for typical  $T_c/T_d \approx 0.05$ – $0.2$

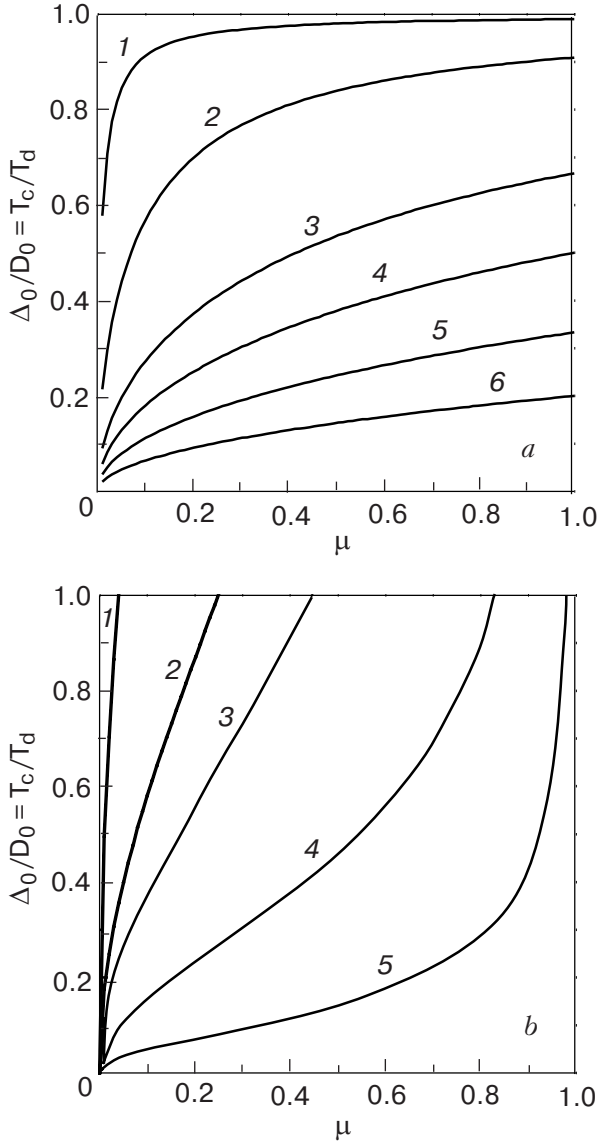


Fig. 1. Contour plot of the ratios  $H_p/H_p^{BCS}$ : 1.01 (1); 1.1 (2); 1.5 (3); 2 (4); 3 (5); 5 (6) (panel a) and  $H_p/H_p^{CDWM}$ : 5 (1); 2 (2); 1.5 (3); 1.1 (4); 1.01 (5) (panel b) on the plane  $(T_c/T_d, \mu)$ . Here  $H_p$ ,  $H_p^{BCS}$ , and  $H_p^{CDWM}$  are the paramagnetic limits for superconductors with charge-density-waves (CDWs), BCS spin-singlet superconductors, and CDW metals, respectively,  $T_c$  and  $T_d$  are the observed critical temperatures of the superconducting and CDW transitions, respectively, and  $\mu$  is the portion of the nested Fermi surface sections, where the CDW gap develops.

(some A15 compounds are rare exceptions [7,8]) and moderate values of  $\mu \approx 0.3-0.5$ , the augmentation of the paramagnetic limit (9) becomes very large. Of course, this outcome may be essentially reduced by the spin-orbit scattering [5]. At the same time, the Pauli limitation on  $H_p^{CDWM}$  is not so conspicuous, because the very role of superconductivity in the  $\Delta-\tilde{\Sigma}$  symbiosis is subdominant.

There is another way of representing the results. To this end a primordial superconducting gap  $\Delta_*$  at  $T = 0$

in the absence of CDWs is introduced. The observable superconducting order parameter  $\Delta_0$  can be expressed in terms of the bare input parameters in the following way [40]:

$$\Delta_0 = \Sigma_* \left( \frac{\Delta_*}{\Sigma_*} \right)^{\frac{1}{1-\mu}}. \quad (11)$$

Then the increase of the relevant paramagnetic limit over their primordial values is given by the formulas

$$\left( \frac{H_p}{H_p^{BCS}} \right)^2 = (1-\mu) + \mu \left( \frac{\Sigma_*}{\Delta_*} \right)^{\frac{2}{1-\mu}} \quad (12)$$

and

$$\left( \frac{H_p}{H_p^{CDW}} \right)^2 = 1 + \frac{(1-\mu)}{\mu} \left( \frac{\Delta_*}{\Sigma_*} \right)^{\frac{2}{1-\mu}}. \quad (13)$$

The level lines of  $H_p/H_p^{BCS}$  and  $H_p/H_p^{CDW}$  on the phase planes  $(\Delta_*/\Sigma_*, \mu)$  are shown in Fig. 2. It is clear from the plots that the smaller the ratio between the superconducting and CDW coupling constants the larger the excess of the paramagnetic limit.

The dimensionless parameters  $\Delta_*/\Sigma_*$  and  $\mu$  are independent of one another. As has been mentioned above, the latter can be experimentally determined, in particular, by resistive, specific heat, or optical measurements [7,8]. On the other hand, the bare gaps  $\Delta_*$  and  $\Sigma_*$  are hardly measurable because to get rid of either superconductivity or CDWs it is necessary to apply pressure, external magnetic field, or alloying. Therefore, various background electronic and crystal lattice properties would be inevitably altered, including gaps (some insight can be obtained from [11,44,45]).

Physically, the rise of  $H_p$  over  $H_p^{BCS}$  and  $H_p^{CDW}$  in CDW superconductors is quite natural. Both Cooper and electron-hole pairings are simultaneously depressed by the paramagnetic effect, whereas, while calculating  $H_p^{BCS}$  and  $H_p^{CDW}$ , the detrimental influence of the external field  $H$  on either of the order parameters (energy gaps) is taken into account. Therefore, larger fields  $H$  are required to produce the same effect as in the absence of a partner gap.

It is of interest that recently the enhancement of the paramagnetic limit for superconductors has been also found theoretically for a model related to the CDW model and taking into account the Van Hove singularity of the two-dimensional electron density of states [46].

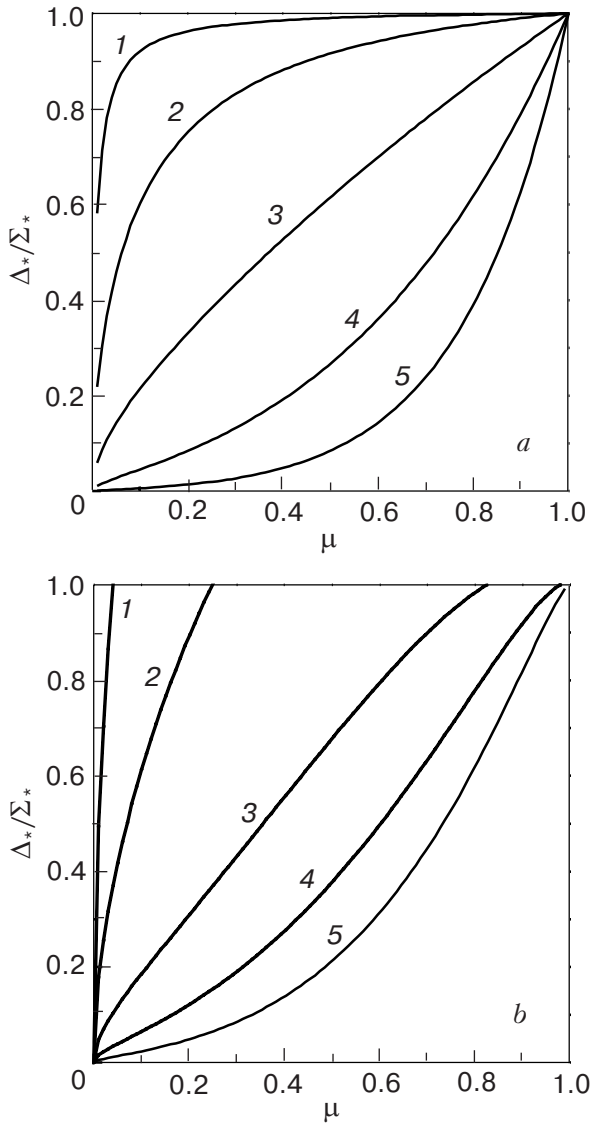


Fig. 2. Contour plot of the ratios  $H_p/H_p^{BCS}$ : 1.01 (1); 1.1 (2); 2 (3); 10 (4); 100 (5) (panel a) and  $H_p/H_p^{CDWM}$ : 5 (1); 2 (2); 1.1 (3); 1.01 (4); 1.001 (5) (panel b) on the plane  $(\Delta_*/\Sigma_*, \mu)$ . Here,  $\Delta_*$  and  $\Sigma_*$  are bare values of the order parameters in parent phases with only Cooper or CDW pairing, respectively.

### 3. Discussion

From the aforesaid it becomes clear that there is a unique Pauli limit in the mixed phase, which, in principle, can be attributed either to the superconducting or dielectric order parameters. Since in the case of the coexistence between  $\Delta$  and  $\tilde{\Sigma}$  experimentalists are most often interested in superconducting properties, the apparent exceeding of the Clogston–Chandrasekhar paramagnetic limit is interpreted without any reference to CDWs. Therefore, to verify our theory it would be desirable to prove the coexistence between CDWs and superconductivity in the same samples

where  $H_p > H_p^{BCS}$ . Unfortunately, such a direct verification is still lacking.

In principle, photoemission experiments might confirm simultaneous superconducting and CDW gapping of FSs and give FS momentum-space maps in the high- (ungapped) and low- $T$  (gapped) states [47]. In particular, such measurements might verify or disprove the strong-mixing concept discussed in the previous section. There are, however, methodological difficulties, which can hamper the unambiguous identification of the magnitudes as well as the directional and temperature dependences of  $\Delta$  and  $\Sigma$  (see, e.g., the analysis in Ref. 48 as applied to  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ ). Another important point is a three-dimensionality of the FS in cuprates [49]. If such warnings are ignored, the situation with gapping in photoemission spectra for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  (a high- $T_c$  oxide, the most suspicious from the CDW point of view) looks as follows [47]. The superconducting gap  $\Delta$  has a  $d$ -wave momentum dependence in the  $k_x - k_y$  plane with definite nodes. The same features are appropriate to pseudogaps, earlier identified by us as CDW ones [7,8]. Therefore, a clear-cut division of the cuprates' FS into two parts, one non-nested and gapped by  $\Delta$  and the other nested and gapped both by  $\Sigma$  and  $\Delta$  [see Eq. (6)], is not confirmed so far.

FSs and their gapping in layered dichalcogenides have been studied extensively by the photoemission method as well as by tunneling. In particular, the tunnel measurements [50] for  $2H$ -polytype compounds showed a conspicuous anticorrelation between  $\Sigma$  (or  $T_d$ ) and  $T_c$ . For  $2H\text{-NbSe}_2$  the CDW gap  $\Sigma \approx 34$  meV is the smallest nonzero one, whereas  $T_c$  is 7.2 K. Nevertheless,  $\Sigma$  has escaped detection by photoemission, although a much smaller superconducting gap was disclosed [51,52]! The authors of Ref. 52 believe that this result is due to the fact that the nested FS portion ( $\mu$  in our terms) is tiny. This explanation does not seem satisfactory, since all FS sheets and all directions in the  $\mathbf{k}$ -space were investigated. At the same time, a superconducting gapping was found for the  $\Gamma$ -centered [51] and  $K$ -centered [52] FS cylinders. Notwithstanding substantially different electron–phonon coupling strengths at various points of FS cylinders surrounding the  $K$ -point, the gap  $\Delta \approx 1$  meV is uniform there. This behavior counts in favor of the strong-mixing paradigm adopted here. All the preceding means that the microscopic relationships between two types of gapping in layered dichalcogenides are far from being resolved.

Let us turn back to the paramagnetic properties of CDW superconductors. It seems quite plausible that the phenomenon predicted in this article has already been observed in the C15 compound  $\text{Hf}_{1-x}\text{Zr}_x\text{V}_2$ , where  $H_{c2}(T) = 230$  or  $208$  kG for  $x = 0.5$  and  $0.6$ ,

respectively, and  $H_p^{BCS} \leq 190$  kG if the simplest possible estimation is made. On the other hand, in these solid solutions the CDW gapping was directly found by resistive measurements [53].

More recently necessary correlations between the increase of the paramagnetic limit and the CDW appearance have been revealed for organic superconductors. For example,  $H_{c2}(0)$  in the layered  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> with  $T_c \approx 10.4$  K and the FS prone to nesting [54], overcomes the corresponding  $H_p^{BCS}$  [55]. At the same time, the  $T$ -dependence of the resistance for this compound demonstrates a high and wide peak in the range 85–100 K interrupting the metallic trend appropriate both to low and room temperatures. Most probably, this behavior reflects the partial CDW-gapping [56]. The competition between CDW insulating state and superconductivity, triggered by an external pressure  $P$  in the related compound (BEDT-TTF)<sub>3</sub>Cl<sub>2</sub>·2H<sub>2</sub>O, can be considered as additional indirect evidence for the possible CDW presence in the superconducting state of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [54].

$\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is another charge-transfer salt with the  $\kappa$ -packing arrangement, where  $H_{c2}(0)$  conspicuously exceeds  $H_p^{BCS}$  [57]. It is remarkable that this substance is an insulator at ambient pressure but becomes metallic and superconducting for  $P > 0.3$  kbar. In view of such a proximity between dielectric and superconducting phases, it seems quite possible that  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl retains nesting properties of its FS for higher  $P$ . The observed positive curvature of  $H_{c2}(T)$  in the neighborhood of  $T_c$  [57], a feature appropriate to superconductors with density waves [58], agrees with the assumption made. At the same time, at larger  $P = 6$  kbar the critical temperature  $T_c$  reaches a rather high value of 12.8 K [54]. In the framework of our model [7,8,36] it corresponds to the FS distortion with  $\mu \rightarrow 0$ . The authors of Ref. 57 point out that spin-orbit scattering cannot lead to  $H_{c2}(0)$  exceeding  $H_p^{BCS}$  in the case discussed, since the Shubnikov-de Haas quantum oscillations in this compound are distinctly seen under pressure [54].

In the layered superconductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>NH<sub>4</sub>Hg(SCN)<sub>4</sub> the value  $H_{c2}(0)$  is comparable to  $H_p^{BCS}$  [59]. This salt with  $T_c \approx 1$  K is the only superconductor from the family  $\alpha$ -(BEDT-TTF)<sub>2</sub>MHg(SCN)<sub>4</sub>, while other sister compounds demonstrate the ground state of the density-wave type and  $T_d \approx 8$  K for M = K, Tl or 10 K for M = Rb [54]. A comparison of critical temperatures shows that density-wave correlations are stronger than superconducting ones, which imply large  $\Sigma_*/\Delta_*$  and hence favors the increase of the ratio  $H_p/H_p^{BCS}$ . It should be noted that the CDW nature of the low- $T$  in-

ulating state in non-superconducting salts stems from the observed paramagnetic effects [21,24,30,32,33,60] not appropriate to the SDW phase [19].

Application of the external pressure  $P$  to the initially insulating compound  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> leads to a complete suppression of CDWs for  $P > P_0 \approx 2.5$  kbar and an appearance of superconductivity with  $T_c \approx 0.1$  K [61]. This agrees well with our concept, and one should expect that  $H_{c2}(0)$  will exceed  $H_p^{BCS}$  under pressure  $P < P_0$ , when the CDW is not completely destroyed. Such a behavior is similar to what has been revealed in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl [57]. On the other hand, the superconducting transitions become extremely broad at pressures below  $P_0$ , demonstrating something like incomplete superconductivity [61], which is not covered by our theory [7,8]. However, this behavior may also stem from experimental artefacts, such as non-attained thermal equilibrium or internal strains. In any case, magnetic studies of  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> would be very important to elucidate the nature of CDW, superconducting, and superconducting + CDW phases.

A new oxide KOs<sub>2</sub>O<sub>6</sub> with a defect pyrochlore structure and  $T_c = 9.6$  K is the most recently synthesized superconductor with  $H_{c2} > H_p^{BCS}$  [62]. Since many oxides exhibit structural metal-insulator transitions with low- $T$  phases of the CDW nature [7,8,63–65], it would be of interest to check whether CDWs really coexist with superconductivity in this compound.

To summarize, we have obtained simple formulas describing the increase of the Pauli paramagnetic limit for  $H_{c2}(0)$  in CDW superconductors over the Clogston-Chandrasekhar value of the BCS theory as well as over the paramagnetic limit in the partially gapped normal CDWM phase. The similarity of the paramagnetic properties for  $s$ -wave superconductors and CDW partially gapped metals and the interplay of the two coexisting order parameters are responsible for the effect. There are strong experimental grounds to link the observed experimental data with the proposed concept.

### Acknowledgements

A.M. Gabovich is grateful to the Japan Society for the Promotion of Science for support of his visit to the Hiroshima University (Grant ID No. S-03204) and to the Mianowski Foundation for support of his visit to Warsaw University. The research has been partly supported by the NATO grant PST.CLG.979446 and the grants COE (No. 13CE2002) and Scientific Research (No. 15540346) of the Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors are also grateful to Jun Akimitsu (Tokyo),

Serguei Brazovskii (Kyoto), Kenji Ishida (Kyoto), Yoshiteru Maeno (Kyoto), and Mai Suan Li (Warsaw) for fruitful discussions of the paramagnetic properties of the charge-density-wave state.

1. A.M. Clogston, *Phys. Rev. Lett.* **9**, 266 (1962).
2. B.S. Chandrasekhar, *Appl. Phys. Lett.* **1**, 7 (1962).
3. A.A. Abrikosov, *Fundamentals of the Theory of Metals*, North-Holland, Amsterdam (1987).
4. P. Fulde, *Adv. Phys.* **22**, 667 (1973).
5. P.M. Tedrow and R. Meservey, *Phys. Rev. Lett.* **43**, 384 (1979).
6. R. Meservey and P.M. Tedrow, *Phys. Rep.* **238**, 173 (1994).
7. A.M. Gabovich and A.I. Voitenko, *Fiz. Nizk. Temp.* **26**, 419 (2000) [*Low Temp. Phys.* **26**, 305 (2000)].
8. A.M. Gabovich, A.I. Voitenko, and M. Ausloos, *Phys. Rep.* **367**, 583 (2002).
9. G. Grüner, *Density Waves in Solids*, Addison-Wesley Publishing Company, Reading, Massachusetts (1994), p. 259.
10. B.I. Halperin and T.M. Rice, *Solid State Phys.* **21**, 115 (1968).
11. Yu.V. Kopaev, *Trudy Fiz. Inst. Akad. Nauk SSSR* **86**, 3 (1975).
12. I.V. Krive, A.S. Rozhavskii, and I.O. Kulik, *Fiz. Nizk. Temp.* **12**, 1123 (1986) [*Sov. J. Low Temp. Phys.* **12**, 635 (1986)].
13. W. Kohn and D. Sherrington, *Rev. Mod. Phys.* **42**, 1 (1970).
14. M.A. Eggington and A.J. Leggett, *Collective Phenomena* **2**, 81 (1975).
15. W. Dieterich and P. Fulde, *Z. Phys.* **265**, 239 (1973).
16. T. Tiedje, J.F. Carolan, A.J. Berlinsky, and L. Weiler, *Canad. J. Phys.* **53**, 1593 (1975).
17. M. Matos, G. Bonfait, R.T. Henriques, and M. Almeida, *Phys. Rev.* **B54**, 15307 (1996).
18. D. Graf, J.S. Brooks, E.S. Choi, S. Uji, J.C. Dias, M. Almeida, and M. Matos, *Phys. Rev.* **B69**, 125113 (2004).
19. R.H. McKenzie, *cond-mat/9706235*.
20. D. Jérôme, T.M. Rice, and W. Kohn, *Phys. Rev.* **158**, 462 (1967).
21. D. Andres, M.V. Kartsovnik, W. Biberacher, H. Weiss, E. Balthes, H. Müller, and N. Kushch, *Phys. Rev.* **B64**, 161104 (2001).
22. N. Harrison, C.H. Mielke, A.D. Christianson, J.S. Brooks, and M. Tokumoto, *Phys. Rev. Lett.* **86**, 1586 (2001).
23. N. Harrison, *Phys. Rev.* **B66**, 121101 (2002).
24. D. Andres, M.V. Kartsovnik, P.D. Grigoriev, W. Biberacher, and H. Müller, *Phys. Rev.* **B68**, 201101 (2003).
25. N. Harrison, J. Singleton, A. Bangura, A. Ardavan, P.A. Goddard, R.D. McDonald, and L.K. Montgomery, *Phys. Rev.* **B69**, 165103 (2004).
26. A. Bjeliš and K. Maki, *Phys. Rev.* **B42**, 10275 (1990).
27. D. Zanchi, A. Bjeliš, and G. Montambaux, *Phys. Rev.* **B53**, 1240 (1996).
28. N. Biskup, J.A.A.J. Perenboom, J.S. Brooks, and J.S. Qualls, *Solid State Commun.* **107**, 503 (1998).
29. A. Bjeliš, D. Zanchi, and G. Montambaux, *cond-mat/9909303*.
30. J.S. Qualls, L. Balicas, J.S. Brooks, N. Harrison, L.K. Montgomery, and M. Tokumoto, *Phys. Rev.* **B62**, 10008 (2000).
31. P. Christ, W. Biberacher, M.V. Kartsovnik, E. Steep, E. Balthes, H. Weiss, and H. Müller, *Pis'ma Zh. Éksp. Teor. Fiz.* **71**, 437 (2000) [*JETP Lett.* **71**, 300 (2000)].
32. M.V. Kartsovnik, D. Andres, W. Biberacher, C. Christ, E. Steep, E. Balthes, H. Weiss, H. Müller, and N.D. Kushch, *Synth. Met.* **120**, 687 (2001).
33. A.G. Lebed, *Pis'ma Zh. Éksp. Teor. Fiz.* **78**, 170 (2003).
34. N. Harrison, L. Balicas, J.S. Brooks, and M. Tokumoto, *Phys. Rev.* **B62**, 14212 (2000).
35. H. Fröhlich, *Proc. Roy. Soc.* **A223**, 296 (1954).
36. G. Bilbro and W.L. McMillan, *Phys. Rev.* **B14**, 1887 (1976).
37. A.M. Gabovich, A.S. Gerber, and A.S. Shpigel, *Phys. Status Solidi* **B141**, 575 (1987).
38. A.M. Gabovich, E.A. Pashitskii, and A.S. Shpigel, *Pis'ma Zh. Éksp. Teor. Fiz.* **28**, 302 (1978) [*JETP Lett.* **28**, 277 (1978)].
39. A.M. Gabovich, E.A. Pashitskii, and A.S. Shpigel, *Zh. Éksp. Teor. Fiz.* **77**, 1157 (1979) [*Sov. Phys. JETP* **50**, 583 (1979)].
40. A.M. Gabovich, M.S. Li, H. Szymczak, and A.I. Voitenko, *J. Phys.: Condens. Matter* **15**, 2745 (2003).
41. L.D. Landau and E.M. Lifshits, *Electrodynamics of Continuous Media*, Nauka, Moscow (1982), in Russian.
42. Yu.A. Izyumov and Yu.N. Skryabin, *Phys. Status Solidi* **B61**, 9 (1974).
43. M.A. Tanatar, M. Suzuki, T. Ishiguro, H. Tanaka, H. Fujiwara, H. Kobayashi, T. Toito, and J. Yamada, *Synth. Met.* **137**, 1291 (2003).
44. *Problem of High-Temperature Superconductivity*, V.L. Ginzburg and D.A. Kirzhnits (eds.), Nauka, Moscow (1977), in Russian.
45. E.G. Maksimov, *Usp. Fiz. Nauk* **170**, 1033 (2000).
46. R.G. Dias and J.A. Silva, *Phys. Rev.* **B67**, 092511 (2003).
47. A. Damascelli, Z. Hussain, and Z-X. Shen, *Rev. Mod. Phys.* **75**, 473 (2003).
48. A.A. Kordyuk, S.V. Borisenko, M. Knupfer, and J. Fink, *Phys. Rev.* **B67**, 064504 (2003).
49. N.E. Hussey, M. Abdel-Jawad, A. Carrington, A.P. Mackenzie, and L. Balicas, *Nature* **426**, 814 (2003).
50. C. Wang, B. Giambattista, C.G. Slough, R.V. Coleman, and M. Subramanian, *Phys. Rev.* **B42**, 8890 (1990).
51. T. Kiss, T. Yokoya, A. Chainani, S.S. Nohara, and H. Takagi, *Physica* **B312-313**, 666 (2002).
52. T. Valla, A.V. Fedorov, P.D. Johnson, P-A. Glans, C. McGuinness, K.E. Smith, E.Y. Andrei, and H. Berger, *Phys. Rev. Lett.* **92**, 086401 (2004).

53. V.M. Pan, V.G. Prokhorov, and A.S. Shpigel, *Metal Physics of Superconductors*, Naukova Dumka, Kiev (1984), in Russian.
54. J. Singleton, *Rep. Prog. Phys.* **63**, 1111 (2000).
55. F. Zuo, J.S. Brooks, R.H. McKenzie, J.A. Schlueter, and J.M. Williams, *Phys. Rev.* **B61**, 750 (2000).
56. H. Mori, *Int. J. Mod. Phys.* **B8**, 1 (1994).
57. Y. Shimojo, T. Ishiguro, H. Yamochi, and G. Saito, *J. Phys. Soc. Jpn.* **71**, 1716 (2002).
58. A.M. Gabovich and A.S. Shpigel, *Phys. Rev.* **B38**, 297 (1988).
59. Y. Shimojo, T. Ishiguro, M.A. Tanatar, A.E. Kovalev, H. Yamochi, and G. Saito, *J. Phys. Soc. Jpn.* **71**, 2240 (2002).
60. D. Andres, M.V. Kartsovnik, W. Biberacher, T. Togonidze, H. Weiss, E. Balthes, and N. Kushch, *Synth. Met.* **120**, 841 (2001).
61. D. Andres, M.V. Kartsovnik, W. Biberacher, K. Neumaier, and H. Müller, *J. Phys. IV (Paris)* **12**, Proceedings 9, 87 (2002).
62. S. Yonezawa, Y. Muraoka, Y. Matsushita, and Z. Hiroi, *J. Phys.: Condens. Matter* **16**, L9 (2004).
63. J.M. Honig and L.L. Van Zandt, *Annu. Rev. Mater. Sci.* **5**, 225 (1975).
64. A.M. Gabovich and D.P. Moiseev, *Usp. Fiz. Nauk* **150**, 599 (1986) [*Sov. Phys. Usp.* **29**, 1135 (1986)].
65. A.K. Raychaudhuri, *Adv. Phys.* **44**, 21 (1995).