# Anisotropy of magnetic properties of exotic superconductors

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(Submitted 1 July 1991)
Zh. Eksp. Teor. Fiz. **100**, 1699–1710 (November 1991)

We obtain the orientational dependence of the upper critical field in a plane passing through a high-symmetry axis of an exotic rhombohedral or hexagonal superconductor. We show that the angular dependence of the upper critical field becomes more nonmonotonic only in a rhombohedral exotic superconductor. A distinctive asymmetry of the upper critical field and of the fluctuation diamagnetism near the transition point is obtained also for a rhombohedral crystal.

## 1. INTRODUCTION

The possible forms of superconductivity were first classified in discussions of the unusual properties of superconductors with heavy fermions.[1,2] The superconductivity attracting much attention was that of superconductors known to have nontrivial pairing (and called exotic) and described in the Ginzburg–Landau theory by a multicomponent order parameter. It appears that the heavy-fermion hexagonal superconductor $UPt_3$ is exotic. This is attested to by many experimental data, viz., the polarization anisotropy of the transverse-ultrasound absorption,[3] the frequency and low-temperature dependence of the magnetic-field penetration depth,[4,5] and also the phase diagram in the $H$–$T$ plane, a diagram containing several regions with different superconducting-state symmetries.[6–10] It can be deduced from most of these experiments that the superconducting gap on the Fermi surface is zero on a line located in a plane perpendicular to the hexagonal axis (and also at points on the intersection of the hexagonal axis with the Fermi surface[4]). This case offers a rare opportunity of uniquely determining the number of complex components of the superconductor order parameter solely from knowledge of the locations of the superconducting-gap zeros.

An important role in the identification of superconductors with nontrivial pairing can be assumed by a study of the anisotropy of their magnetic properties. Thus, the anisotropy of the upper critical field in tetragonal exotic superconductors should become manifest, generally speaking, even if the field is in a plane perpendicular to the tetragonal axis.[11,12] There is no such anisotropy in ordinary tetragonal superconductors. An unusual anisotropy in the basal plane of a tetragonal metal should result also from fluctuation diamagnetism (more accurately, from that part of the induced magnetic moment which is nonlinear in the field) in the normal phase near the transition into a superconductor with nontrivial pairing.[13] The anisotropy of the lower critical field in such superconductors can also have distinctive peculiarities.[14,15]

An unusual orientation dependence of the upper critical field can occur, generally speaking, not only in a plane perpendicular to a high-symmetry axis, but also in a plane passing through this axis. Attention was attracted in this connection by the measured $H_{c2}$ anisotropy in a plane passing through a threefold axis in a Chevrel phase of $Cu_{1.8}Mo_6S_8$ with rhombohedral crystal symmetry.[16,17] The resultant anisotropy cannot be described by the usual Ginzburg–Landau theory with anisotropic mass. To explain the experimental anisotropy obtained in Ref. 18 it was proposed that $Cu_{1.8}Mo_6S_8$ is an exotic superconductor characterized in the Ginzburg–Landau theory by a two-component complex vector as the order parameter. Numerical calculations[18] yielded the Ginzburg–Landau functional coefficients most suitable for reconciling the numerical data with experiment.

The angular dependence of the upper critical field under the above condition, however, has no analytic description. Since "turning off" the rhombohedral distortion of the crystal leads to hexagonal symmetry, this situation is also closely related to the anisotropy of the upper critical field in a plane passing through a sixfold axis in an hexagonal exotic superconductor, e.g., in $UPt_3$. This question is dealt with in Ref. 19, where the analysis implies that the unusual anisotropy of $H_{c2}$ in general exists already in an hexagonal exotic superconductor, meaning that there are grounds for seeking a specific $H_{c2}$ anisotropy of the "rosette" type in $UPt_3$. The relatively small rhombohedral distortion of the $Cu_{1.8}Mo_6S_8$ crystal has according to Ref. 19 practically no effect on the $H_{c2}$ anisotropy. It follows from our results, in particular, that the above statements of Ref. 19 are incorrect.

In Sec. 2 of this paper we obtain approximate expressions that describe in sufficient (perturbation-theory) approximation the anisotropy of the upper critical field in hexagonal and rhombohedral superconductors when the field is not in a plane passing through a sixfold or threefold axis, respectively. We show that anisotropy of the "rosette" type exists only in a rhombohedral-symmetry crystal. The reason is that for rhombohedral superconductors with nontrivial pairing the Ginzburg–Landau functional has second-order gradient terms containing products of derivatives of various order-parameter components along different crystallographic axes in the particular plane [see the terms with coefficient $P_4$ in (1)]. No such terms are present in the free-energy functionals of hexagonal exotic superconductors. A characteristic feature of the obtained $H_{c2}$ anisotropy near $T_c$ in the case of rhombohedral exotic superconductor is its symmetry with respect to reflections of the field direction in the two Cartesian planes perpendicular to the initial coordinate plane in which the magnetic field is located. Since we are dealing with the point group $D_{3d}$ and the magnetic field is by assumption in one of the three symmetry planes of this group, the asymmetry in question is generally speaking quite feasible (the two other Cartesian planes are not symmetry planes), but is absent from ordinary superconductors near $T_c$. Our analytic results for the anisotropy of the upper criti-

 0038-5646/91/110939-06$03.00  

cal field are in good agreement with Burlachkov's[18] calculations of the actual Ginzburg–Landau functional coefficients.

In Sec. 3 we determine the specific anisotropy of the fluctuational diamagnetism in a rhombohedral superconductor with nontrivial pairing. We show that the part, nonlinear in field, of the induced magnetic moment in the normal magnetic field has in the normal phase near $T_c$ the same specific asymmetry as the upper critical field with respect to reflections of the magnetic-field direction. Measurements of the anisotropy of the fluctuation diamagnetism in the normal phases of $Cu_{1.8}Mo_6S_8$ in the vicinity of $T_c$ may be useful for an independent verification of the assumption that the pairing in this compound is not trivial.

## 2. ANISOTROPY OF THE UPPER CRITICAL FIELD IN RHOMBOHEDRAL AND HEXAGONAL EXOTIC SUPERCONDUCTORS

A feature of a rhombohedral superconductor with nontrivial pairing is a two-component complex order parameter. If the spin-orbit interaction is strong enough, the Ginzburg–Landau functional, accurate to second-order invariants, is in this case

$$F=\int dV\{a\eta_i^*\eta_i+P_1\partial_i^*\eta_j^*\partial_i\eta_j+P_2\partial_z^*\eta_i^*\partial_z\eta_i + P_3(\partial_i^*\eta_j^*\partial_j\eta_i+\partial_i^*\eta_i^*\partial_j\eta_j)+[P_4(\partial_z^*\eta_x^*\partial_x\eta_x -\partial_z^*\eta_y^*\partial_x\eta_y-\partial_z^*\eta_x^*\partial_y\eta_y-\partial_z^*\eta_y^*\partial_y\eta_x)+\text{c.c.}]\}. \quad (1)$$

Here $a=\alpha(T-T_c)$, $\partial_k=\partial/\partial x_k-2ieA_k/c$; the $z$ and $y$ axes are respectively directed along threefold and twofold axes, and the subscripts $i$ and $j$ take on the values $x$ and $y$. For the crystal class $D_{3d}$ it follows from the foregoing that the Cartesian $x$ axis lies in a symmetry plane passing through $z$ and perpendicular to $y$.

From the condition that the sum of the gradient terms in (1) be positive-definite we obtain the following constraints on the coefficients $P_j$ ($j=1$–$4$):

$$P_1>0,\ |P_3|<P_1,\ P_1+3P_3>0,\ P_2(P_1+P_3)>2|P_4|^2. \quad (2)$$

Hence, in particular,

$$P_2>0;\ \frac{P_3}{P_1}<1 \text{ and } \frac{|P_4|}{(P_1P_2)^{1/2}}<1, \text{ if } P_3>0;$$
$$\frac{|P_3|}{P_1}<\frac{1}{3} \text{ and } \frac{|P_4|}{(P_1P_2)^{1/2}}<\frac{1}{2^{1/2}}, \text{ if } P_3<0. \quad (3)$$

It is evident from (3) that the parameters $|P_3|/P_1$ and $|P_4|/(P_1P_2)^{1/2}$ can always be regarded as small enough. We shall use hereafter perturbation theory in terms of these parameters, up to second-order terms inclusive, assuming the coefficient $P_4$ to be real. Note that in Eq. (1) only one gradient invariant, contained in the square brackets with the coefficient $P_4$, pertains to rhombohedral symmetry. The remaining invariants in (1) have cylindrical symmetry for rotations around the $z$ axis. Putting $P_4=0$ in (4) we obtain the Ginzburg–Landau free energy for an hexagonal superconductor with nontrivial pairing.[1)] If, however, $P_3=P_4=0$ expression (1) takes the form of a sum of two perfectly analogous independent Ginzburg–Landau functionals for ordinary uniaxial superconductors with anisotropic mass ($P_{1,2}\propto m_{1,2}^{-1}$). Since the orientational dependence of the upper critical field and of the fluctuation diamagnetism is well known for ordinary uniaxial superconductors, it is fairly easy to determine these quantities by perturbation theory for nonzero $P_3$ and $P_4$. Matters become somewhat more complicated for level crossing in first-order perturbation theory.

For a magnetic field $\mathbf{B}=B(\sin\alpha, 0, \cos\alpha)$ located in the $xz$ plane we choose a vector potential $\mathbf{A}=(0, A_y, 0)$, where $A_y=B(x\cos\alpha-z\sin\alpha)$. We express the free energy in the form

$$F=\int dV\{a\eta_i^*\eta_i+\eta_i^*\hat{H}_{ij}\eta_j\}, \quad (4)$$

where $\hat{H}_{ij}$ is a matrix differential operator, and the subscripts $i$ and $j$ take on the two values 1 and 2 [corresponding to the subscripts $x$ and $y$ in (1)].

We change in (4) to new integration variables

$$x'=\left(\frac{P_2}{P_1}\right)^{1/4}\frac{\sin\alpha}{D(\alpha)}x+\left(\frac{P_1}{P_2}\right)^{1/4}\frac{\cos\alpha}{D(\alpha)}z,\quad y'=\frac{1}{P_1^{1/2}}y, \quad (5)$$
$$z'=-\frac{\cos\alpha}{D(\alpha)}x+\frac{\sin\alpha}{D(\alpha)}z,$$

where

$$D(\alpha)=(P_1\cos^2\alpha+P_2\sin^2\alpha)^{1/2}. \quad (6)$$

It is convenient next to represent the operator $\hat{H}_{ij}$ by the sum $\hat{H}_{ij}=\hat{H}_{ij}^{(0)}+\hat{V}_{ij}$, where the perturbation operator $\hat{V}_{ij}$ includes the terms containing the coefficients $P_3$ and $P_4$. Using in (4) the new coordinates (5) we obtain for the unperturbed operator $\hat{H}_{ij}^{(0)}=\hat{H}^{(0)}\delta_{ij}$, where $\hat{H}^{(0)}$ has the form of the usual Hamiltonian for a nonrelativistic isotropic-mass charged particles in a magnetic field. Compared with the degeneracy multiplicity of the Landau levels, the eigenvalues $E_n^{(0)}$ of the operator $\hat{H}_{ij}^{(0)}$ are additionally doubly degenerate. To each level $E_n^{(0)}$ there correspond some two independent combinations of solutions of form $\boldsymbol{\eta}_{1,n}=(\eta_n^{(0)},0)$ and $\boldsymbol{\eta}_{2,n}=(0,\eta_n^{(0)})$, where $\eta_n^{(0)}$ is the wave function of a charged particle on the $n$th Landau level. The perturbation $\hat{V}_{ij}$ lifts just this double degeneracy. Note, however, that for any value of the angle $\alpha$ and for any Landau level there is satisfied identically the relation $(\hat{V}_{12})_{nn}=0$, where the matrix elements are taken over the functions $\eta_n^{(0)}$ and $\hat{V}_{12}=\hat{V}_{21}$. From the standpoint of the electron-term crossing theory (see, e.g., Ref. 20) it is therefore natural to have level crossing at definite field orientations, i.e., the degeneracy is not lifted for certain values of the angle $\alpha$. As a result, the standard second-order perturbation-theory equations for degenerate levels do not hold in the vicinities of such angle values. The correct zeroth-approximation eigenfunctions are also different in these angle intervals. The pertinent vicinities of the two angles $\alpha_{1,2}$ are given here by

$$\alpha_1=0,\ P_2P_3\sin\alpha_2=-2P_1P_4\cos\alpha_2. \quad (7)$$

The level-crossing condition satisfied for the angles $\alpha_{1,2}$ in first-order perturbation theory is

$$(\hat{V}_{11}(\alpha_{1,2}))_{nn}=(\hat{V}_{22}(\alpha_{1,2}))_{nn}. \quad (8)$$

Disregarding the term crossing and using the usual perturbation theory for degenerate levels,[20] we obtain for the eigenvalues of the operator $\hat{H}_{ij}$ to second order in the powers of $P_3$ and $P_4$

$$E_{n,1}(p_{x'},\alpha)=\frac{4|e|B}{c}P_1^{1/2}D(\alpha)f_1(\alpha)(n+{}^1/_2)+g_1(\alpha)p_{x'}^2, \quad (9)$$

$$E_{n,2}(p_{x'},\alpha)=\frac{4|e|B}{c}P_1^{1/2}D(\alpha)f_2(\alpha)(n+{}^1/_2)+g_2(\alpha)p_{x'}^2. \quad (10)$$

The functions $f_{1,2}(\alpha)$ are given by

$$f_1(\alpha)=1+\frac{\cos\alpha}{D^2(\alpha)}(P_3\cos\alpha-P_4\sin\alpha)-\frac{1}{2P_1D^2(\alpha)}(P_3\cos\alpha+P_4\sin\alpha)^2-\frac{\cos^2\alpha}{2D^4(\alpha)}(P_3\cos\alpha-P_4\sin\alpha)^2, \quad (11)$$

$$f_2(\alpha)=1+\frac{P_3}{P_1}+\frac{P_4\sin\alpha\cos\alpha}{D^2(\alpha)}-\frac{1}{2P_1D^2(\alpha)}(P_3\cos\alpha+P_4\sin\alpha)^2-\frac{1}{2}\left(\frac{P_3}{P_1}-\frac{P_4\sin\alpha\cos\alpha}{D^2(\alpha)}\right)^2. \quad (12)$$

We shall not need below explicit expressions for $g_{1,2}(\alpha)$. It suffices to note that they satisfy the relation

$$g_1(\alpha)f_1^2(\alpha)=g_2(\alpha)f_2^2(\alpha)=1+\frac{2P_3}{P_1}-\frac{2P_4^2}{P_1P_2}-\frac{P_3^2}{P_1^2}\equiv Q. \quad (13)$$

All the above results will be needed in the next section to calculate the anisotropy of the fluctuation diamagnetism. To find the upper critical field, however, it suffices to consider only the Landau ground level $n=0$, putting also $p_{x'}=0$. We get then from (9) and (10)

$$H_{c2}=\frac{|a|c}{2|e|P_1^{1/2}D(\alpha)}\max\left\{\frac{1}{f_1(\alpha)},\frac{1}{f_2(\alpha)}\right\}. \quad (14)$$

A more accurate calculation of the orientation dependence of the upper critical field, with allowance for the lifting of the level crossing in second-order perturbation theory, is also possible. Let us illustrate the procedure briefly. We are interested in the eigenvalues, obtained by perturbation theory, of the equation

$$(\hat{H}_0+\hat{V})_{ij}\eta_j=E\eta_i. \quad (15)$$

In the zeroth approximation we have

$$\hat{H}_{0,ij}=\hat{H}_0\delta_{ij},\quad \hat{H}_0\eta_n^{(0)}=E_n^{(0)}\eta_n^{(0)}. \quad (16)$$

Putting

$$\eta_1=\sum_m c_m\eta_m^{(0)},\quad \eta_2=\sum_m d_m\eta_m^{(0)}, \quad (17)$$

we obtain in the usual manner

$$(E-E_k^{(0)})c_k=\sum_m[(\hat{V}_{11})_{km}c_m+(\hat{V}_{12})_{km}d_m],$$
$$(E-E_k^{(0)})d_k=\sum_m[(\hat{V}_{21})_{km}c_m+(\hat{V}_{22})_{km}d_m]. \quad (18)$$

Since $(\hat{V}_{12})_{nn}=(\hat{V}_{21})_{nn}=0$, we must, for the vicinity of the angles (8), consider jointly terms of first and second order of smallness in some of the relations (18). This leads in general to rather unwieldy equations, but an explicit calculation of the matrix elements $(\hat{V}_{ij})_{km}$ from the oscillator wave functions $\eta_n^{(0)}$ simplifies (18) substantially. Thus, in the case $p_{x'}=0$, the perturbed Landau ground level is connected in (18) only with the $n=2$ level. The result for the ground energy level with allowance for perturbation is a quadratic equation whose solution yields for the upper critical field the expression

$$H_{c2}(\alpha)=\frac{|a|c}{2|e|P_1^{1/2}D(\alpha)}\left\{1+\frac{P_3}{2P_1}\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\cdot\left[1-\frac{P_3}{2P_1}\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\right]-\frac{P_4\sin^2\alpha}{2P_1D^2(\alpha)}\left[P_4\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)+\frac{P_2P_3\sin\alpha\cos\alpha}{D^2(\alpha)}\right]-\frac{1}{2}\mathcal{F}^{1/2}(\alpha)\right\}^{-1}, \quad (19)$$

$$\mathcal{F}(\alpha)=\frac{\sin^2\alpha}{D^4(\alpha)}\left\{\left[\frac{P_2P_3\sin\alpha}{P_1}\left(1-\frac{P_3}{2P_1}\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\right)+2P_4\cos\alpha\left(1+\frac{P_2P_3\sin^2\alpha}{2P_1D^2(\alpha)}\right)\right]^2-\frac{P_4^2}{P_1^2}\left[P_3\cos\alpha\left(3+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)+P_4\sin\alpha\left(1-\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\right]^2\right\}+\frac{1}{D^2(\alpha)P_1^3}\left(P_3^2+P_4^2\sin^2\alpha\frac{P_1}{D^2(\alpha)}\right)\times\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\left[(P_3\cos\alpha+P_4\sin\alpha)^2+\frac{P_1\cos^2\alpha}{D^2(\alpha)}(P_3\cos\alpha-P_4\sin\alpha)^2\right]. \quad (20)$$

The orientation dependence[2)] of $H_{c2}(\alpha)$ that follows from (19) and (20) is shown in Fig. 1 (curve 1) for the case when the coefficients in (1) satisfy the relations

$$P_1:P_2:P_3:P_4=1:1.34:0.11:-0.24, \quad (21)$$

suggested in Ref. 18 on the basis of a numerical analysis of problem and comparison with experiment. This relation agrees well with the numerical results of Ref. 18. The standard perturbation-theory expression (14) (dashed curve of Fig. 1) also describes well the $H_{c2}(\alpha)$ angular dependence, except at relatively narrow vicinities of the angles $\alpha_{1,2}$ [see Eqs. (7) and (8)].

The equation for the angular dependence $H_c(\alpha)$ is much simpler for an hexagonal superconductor ($P_4=0$) and we obtain in place of (19) and (20)

$$H_{c2}(\alpha)=\frac{|a|c}{2|e|P_1^{1/2}D(\alpha)}\left\{1+\frac{P_3}{2P_1}\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\times\left[1-\frac{P_3}{2P_1}\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\right]-\frac{|P_3|}{2P_1D^2(\alpha)}\left[P_2^2\sin^4\alpha\left(1-\frac{P_3}{2P_1}\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)\right)^2+\frac{P_3^2\cos^2\alpha}{P_1}D^2(\alpha)\left(1+\frac{P_1\cos^2\alpha}{D^2(\alpha)}\right)^2\right]^{1/2}\right\}^{-1}. \quad (22)$$

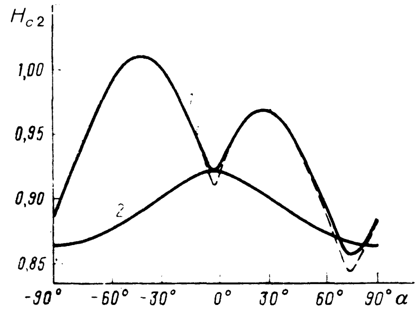


FIG. 1. Orientation dependence of the lower critical field in units of $H_{c2}^{(0)}(\alpha=0)$ [see (29)] for the values of the coefficients (21). Rhombohedral superconductor [curve 1—Eq. (19); dashed curve—Eq. (14)]. Hexagonal superconductor ($P_4=0$)—curve 2 [Eq. (22)].

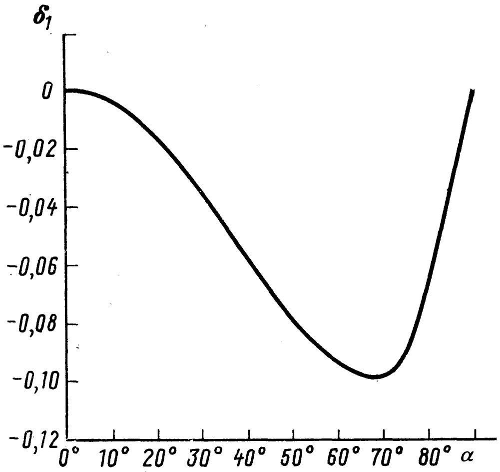


FIG. 2. Asymmetry $\delta_1(\alpha)$ of upper critical field.

This equation, with the second term in the square root neglected, coincides with the result (14) of the standard perturbation theory for $P_4=0$. If, for example, $(|P_3|/P_2)^{1/2}$ is small, the second term under the square root in (22) is not negligible only in the small angle region $\alpha \lesssim (|P_3|/P_2)^{1/2}$. As seen from (2), however, there are no general constraints on the value of $|P_3|/P_2$, and the interval of $\alpha$ in which the results of (22) differ substantially from those of (14) may generally speaking be quite large. For actual values (21) of the coefficients $P_{2,3}$ we have $(|P_3|/P_2)^{1/2}\simeq 0.29$ and the difference between (22) and (14) at $P_4=0$ is significant in the relatively narrow angle interval $\alpha \lesssim 17°$.

An important qualitative difference exists between the considered $H_{c2}(\alpha)$ dependences for a rhombohedral crystal [see (19) and (20)] and an hexagonal one [see (22)]. According to (19) and (20), the upper critical field of a rhombohedral exotic superconductor passes through four local maxima when rotated through 360° in the plane in question. Accordingly, curve 1 of Fig. 1 has two local maxima in the interval $(-\pi/2, \pi/2)$. According to (22), however, an hexagonal exotic superconductor goes through only two such maxima (as do all other superconductors having one complex order parameter), and only one maximum is present in the interval $(-\pi/2, \pi/2)$. The angular dependence $H_{c2}(\alpha)$ described by Eq. (22) with the coefficients $P_{1,2,3}$ in (21) is also shown in Fig. 1 (curve 2). It is clear therefore that the presence, in a rhombohedral superconductor, of definite additional nonmonotonicities (and accordingly of additional extrema) in the angular dependence of the upper critical field in the plane in question would be incontrovertible evidence of exotic pairing in this superconductor (in accordance with Ref. 18).

There are, however, no such additional nonmonotonicities in an hexagonal superconductor no matter what the type of pairing.[3)] The cause of this disagreement with the result of Ref. 19 is an error in the calculations of this reference. The method proposed there to analyze the anisotropy of $H_{c2}(\alpha)$ is based on an exact solution obtained in Refs. 19 and 27 for the case $\alpha=0$, and is in principle fully valid. But the perturbation-theory analysis of Eq. (12) of Ref. 19 (which is in essence a secular eigenvalue equation) leads to an erroneous solution (14) for $\Lambda_{\min}(\theta)$ (we are using here the notation and the equation numbers of Ref. 19).

The orientation dependence (19), (20) of the upper critical field in an exotic rhombohedral superconductor also has a distinct asymmetry $\delta_1(\alpha)\neq 0$, which can be specified in the form

$$\delta_1(\alpha)=[H_{c2}(\alpha)-H_{c2}(-\alpha)]/H_{c2}(\alpha). \qquad (23)$$

A plot of $\delta_1(\alpha)$ for the values (21) of the coefficients $P_j$ is shown in Fig. 2. Reversal of the sign of the angle $\alpha$ corresponds to reflection of the field direction in the $yz$ plane. A similar asymmetry of $H_{c2}(\alpha)$ obtains also when the field is reflected in the $xy$ plane, i.e., when the angle $\alpha$ in (19) and (20) is replaced by $(\pi-\alpha)$.

### 3. CHARACTERISTIC ASYMMETRY OF FLUCTUATION DIAMAGNETISM IN AN EXOTIC RHOMBOHEDRAL SUPERCONDUCTOR

We shall analyze the fluctuation diamagnetism using the results (9)–(13) including first- and second-order corrections in the framework of ordinary perturbation theory for degenerate levels. Since the transformations (5) change the effective volume $V'$ and the magnetic field $B'$ into

$$V'=\frac{V}{P_1P_2^{1/2}},\quad B'=BP_1^{1/2}D(\alpha), \qquad (24)$$

we obtain for the fluctuation contribution $\Delta F$ to the free energy of the system near $T_c$ at $T>T_c$

$$\Delta F=-\frac{TV2|e|BD(\alpha)}{(2\pi)^2c\,P_1^{1/2}P_2^{1/2}}\sum_{n=0}^{\infty}\left\{\int_{-\infty}^{\infty}dp_{x'}\ln\frac{\pi T}{E_{n,1}(p_{x'},\alpha)+a}+\int_{-\infty}^{\infty}dp_{x'}\ln\frac{\pi T}{E_{n,2}(p_{x'},\alpha)+a}\right\}. \qquad (25)$$

The characteristic anisotropy of the fluctuation diamagnetism in rhombohedral exotic superconductors is manifest only in the nonlinear dependence of the magnetic moment on the applied field (similar to the previously considered[13] case of tetragonal superconductors). This leads to relative smallness of this effect in weak fields $B\ll H_{c2}(\tilde{T})$, where $\tilde{T}=2T_c-T$. The employed Ginzburg–Landau theory, however, can explain the fluctuation diamagnetism near $T_c$ also in strong enough fields $B\gtrsim H_{c2}(\tilde{T})$ [and even under the condition $B\gg H_{c2}(\tilde{T})$], provided the relation $B\ll H_{c2}(0)$ is satisfied (under real conditions, $H_{c2}(0)$ in the last inequality can be preceded by a small numerical factor[28]). In the $Cu_{1.8}Mo_6S_8$ Chevrel phase we have $T_c = 10.5$ K, $H_{c2}(0) = 15$ T, and $(dH_{c2}/dT)_{T_c} = 1.9$ T/K (Ref. 29), so that the condition $H_{c2}(\widetilde{T}) \lesssim B \ll H_{c2}(0)$ is satisfied in a sufficiently wide range of fields and temperatures near $T_c$. We shall therefore consider next the case of strong fields $B > H_{c2}(\widetilde{T})$, where the nonlinear effects are large.

It is convenient to change over in the first and second integrals of (25) to new integration variables $q_{1,2} = g_{1,2}^{(1/2)}(\alpha)p_{x'}$, where the functions $g_{1,2}(\alpha)$ are defined in Eqs. (9)–(13). Next, following Prange's method,[30] we write the resultant expression for the free energy in the form

$$\Delta F = -\frac{TV}{2\pi}\frac{1}{2P_1P_2^{1/2}Q'^{1/2}}\sum_{j=1,2}\int_0^\infty dt \int_{-\infty}^{\infty}\frac{dq_j}{2\pi} \times \ln\left(\frac{\pi T}{t+q_j^2+a}\right)\left[G'\left(\frac{t}{b_j}\right)+1\right], \qquad (26)$$

where

$$b_{1,2}(\alpha) = \frac{4|e|B}{c}P_1^{1/2}D(\alpha)f_{1,2}(\alpha), \quad G'(x) = dG(x)/dx, \qquad (27)$$

while the function $G(x)$ is equal to $(-x)$ in the interval $(-1/2, 1/2)$ and $G(x+1) = G(x)$.

Note that in (26) the entire dependence on the magnetic field and on its orientation in the $xz$ plane is contained only in the quantities $b_{1,2}$ in the argument of the function $G(x)$. Taking this into account, we arrive at the following expression for the components of the induced magnetic moment

$$M_{x,z} = -\frac{2|e|^{1/2}TB^{1/2}D^{1/2}(\alpha)}{\pi Q'^{1/2}P_1^{1/4}P_2^{1/2}}\left\{f_1^{1/2}(\alpha)\Phi(\gamma_1)\frac{\partial}{\partial B_{x,z}}[BD(\alpha)f_1(\alpha)] + f_2^{1/2}(\alpha)\Phi(\gamma_2)\frac{\partial}{\partial B_{x,z}}[BD(\alpha)f_2(\alpha)]\right\}. \qquad (28)$$

Here

$$\gamma_{1,2}(B,\alpha) = \frac{\widetilde{B}P_1^{1/2}}{Bf_{1,2}(\alpha)D(\alpha)}, \quad \widetilde{B} = \frac{ac}{4|e|P_1} = \frac{1}{2}H_{c2}^{(0)}\ (\alpha=0), \qquad (29)$$

and $H_{c2}^{(0)}(\alpha = 0)$ is the upper critical field oriented along the $z$ axis in the zeroth perturbation-theory approximation at the temperature $\widetilde{T} = 2T_c - T$. The function $\Phi(x)$ is defined as

$$\Phi(x) = \frac{1}{8(x+1/2)^{1/2}} - \frac{1}{32}\sum_{n=1}^{\infty}\zeta_n^3(x)\left(1+\frac{x}{d_n(x)}\right), \qquad (30)$$

where

$$d_n(x) = [(n+x)^2 - 1/4]^{1/2}, \quad \zeta_n(x) = [1/2(n+x) + 1/2 d_n(x)]^{-1/2}. \qquad (31)$$

By analogy with (23), let us consider the asymmetry of the induced magnetic moment[4])

$$\delta(\alpha) = [M(\alpha) - M(-\alpha)]/M(\alpha), \qquad (32)$$

where $M = (M_x^2 + M_z^2)^{1/2}$. A plot of $\delta(\alpha)$ is shown in Fig. 3, for the values (21) of the coefficients $P_j$ and for different values of the parameter $\beta = B/\widetilde{B}$, i.e., of the magnetic field. The asymmetry is a maximum in the limit $B \gg \widetilde{B} \to \infty$, where the diamagnetic response is nonlinear.

The analytical solution for $\delta(\alpha)$ in general case is quite

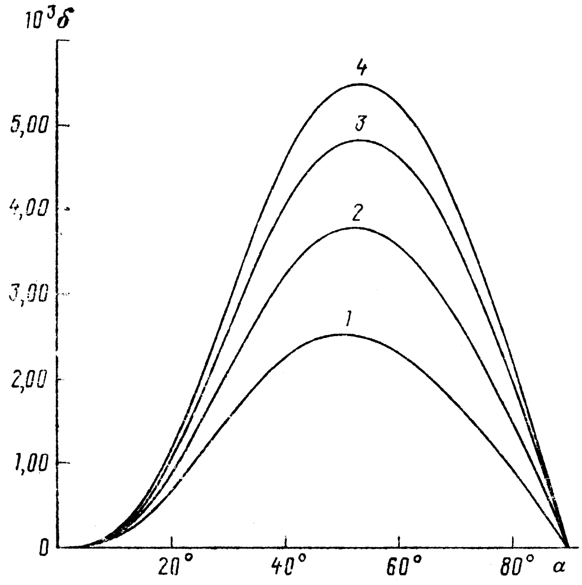


FIG. 3. Asymmetry $\delta(\alpha)$ of induced magnetic moment ($10^{-3}$ scale). Curves 1–4 correspond to $\beta = 1, 2, 4$, and 10, respectively ($\beta = B/\widetilde{B}$).

cumbersome; but it simplifies in the $\beta = (B/\widetilde{B}) \to \infty$ limit, when it takes the following form:

$$\delta_\infty(\alpha) = -P_3P_4P_2\sin^3\alpha\cos\alpha \times \frac{3P_1\cos^2\alpha(P_2/P_1 - 1/2) + P_2\sin^2\alpha(P_2/2P_1 + 1)}{2(P_1\cos^2\alpha + P_2\sin^2\alpha)^2(P_1^2\cos^2\alpha + P_2^2\sin^2\alpha)}. \qquad (33)$$

The plot of $\delta(\alpha)$ shown in Fig. 3 for $\beta = 10$ is quite close to $\delta_\infty(\alpha)$ described by (33) with the coefficients (21).

It follows from (33) that $\delta_\infty(\alpha)$ is small because $(P_3P_4/P_{1,2}^2)$ is small. According to (2) and (3) its value could generally speaking be several times ten percent. For the specific values (21) of the coefficients $P_j$, however, we have $(P_3P_4/P_1^2) \simeq 0.03$. As a result, as seen from Fig. 3, the asymmetry in the considered actual case is small, $\simeq 0.5\%$ of the total induced magnetic moment. It seems experimentally feasible, nonetheless, to use measurements of $\delta(\alpha)$ in the field region $B > 2\widetilde{B}$ to study the type of pairing in $Cu_{1.8}Mo_6S_8$.

Since we have used in this section standard perturbation theory for degenerate level, one might question whether the present results [see (33) and Fig. 3] are valid in the vicinities of the angles $\alpha_{1,2}$, where level crossing takes place in first-order perturbation theory [see (7) and (8)]. Recall that in Sec. 2 the results obtained by standard perturbation theory for the angular dependence of the upper critical field and for degenerate levels had to be modified precisely for the purpose of describing correctly the behavior of $H_{c2}(\alpha)$ near the angles $\alpha_{1,2}$. Incidentally, for the specific values (21) of the coefficients $P_j$, when $\alpha_1 = 0°$ and $\alpha_2 \approx 73°$, these vicinities turn out to be quite narrow, as follows from Fig. 1. Moreover, it is evident from Fig. 3 that the angle interval of greatest interest for the asymmetry of the fluctuation diamagnetism in the case (21) is approximately from 40° to 60°–65°, which does not contain the immediate vicinity of the angle $\alpha_2 \simeq 73°$ (let alone the vinicity of $\alpha_1 = 0°$).

It should nevertheless be noted that in the problem of fluctuation diamagnetism (in contrast to the problem of the upper critical field) it is actually correct to use standard second-order perturbation theory for degenerate levels at arbitrary field orientations in the considered plane, and particularly in the vicinities of the angles $\alpha_{1,2}$. Expressions (9) and (10) are actually incorrect when taken separately for the levels $E_{n,1}(p_{x'},\alpha)$ and $E_{n,2}(p_{x'},\alpha)$ if small second-order terms are taken into account near the angles $\alpha_{1,2}$. It can be shown that the sum $E_{n,1}(p_{x'},\alpha) + E_{n,2}(p_{x'},\alpha)$ agrees with the exact expression in which account is taken of the lifting of the level crossing in second-order perturbation theory. We write next the expressions for Eqs. (9) and (10) in the form

$$E_{n,1}(p_{x'},\alpha) = \widetilde{E}_{n,1}(p_{x'},\alpha) + \Delta E_{n,1}(p_{x'},\alpha),$$

$$E_{n,2}(p_{x'},\alpha) = \widetilde{E}_{n,2}(p_{x'},\alpha) + \Delta E_{n,2}(p_{x'},\alpha).$$

Here $\widetilde{E}_{n,1}$ and $\widetilde{E}_{n,2}$ are the correct values of the energy levels in second-order perturbation theory, while $\Delta E_{n,1}$ and $\Delta E_{n,2}$ are the deviations from these correct values, which are of second order of smallness. According to the foregoing, $\Delta E_{n,1} + \Delta E_{n,2} = 0$. On the other hand, expanding (25) in powers of $\Delta E_{n,1}$ and $\Delta E_{n,2}$ and retaining only the first correction (which of second order of smallness in the parameters $P_3$ and $P_4$), we obtain in the equation for the correction the very sum $\Delta E_{n,1} + \Delta E_{n,2}$, meaning zero. Therefore, in second-order perturbation, allowance for the lifting of the level crossing does not change the results of the present section for the fluctuation diamagnetism.

[1)] Under the additional assumption, already made in (1), of approximate electron–hole symmetry at the Fermi surface.

[2)] In view of the symmetry of $H_{c2}(\alpha)$ with respect to the inversion operation corresponding to $\alpha \to \alpha + \pi$, it suffices to consider the variation of the angle $\alpha$ in the interval $(-\pi/2, \pi/2)$.

[3)] An angle dependence (22) leads only to an insignificant stretch in a narrow interval of $[\alpha \leqslant (|P_3|/P_2)^{1/2}]$ angles of $H_{c2}/(\alpha)$ ellipse described in eq. 14. We do not consider here the influence of antiferromagnetic ordering on the anisotropic properties of the superconducting state. It is known that this influence can lead to important consequences for $UPt_3$ and to certain other superconductors with heavy fermions.[21–26]

[4)] Just as in the problem with the upper critical field, it would be possible to consider also the $M(\alpha) - M(\pi - \alpha)$ asymmetry.


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Translated by J. G. Adashko