


## Type-II character and anisotropic superconductivity in natural superconducting covellite

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# Type-II character and anisotropic superconductivity in natural superconducting covellite

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We report a comprehensive investigation of the superconducting properties of the mineral superconductor covellite (CuS) using high-quality single crystals. First, we establish that CuS is an intrinsic type-II superconductor, correcting its long-standing classification as type-I. Second, a complete set of anisotropic superconducting parameters is determined, including the critical fields, penetration depth and coherence length, which yield a Ginzburg–Landau parameter $\kappa \sim 1.5$ and a moderate anisotropy of $\gamma \sim 2$. Our results indicate that this type-II superconductivity can be well-described by a conventional, weak-coupling, single-band s-wave pairing mechanism. This work fills a long-standing gap in the understanding of this archetypal superconductor.

**Keywords:** type-II superconductivity, critical parameters, anisotropy, covellite

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## 1. Introduction

The interplay between structural motifs and electronic properties is crucial for understanding and discovering novel superconductors. In cuprate superconductors, for instance, the quasi-two-dimensional $CuO_2$ planes are widely recognized as the essential structural element hosting high-temperature superconductivity.[1,2] Covellite (CuS), another system based on copper-anion layers, provides an interesting and historically significant counter case. As a rare natural mineral in which superconductivity was discovered,[3–6] CuS is a material with a simple chemical formula but a complex crystal structure, and it has found numerous applications in fields such as batteries,[7,8] plasmonics[9,10] and photocatalysis.[11,12] It possesses a hexagonal structure at room temperature and undergoes a structural phase transition around 55 K to an orthorhombic phase,[13] the origin of which is still unclear,[14,15] but has been tentatively linked to a charge density wave instability.[16] Its electronic structure is known to be complex and quasi-two-dimensional as shown by calculations[14,17–20] and angle-resolved photoemission spectroscopy (ARPES) measurements.[21]

Despite these complexities, the superconductivity in CuS, discovered decades ago, has long been considered to be of the simple type-I classification.[3,6] The emergence of type-I superconductivity is rare in materials with such a complex electronic structure, as it is typically observed in simple elemental metals. Strikingly, for such a historically important system, a systematic investigation of its fundamental superconducting parameters and their anisotropy, performed on high-quality single crystals, has been conspicuously absent from the literature.

In this work, we address this long-standing gap by performing a comprehensive study of the superconducting properties of high-quality CuS single crystals. Our results unambiguously establish CuS as a type-II superconductor. Through detailed measurements and analysis of its upper and lower critical fields, we have determined its key superconducting parameters, including the penetration depth ($\lambda$), coherence length ($\xi$), and Ginzburg–Landau parameter ($\kappa$). The behavior of these parameters points towards a conventional s-wave pairing mechanism with quasitwo-dimensional features, which is consistent with its electronic structure. Our findings provide a modern, self-consistent physical picture of superconductivity in CuS, filling a crucial void in the understanding of this archetypal mineral superconductor and offering a solid base for future research on covellite.

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## 2. Methods

CuS single crystals were synthesized via a high-temperature solution method.[5] High-purity copper (Cu, Alfa Aesar, 99.9%) and sulfur powder (S, Aladdin, 99.999%) were thoroughly mixed and pressed into pellets in an argon-filled glove box, then sealed in a quartz tube under vacuum. The sealed tube was heated under appropriate conditions to ensure the complete formation of CuS precursors, which were subsequently ground into fine powders and mixed with flux. The mixture was then resealed in a fresh quartz ampoule under vacuum conditions. The ampoule was placed in a two-zone horizontal furnace and maintained at a temperature gradient of 2 K/cm for over two weeks. Finally, dark-blue hexagonal-plate-shaped single crystals with millimeter size were obtained through ultrasonic cleaning in deionized water.

The x-ray diffraction (XRD) data were collected at room temperature on a diffractometer (Rigaku SmartLab, 9 kW) equipped with two Ge (220) monochromators. Magnetization measurements (down to 400 mK) were conducted using an MPMS-3 SQUID magnetometer equipped with a He-3 option. The electrical transport data were obtained using a Lakeshore Model 372 AC resistance bridge in a dilution refrigerator (down to 300 mK).

## 3. Results and discussion

The representative XRD pattern of the CuS single crystal, shown in Fig. 1(a), confirms the single preferred (00l) orientation. The lattice parameter $c$ is calculated to be 16.36 Å, slightly larger than previous reported values of 16.31 Å[5] and 16.34 Å.[13]

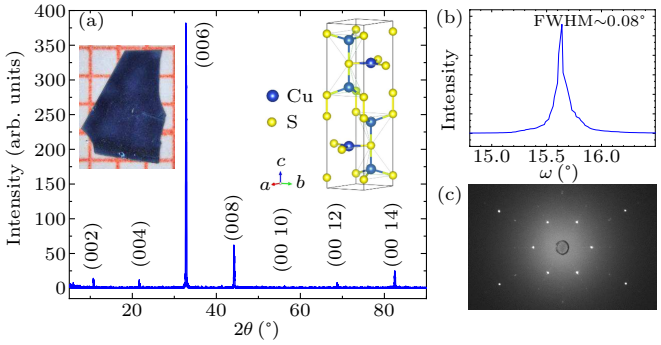



**Fig. 1.** Structural characterization of the CuS single crystal. (a) Single-crystal XRD pattern, with peaks indexed to the hexagonal structure of covellite. The inset shows the crystal lattice structure. (b) X-ray rocking curve of the (006) reflection. The FWHM of 0.08° indicates high crystalline quality. (c) Laue diffraction of CuS.

The full width at half maximum (FWHM) of the x-ray rocking curve for the (006) reflection of the CuS sample was measured to be 0.08° (Fig. 1(b)). This small value indicates a high degree of crystalline perfection, characterized by a narrow orientational distribution of mosaic blocks and a low dislocation density. The high quality of the single crystal is also identified by Laue diffraction pattern, as shown in Fig. 1(c). The observed sharp and well-defined diffraction spots are perfectly indexed to the space group $P6_3/mmc$.

The superconducting properties of the CuS single crystal were characterized by electrical resistivity and magnetic susceptibility measurements. The high quality of the sample is evidenced by a residual-resistivity ratio (RRR) of 65 (inset of Fig. 2(a)), which indicates high chemical purity and low defect density. The onset and zero-resistance superconducting transition temperatures were determined to be $T_c^{onset} \approx 1.2$ K and $T_c^{zero} \approx 1.0$ K, respectively. We note that the $T_c$ of our sample is slightly lower than the values of up to 1.6 K reported.[6,22,23] We speculate that this sensitivity of $T_c$ may be related to subtle variations in stoichiometry, such as the Cu:S ratio. A systematic study of this relationship will be the subject of future work. Notably, the magnetization measurements (Fig. 2(b)) exhibit a clear bifurcation between the zero-field-cooled (ZFC) and field-cooled (FC) curves below $T_c$. This behavior is a hallmark of magnetic flux pinning in a type-II superconductor.[24] Although a similar ZFC–FC splitting can arise from flux trapping in defective type-I superconductors, the demonstrated high crystalline quality of our sample and the shape of the FC curve suggests that this is an intrinsic type-II property, contrary to some earlier reports suggesting it to be type-I.[3,6]

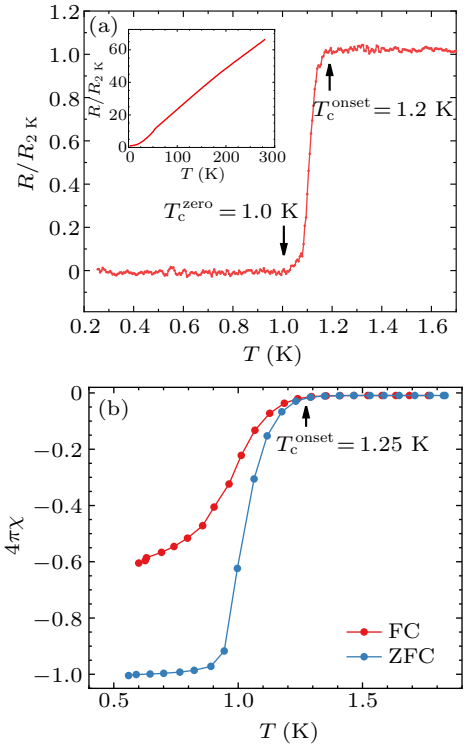



**Fig. 2.** Basic superconducting properties of CuS. (a) Temperature dependence of the electrical resistance showing the superconducting transition. The onset ($T_c^{onset}$) and zero-resistance ($T_c^{zero}$) temperatures are approximately 1.2 K and 1.0 K, respectively. The inset displays the resistance over a wide temperature range, yielding a RRR of 65. (b) Temperature dependence of the DC magnetic susceptibility measured in the ZFC and FC protocols under a small magnetic field, confirming bulk superconductivity and showing a clear bifurcation characteristic of a type-II superconductor.

To systematically investigate the anisotropic superconductivity of CuS, we measured magnetoresistance ($R$–$H$) and

magnetization ($M$–$H$) at various temperatures with the magnetic field oriented in-plane ($\mu_0 H \parallel ab$) and out-of-plane ($\mu_0 H \parallel c$), as shown in Fig. 3. From the transport data, the superconducting transitions are sharp and the $R$–$H$ curves remain largely parallel, indicating high sample homogeneity. We defined the upper critical field $\mu_0 H_{c2}$ using the 50% criterion of the normal-state resistance $R_n$, and constructed the temperature-field phase diagram in Fig. 3(c). The data exhibit a clear anisotropy and are well-described by the single-band Ginzburg–Landau model . The fits yield zero-temperature upper critical fields of $\mu_0 H_{c2}^{ab} \approx 18$ mT and $\mu_0 H_{c2}^{c} \approx 9$ mT. Thus the coherence lengths are found to be $\xi_{ab} = 191$ nm and $\xi_c = 96$ nm, respectively. Using the Drude model, the mean free path of CuS was estimated to be $10^3$ nm from the Hall coefficient[15] and resistivity. Since this value is significantly larger than the obtained coherence length, our sample is in the clean limit. The resulting superconducting anisotropy parameter is thus $\gamma = \xi_{ab}/\xi_c \sim 2$. This anisotropy quantitatively matches the estimation from normal-state properties, where a reported resistivity anisotropy of $\rho_c/\rho_{ab} \sim 6$[25] implies a Fermi velocity anisotropy of $v_F^{ab}/v_F^{c} \sim 2.45$. Since $\xi_0 = \hbar v_F/\pi\Delta_0$, $\gamma = \xi_{ab}/\xi_c \sim v_F^{ab}/v_F^{c}$. This self-consistency strongly suggests that the same electronic band that governs the normal-state transport is also responsible for the superconducting pairing. Furthermore, this quasi-2D superconductivity is also consistant with the reported calculation works which suggests a quasi-2D electronic structure.[14,17–21]

The anisotropic nature of CuS is further corroborated by the magnetization measurements shown in Figs. 3(d) and 3(e). For both magnetic field orientations, the magnetization is initially linear and diamagnetic, then reaches a peak before gradually decreasing, which is the characteristic behavior of a type-II superconductor evolving from the Meissner state to a state with significant flux pinning. After correcting for the demagnetization factor, the lower critical field, the values of $\mu_0 H_{c1}$ were extracted using a 5% deviation criterion from the initial linear $M$–$H$ response. The resulting $\mu_0 H_{c1}(T)$ data, plotted in Fig. 3(f), reveal an anisotropy of $\mu_0 H_{c1}^{c}/\mu_0 H_{c1}^{ab} \sim 2$, which is inverse to that of $\mu_0 H_{c2}$, in agreement with the anisotropic G-L theory.

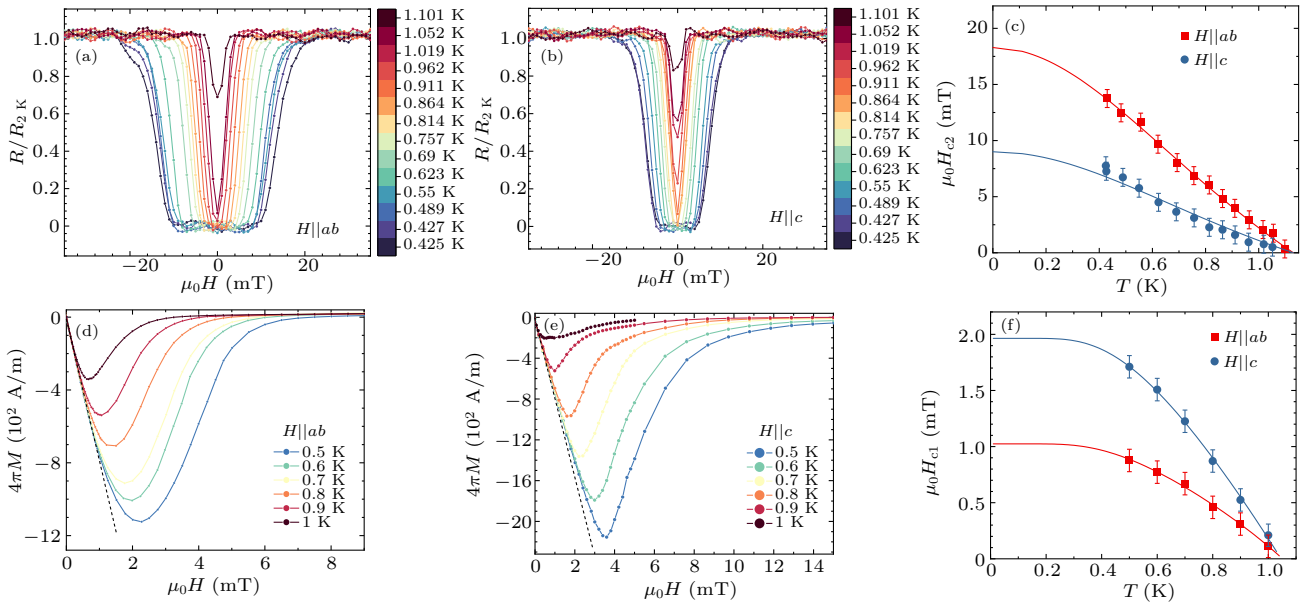



**Fig. 3.** Anisotropic $\mu_0 H_{c2}$ and $\mu_0 H_{c1}$ of CuS. (a), (b) Magnetoresistance $R(H)$ curves at various temperatures for magnetic fields oriented out-of-plane ($H \parallel c$) and in-plane ($H \parallel ab$), respectively. (c) The upper critical field $\mu_0 H_{c2}$ as a function of temperature for both field directions. The solid lines are linear fits based on the Ginzburg–Landau model. (d), (e) Isothermal magnetization hysteresis loops $M(H)$ at a low temperature for $H \parallel c$ and $H \parallel ab$, respectively, after demagnetization factor correction. $\mu_0 H_{c1}$ is identified as the field where the $M$–$H$ curve first deviates from the initial linear fit by a 5% criterion. (f) The lower critical field $\mu_0 H_{c1}$ as a function of temperature. The solid lines are fits to a single-band s-wave model, which describes the temperature dependence of the superfluid density.

Since $\mu_0 H_{c1}$ is proportional to the superfluid density ($\rho_s \propto \lambda^{-2}$), we fitted the $\mu_0 H_{c1}(T)$ data to model the temperature dependence of $\rho_s$ by a semi-classical approach.[26] As shown by the solid lines in Fig. 3(f), the data are well-described by a simple, single-band, weak-coupling s-wave model. Although we cannot definitively exclude more complex pairing symmetries without measurement at much lower temperatures (typically $0.1T_c$), all the analyses consistently point towards a conventional s-wave pairing mechanism. The fit yields a normalized gap of $\Delta(0)/k_B T_c \approx 1.8$, corresponding to a gap size of $\Delta(0) \approx 0.17$ meV, which is in close agreement with the BCS value. From this analysis, we obtained the zero-temperature lower critical fields $\mu_0 H_{c1}^{ab}(0) = 1$ mT and $\mu_0 H_{c1}^{c}(0) = 2$ mT. The GL parameters $\kappa_{ab}$ and $\kappa_c$ are obtained by numerically solving the relation $H_{c1}/H_{c2} = (\ln\kappa + 0.5)/2\kappa^2$ for the respective field orientations. And the penetration depths are calculated from the GL definitions: $\lambda_{ab}$ is found using $\kappa_c$ via $\lambda_{ab} = \kappa_c \xi_{ab}$, and $\lambda_c$ is determined using $\kappa_{ab}$ from the relation $\lambda_c = \left(\kappa_{ab}^2 \xi_{ab} \xi_c\right)/\lambda_{ab}$, which is derived from the definition $\kappa_{ab} = \sqrt{\lambda_{ab}\lambda_c/(\xi_{ab}\xi_c)}$. The magnetic penetration depths are

estimated to be $\lambda_{ab}(0) \approx 290$ nm and $\lambda_c(0) \approx 1252$ nm, and the Ginzburg–Landau parameter for $\mu_0 H \parallel c$ and $\mu_0 H \parallel ab$ was found to be $\kappa_c \approx 1.5$ and $\kappa_{ab} \approx 4.2$, which are both well above the type-II superconductivity criterion of $1/\sqrt{2}$, thus confirming the type-II nature of CuS.

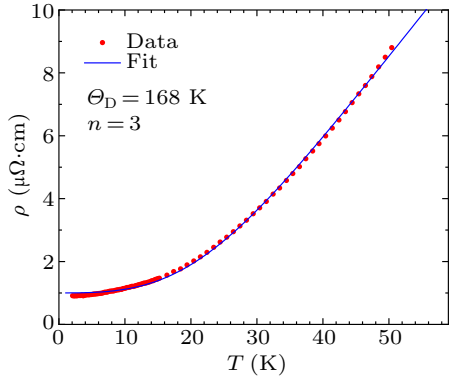



**Fig. 4.** Normal-state resistivity analysis of CuS. Temperature dependence of the normal-state resistance below the structural transition at 55 K. The solid line represents a fit to the Bloch–Grüneisen formula, which yields an exponent $n \approx 3$ and a Debye temperature of $\Theta_D = 168$ K.

Conventional superconductivity, such as that observed in CuS, is typically mediated by electron–phonon coupling (EPC). To gain insight into the EPC strength and scattering mechanisms in our system, we analyzed the low-temperature normal-state resistivity by the Bloch–Grüneisen (B-G) model, as formulized by Wilson's theory:[27,28]

$$\rho(T) = C\left(\frac{T}{\theta_D}\right)^n \int_0^{\theta_D/T} \frac{x^n}{(e^x - 1)\left(1 - e^{-x}\right)} dx.$$

The data were fitted exclusively below the structural phase transition at 55 K to ensure that the analysis was performed within a single crystallographic phase. The resistivity data, normalized to the value at 2 K, were used for the fitting, and the resulting behavior is consistent with that reported in the literature.[6] As shown in Fig. 4, the fit yields a power-law exponent of $n \approx 3$. This value deviates from the $n = 5$ exponent expected for simple metals dominated by intra-band electron–phonon scattering. Instead, $n \approx 3$ is typically attributed to dominant inter-band scattering, which is consistent with the complex, multi-band electronic structure of CuS. By setting $n = 3$, the fit provides a Debye temperature of $\Theta_D = 168$ K, a value in excellent agreement with the 184 K obtained from previous specific heat measurements,[29] thus validating our analysis. The prefactor $C$ is a constant related to the electron–phonon coupling strength and it is found to be 84 μΩ·cm·K$^{-3}$, which is comparable to that of similar weak coupling systems.[30] And the electron–phonon coupling strength of this system can be estimated using the McMillan formula,[31] which is approximately 0.51, similarly a characteristic of a weak-coupling superconductor.

## 4. Conclusions

In summary, we have presented a systematic investigation of the superconducting critical parameters and their anisotropy in covellite (CuS), a rare natural mineral superconductor. Our analysis of the superconducting transition and critical fields demonstrates that CuS is a typical type-II superconductor, resolving prior ambiguities concerning a possible type-I classification. The temperature dependence of the upper and lower critical fields can be well-described by a conventional, single-band Ginzburg–Landau theory, indicating an s-wave pairing symmetry. Despite its complex band structure, which gives rise to normal-state transport behavior indicative of inter-band interactions, its superconducting properties remain remarkably simple. Furthermore, the measured superconducting anisotropy is quantitatively consistent with the anisotropy of its electronic structure, revealing a quasi-two-dimensional character. These findings provide a comprehensive picture of the superconductivity in CuS and serve as a valuable case for studying superconductivity in similar systems.

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## References

[1] Hu J 2016 *Sci. Bull.* **61** 561
[2] Keimer B, Kivelson S A, Norman M R, Uchida S and Zaanen J 2015 *Nature* **518** 179
[3] Di Benedetto F, Borgheresi M, Caneschi A, Chastanet G, Cipriani C, Gatteschi D, Pratesi G, Romanelli M and Sessoli R 2006 *European Journal of Mineralogy* **18** 283
[4] Meissner W 1929 *Zeitschrift für Physik* **58** 570
[5] Gonsçalves A, Lopes E, Casaca A, Dias M and Almeida M 2008 *Journal of Crystal Growth* **310** 2742
[6] Casaca A, Lopes E, Gonsçalves A and Almeida M 2011 *J. Phys.: Condens. Matter* **24** 015701
[7] Chung J S and Sohn H J 2002 *Journal of Power Sources* **108** 226
[8] Jiang K, Chen Z and Meng X 2019 *ChemElectroChem* **6** 2825
[9] Wei T, Liu Y, Dong W, Zhang Y, Huang C, Sun Y, Chen X and Dai N 2013 *ACS Appl. Mater. Interfaces* **5** 10473
[10] Xie Y, Carbone L, Nobile C, Grillo V, D'agostino S, Della Sala F, Giannini C, Altamura D, Oelsner C and Kryschi C 2013 *ACS Nano* **7** 7352
[11] Basu M, Sinha A K, Pradhan M, Sarkar S, Negishi Y and Pal T 2010 *Environmental Science & Technology* **44** 6313
[12] Kuchmii S Y, Korzhak A, Raevskaya A and Kryukov A 2001 *Theoretical and Experimental Chemistry* **37** 36
[13] Fjellvag H, Grenvøld F, Stølen S, Andresen A F, Müller-Käfer R and Simon A 1988 *Zeitschrift für Kristallographie-Crystalline Materials* **184** 111
[14] Mazin I 2012 *Phys. Rev. B* **85** 115133
[15] Nozaki H, Shibata K and Ohhashi N 1991 *Journal of Solid State Chemistry* **91** 306

[16] Gainov R, Dooglav A, Pen'kov I, Mukhamedshin I, Mozgova N, Evlampiev I and Bryzgalov I 2009 *Phys. Rev. B* **79** 075115
[17] Arora S, Kabra K, Joshi K, Sharma B and Sharma G 2020 *Physica B* **582** 311142
[18] Soares Jr A L, Dos Santos E C, Morales-García A, Heine T, De Abreu H A and Duarte H A 2016 *2D Mater.* **4** 015041
[19] Morales-García A, Soares Jr A L, Dos Santos E C, De Abreu H A and Duarte H L A 2014 *The Journal of Physical Chemistry A* **118** 5823
[20] Liang W and Whangbo M-H 1993 *Solid State Commun.* **85** 405
[21] Antezak A, Kato T, Rezende-Gonsçalves P, Fortuna F, Rosmus M, Olszowska N, Santander-Syro A F and Frantzeskakis E 2025 *Phys. Rev. B* **112** 115103
[22] Nakajima T, Isino M and Kanda E 1970 *J. Phys. Soc. Jpn.* **28** 369
[23] Buckel W and Hilsch R 1950 *Zeitschrift für Physik* **128** 324
[24] Tinkham M 2004 *Introduction to Superconductivity*
[25] Saito S H, Kishi H, Nié K, Nakamaru H, Wagatsuma F and Shinohara T 1997 *Phys. Rev. B* **55** 14527
[26] Prozorov R and Giannetta R W 2006 *Superconductor Science and Technology* **19** R41
[27] Ziman J 1964 *Principles of the Theory of Solids*
[28] Wilson A H 1938 *Proc. Roy. Soc. Lond. Ser. A Math. Phys. Sci.* **167** 580
[29] Westrum Jr E F, Stølen S and Grønvold F 1987 *The Journal of Chemical Thermodynamics* **19** 1199
[30] Imai Y, Nabeshima F, Yoshinaka T, Miyatani K, Kondo R, Komiya S, Tsukada I and Maeda A 2012 *J. Phys. Soc. Jpn.* **81** 113708
[31] Mcmillan W L 1968 *Phys. Rev.* **167** 331