Some Properties of Superconductors below 1°K. II. Aluminum and Zinc

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Magnetic measurements of the threshold curves of superconducting aluminum and zinc of very high purity have been carried out down to 0.3°K. Calculations have been made therefrom of the entropy differences between the normal and superconducting states and of the specific heats of the electron assemblies in both the normal and superconducting states. The value of the linear term for the normal electronic specific heat for Al was found to be $2.59\times 10^{-4}T$ cal./mole/degree and for Zn $1.36\times 10^{-4}\,T$ cal./mole/degree.

INTRODUCTION

IN continuation of investigations[1] on techniques required for the observation of nuclear paramagnetism the properties of superconducting aluminum and zinc have been studied below 1°K, details of which are reported herewith. A detailed examination has been made of the magnetic properties of these elements in the temperature range 0.3°K to 1°K, since it is considered that these metals will be of value for the establishment of thermal contact switches at very low temperatures.*

Previous work by Daunt and Mendelssohn,[2] on the magnetic properties of superconductors in the liquid helium temperature range, has shown that it is possible therefrom to calculate reliable values for the specific heats of the electron assemblies both in the normal and in the superconducting states. Furthermore such evaluations are free of any obscuring effects of the vibrations of the crystal lattice, as would be present in direct calorimetric observations. The accuracy of our measurements of the magnetic threshold curves of superconducting aluminum and zinc was sufficiently good to enable such evaluations of their specific heats to be carried out by this method for the first time. A comparison of our results with those obtained by other methods disclosed satisfactory agreement and emphasizes the confidence previously established in the reliability of our method.

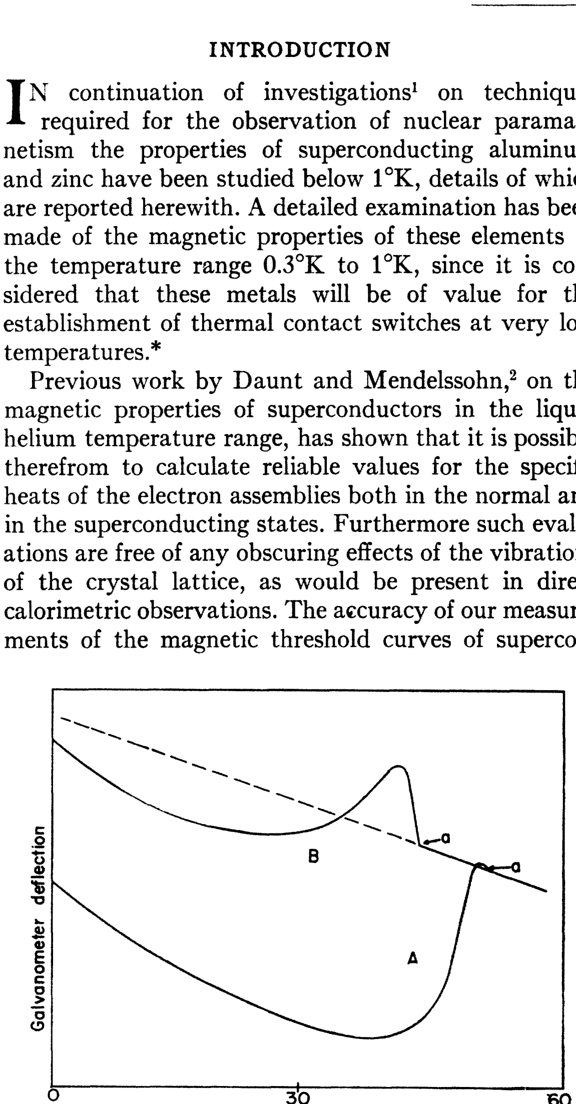

FIG. 1. Change of susceptibility with warm-up time; curve A for zero exterior magnetic field, curve B for a finite applied magnetic field.

EXPERIMENTAL ARRANGEMENTS

Temperatures below 1°K were produced by the magnetic method starting from the temperatures obtained with liquid helium.[3] The paramagnetic salt used was chromium potassium alum, the magnetic field being provided by a large permanent magnet.

To achieve thermal contact between the salt and the superconducting metal under investigation, the metal in the form of small pieces was compressed together with the powdered salt into an ellipsoidal pill under a pressure of 200–300 atmospheres. It was found that good temperature equilibrium was maintained between the salt and the metal by this method down to about 0.2°K, as previously observed by Kurti and Simon[4] and by us,[1] and as is indicated by the agreement between the two sets of measurements reported here for zinc of different average particle size.

The susceptibility of the specimen was measured by the ballistic mutual inductance method,[5] from which measurements both the Curie temperatures and the superconducting transitions could be obtained. The specimen was mounted on a thin-walled glass rod, the lower end of which was fixed to the bottom of a brass vacuum vessel immersed in liquid helium. The mutual inductance used to measure the variation of susceptibility of the specimen was wound around this vacuum vessel and consisted of two secondary coils of 3800 turns each wound in series opposition, and a single layer primary coil of 100 turns per cm. The specimen was mounted coaxially inside one of the secondary coils, the other serving as a compensator. The primary coil produced a measuring field of between 1 and 5 gauss. A solenoidal coil, which could be demounted during the adiabatic demagnetizations, was mounted coaxially

[1] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 715 (1949).
* Detail of experiments carried out on these problems will be published separately.
[2] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **A160**, 127 (1937); Daunt, Horseman, and Mendelssohn, Phil. Mag. **27**, 754 (1939).
[3] Daunt, Heer, and Silvidi, Phys. Rev. **75**, 1113 (1949).
[4] N. Kurti and F. Simon, Proc. Roy. Soc. **A151**, 610 (1935).
[5] N. Kurti and F. Simon, Proc. Roy. Soc. **A149**, 152 (1935); de Haas and Wiersma, Physica **2**, 335 (1935).

TABLE I. Data on the Al and Zn specimens.

No.	Specimen composition	Linear dimensions of metal particles mm	Major axis mm	Minor axis mm	f	Δ
2	Cr alum and Al	1	29	13	0.55	0.008
4	Cr alum and Zn	1–2	38	13	0.63	0.011
5	Cr alum and Zn	0.1–0.5	32	13	0.80	0.013

with the mutual inductance and provided the small fields necessary for the observation of the magnetic transitions of the superconducting metals. All metal joints at liquid helium temperatures were silver soldered to avoid the presence of undesired superconducting material.

It was found that with this arrangement the rate of warming of the specimen at the lowest temperatures was moderately small, thus ensuring good conditions for temperature equilibrium between the salt and the metal. Approximately one hour was required to warm up from 0.3 to 1°K, corresponding to an average heat influx of 8 ergs per second.

In Table I, details of the aluminum and the two zinc specimens are given. The aluminum used in specimen #2 was 30 mesh chips from Coleman and Bell having a purity >99.9 percent. Spectroscopic analysis showed that the amount of other superconducting material present, namely Pb, was probably less than 0.001 percent. The zinc used in specimens #4 and #5 was H-S spectroscopic zinc, Lab. No. 1790B supplied by Johnson, Matthey and Company having a stated purity of 99.999 percent and containing less than 0.0001 percent Pb.

TABLE II. Observed magnetic thresholds for Al and Zn for difference Curie temperatures.

Al (#2)		Zn (#4)		Zn (#5)	
T_s^*(deg)	H_c(gauss)	T_s^*(deg)	H_c(gauss)	T_s^*(deg)	H_c(gauss)
0.734	60.0	0.959	0.0	0.910	0.0
0.688	65.4	0.865	8.8	0.845	13.2
0.636	71.0	0.787	16.4	0.725	22.2
0.600	76.2	0.623	31.6	0.573	37.6
0.526	82.0	0.519	42.0	0.501	42.8
0.454	87.4	0.511	42.2	0.377	53.0
		0.507	42.0		
		0.495	44.2		
		0.447	48.4		
		0.383	52.0		
		0.321	55.0		
		0.283	55.4		

In Table I, f denotes the filling factor, namely the ratio of the distributed density of the powdered salt to the crystalline density and Δ is given by

$$\Delta = cf(4\pi/3 - N),$$

where c is the Curie constant per cc and N the demagnetization factor of the specimen. The listed values of Δ were used in the calculation T_s^*, the extrapolated temperature based on Curie's law for a spherical specimen.[6]

In order to observe the superconducting transitions the specimen was allowed to warm up either in zero magnetic field or in a small d.c. field provided by the external magnetizing coil, susceptibility measurements being made at regular time intervals, a method previously used successfully by Kurti and Simon[4] and by us.[1] Typical curves showing the change of the susceptibility with time are given in Fig. 1, the curve A showing the typical behavior in zero exterior magnetic

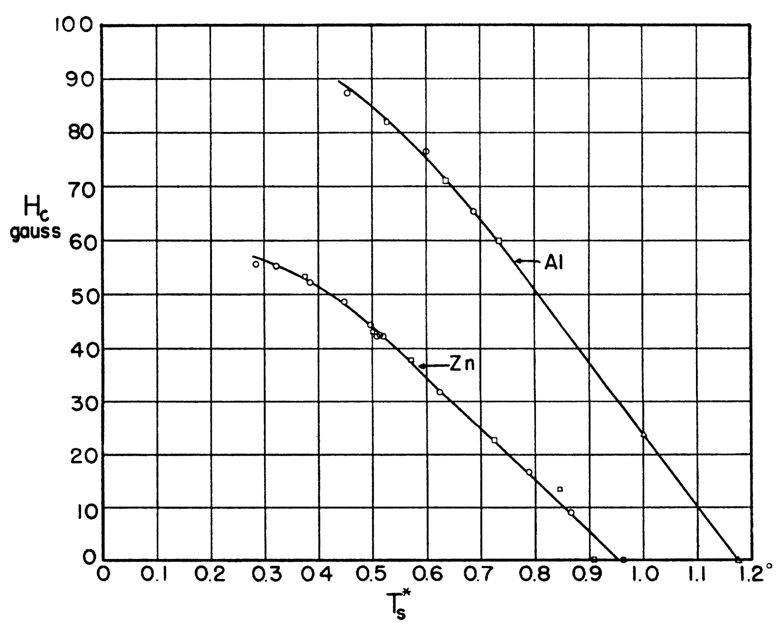

FIG. 2. Observed magnetic threshold for Al and Zn as a function of the Curie temperature T_s^*.

[6] N. Kurti and F. Simon, Phil. Mag. 26, 849 (1938).

TABLE III. Comparison of the values of gamma for Al and Zn obtained by various methods, and the value of the constant A in the equation for the specific heat of superconducting electrons.

	Al	Zn
γ from our experimental ΔS values	2.59×10^{-4} cal./mole/deg.^{2}	1.36×10^{-4} cal./mole/deg.^{2}
γ from Sommerfeld's formula	2.18×10^{-4} cal./mole/deg.^{2} (for $n=3$)	1.80×10^{-4} cal./mole/deg.^{2} (for $n=2$)
γ from calorimetric measurements		
Kok and Keesom*	3.48×10^{-4} cal./mole/deg.^{2}	
Keesom and van den Ende**		1.25×10^{-4} cal./mole/deg.^{2}†
Daunt and Silvidi***		1.50×10^{-4} cal./mole/deg.^{2}
A	5.6×10^{-4} cal./mole/deg.^{4}	4.8×10^{-4} cal./mole/deg.^{4}

* See reference 14.
** See reference 15.
*** See reference 15a.
† This value is obtained from Keesom and van den Ende's measurements by plotting C_V/T against T^2 which yields a straight line the intercept of which on the C/T axis enables the γ-value to be calculated. We are indebted to Mr. A. A. Silvidi for pointing this out to us. This value is somewhat lower than the value given by the interpretation of Burton, Grayson-Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Company, New York, 1940), p. 348, of the same measurements of Keesom and van den Ende.

field and the curve B in a finite applied magnetic field. For both curves a marked kink at the points marked "a" was observed which indicated the disappearance of the last remnants of superconductivity in each specimen at the value of field given by the strength of the applied exterior d.c. field.

For measurements in zero applied magnetic field (curve A in Fig. 1) the specimens showed a susceptibility less than that due to the paramagnetism of the salt on account of the diamagnetism of the superconducting metal, as is shown by the difference between the full curve and the extrapolated dashed curve in Fig. 1. From this diamagnetic component of the total susceptibility it was possible to calculate that for all specimens the full volume of metal became superconducting. The transition from the superconducting state to the normal state was over a broad region owing to the distribution in shape and arrangement of the metal particles in the salt.

For measurements in a finite applied magnetic field (curve B in Fig. 1), the same general features of the warm-up curve were evident with the addition of a marked excess paramagnetism just before the final transition was completed at "a". This excess paramagnetism was due to the large variations possible in the rate of change of susceptibility which can occur in multiply connected superconductors in the intermediate state.

The Curie temperatures corresponding to the transitions at the points "a" could be calculated from the susceptibility calibration curve for the salt specimens made at temperatures above the transition temperatures of the metal concerned.

RESULTS

The observed magnetic thresholds for aluminum and zinc are tabulated in Table II and are shown plotted against the Curie temperatures, T_s^*, in Fig. 2. No significant difference was observed in the results for zinc of two different average particle size. It is estimated that in the temperature range concerned, the differences between the T_s^* values and the absolute temperatures[7] are within the experimental errors which for the magnetic fields are estimated to be ±1 gauss and for T_s^* to be ±0.008 degree for the measurements in finite fields. For the transition in zero field the experimental error in the temperature is greater, being about ±0.025 degree. Other data are given in Table III.

In Fig. 2 the points above 1.0°K for the magnetic threshold curve for aluminum have been taken from Shoenberg's work,[8] the temperatures having been corrected to the 1939 scale proposed by Bleaney and Simon.[9]

The error in the magnetic field depends primarily on estimating the field acting on the small pieces of superconductor imbedded in the salt. The field acting on the interior of a small cavity will be given by

$$H=H_{\text{ext}}+(D-N)\sigma f,$$

where H_{ext} is the exterior applied field, N the demagnetization factor for the entire specimen, D the demagnetization factor for the space occupied by a small superconducting particle, σ the magnetic moment per unit volume and f the filling factor. An accurate evaluation of $(D-N)$ cannot be made since the shapes of the particles were irregular and distributed at random. As long as $(D-N)$ is of the order of unity, errors of the order of 1 percent at 0.5 degree and 2 percent at 0.25 degree may be expected. In the temperature range of our observations therefore, it is assumed that the errors in estimating the magnetic field are within the errors of experimental observation. At lower temperatures the deviations would become large and it would appear that below 0.2 degree, it would be desirable to use particles of regular shape.

DISCUSSION

For aluminum our measurements below 1°K together with those of Shoenberg[8] above 1°K form a satisfactory continuous curve, as shown in Fig. 2.

For zinc the transition temperature of 0.95 degree observed by us lies somewhat higher than the value found by Keesom[10] of 0.81 ± 0.02°K (corrected to 1939 scale).[9] Keesom's measurements, however, were of the electrical resistance of a cold-worked sample and appeared to show a small resistance remaining even at the lowest temperatures.**

[7] See J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937); M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 388 (1937).
[8] D. Shoenberg, Proc. Camb. Phil. Soc. **36**, 84 (1940).
[9] B. Bleaney and F. Simon, Trans. Faraday Soc. **35**, 1205 (1939).
[10] W. H. Keesom, Physica **1**, 123 (1934).
** Some preliminary experiments using Zn, having a purity spectroscopically found to be 99.99 percent which was therefore less pure than the Johnson Matthey zinc of samples #4 and #5 (see Table I), showed transition points in zero magnetic field as low as 0.82 degree. The magnetic measurements made with this

The transition temperature for zinc found by Shoenberg[8] for which the possible observation error was high (±0.05) lies reasonably close to the value given here. Shoenberg's magnetic threshold curve for zinc, however, differs greatly from that given in Fig. 2 due probably to the uncertainty in his measurements which he reported. A comparison of our results with the work on zinc by Lasarew and Esselson[11] is difficult since they based much of their calculations on the results obtained by Shoenberg.

The slopes of the magnetic transition curves for both Al and Zn, being 136 gauss per degree for Al and 98 gauss per degree for Zn at $H=0$, are small, thus placing these superconductors, as would be expected, into the group of "soft" superconductors.[2]

Following the thermodynamic theory of Gorter and Casimir,[12] the difference in entropy between the normal and the superconducting state is given by

$$\Delta S = S_s - S_n = \frac{V}{4\pi} H_c \left(\frac{dH_c}{dT}\right),$$

where V is the atomic volume. The ΔS values calculated from this formula using the magnetic threshold curves of Al and Zn shown in Fig. 2 are plotted against T_s^* in Fig. 3. It is evident that our measurements have been made to temperatures sufficiently low to allow extrapolation towards absolute zero. As has been pointed out previously by Daunt and Mendelssohn[2] for other superconductors, at sufficiently low temperatures ΔS will be proportional to T and can be identified with the total entropy of the electron gas in the normal state. If, according to Sommerfeld,[13] we put the specific heat of the normal electron gas, $C_n = \gamma T$ then

$$\gamma = \left(\frac{d\Delta S}{dT}\right)_{T=0}.$$

The values of γ obtained in this way for Al and Zn are listed in Table III. For comparison with these results, the γ-values calculated according to the simplified Sommerfeld formula[13] neglecting lattice effects are also listed in Table III, together with the γ-values obtained calorimetrically by Kok and Keesom[14] for Al, and by Keesom and van den Ende,[15] and Daunt and Silvidi[15a] for Zn.

The small differences between our results for γ and the values according to the simplified Sommerfeld formula are not surprising in view of the fact that the latter does not take into account the detailed energy spectrum of the metal.[13,16] The agreement between the values obtained from our ΔS values and those obtained calorimetrically is satisfactory in the case of zinc, although some discrepancy exists for the aluminum. The latter may be explained however in view of the fact that the calorimetric values are strongly dependent on the interpretation of the constants for the lattice specific heat, whereas in the values obtained from the ΔS curves the lattice specific heat does not enter in the calculations. These results, together with those previously obtained in a similar manner for other superconductors,[2] give confidence in the reliability of this method of measurement of the specific heat of the normal electrons, and indicate that our threshold curve measurements represent the reversible equilibrium boundary between the normal and the superconducting states.

As previously shown by Kok[17] and by Daunt and Mendelssohn[2] the specific heat of the system of superconducting electrons can also be calculated from the magnetic threshold curves. Such a determination, however, involves a second differentiation of H_c with respect to T, a process which can result in considerable error. On the other hand the calculation can be greatly simplified if it is assumed, as a first approximation, that the threshold curves are parabolic,[17] which leads to T^3 function for the specific heat of the superconducting electrons, given by

$$C_{s.el} = AT^3 = \frac{3VH_0^2}{2\pi T_c^4} \text{ cal./mole/degree},$$

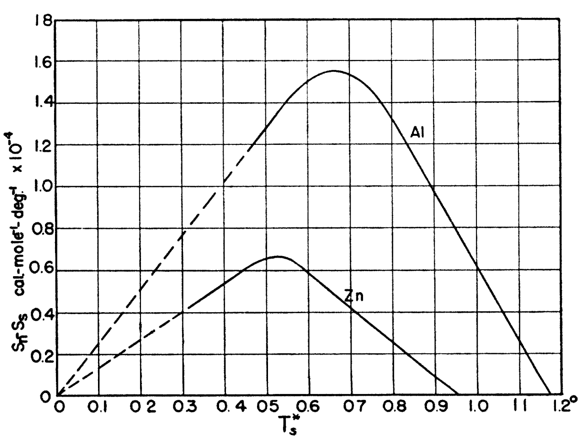

FIG. 3. Calculated values of the difference in entropy ΔS between the normal and the superconducting state plotted as a function of the Curie temperature.

relatively impure zinc have not been used for thermodynamic calculations, as the transitions from the superconducting to the normal state were not reversible.

[11] B. G. Lasarew and B. N. Esselson, J. Phys. U.S.S.R. **15**, 151 (1941).

[12] C. J. Gorter and H. G. B. Casimir, Physica **1**, 305 (1934); Zeits. f. Tech. Physik **15**, 539 (1934).

[13] A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928); Ann. d. Physik **28**, 1 (1937).

[14] J. A. Kok and W. H. Keesom, Physica **4**, 835 (1937).

[15] W. H. Keesom and J. N. van den Ende, Proc. Amst. Akad. Sci. **35**, 143 (1932); Leiden Comm. 219b.

[15a] J. G. Daunt and A. A. Silvidi, to be published shortly.

[16] J. Slater, Phys. Rev. **45**, 794 (1934); N. F. Mott, Proc. Roy. Soc. **A152**, 42 (1936); H. Jones and N. F. Mott, Proc. Roy. Soc. **A162**, 49 (1937); A. Sommerfeld and H. A. Bethe, *Handbuch der Physik* (1933), Vol. 24/2, p. 33.

[17] J. A. Kok, Physica **1**, 1103 (1934).

where V is the atomic volume. The values of A calculated in this way for Zn and Al are given in Table III. The specific heat of the superconducting electrons calculated in this way is 87 times as great as the lattice specific heat for Al (Debye $\theta=419$[14]) and 33 times as great as that for Zn (Debye $\theta=320$[15]). The accuracy of this interpretation of $C_{s.el.}$ is, of course, strongly dependent on the accuracy with which the magnetic threshold curve follows a parabolic law. Our results for Al and Zn as well as those obtained elsewhere[2,18] show that the magnetic threshold curves are not exactly parabolic and consequently it cannot be excluded that for Zn and Al further approximation would lead to some deviation from the T^3 function for $C_{s.el}$.

[18] A. D. Misener, Proc. Roy. Soc. A166, 43 (1938).

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Magnetic Interaction between Neutrons and Electrons*

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The phenomenological interaction operator between neutrons and electrons is usually assumed to be $-\mu\mathbf{s}\cdot\mathbf{B}$. ($\mu\mathbf{s}$ magnetic moment of the neutron, $\mathbf{B}$ magnetic field of the electrons.) Bloch has pointed out that other operators are possible. It is shown that the class of operators considered by Bloch is equivalent with the form $-\mu\mathbf{s}\cdot(\mathbf{H}+4\pi C\mathbf{M})$ where $\mathbf{M}$ is the spin momentum density of the electrons, $\mathbf{H}=\mathbf{B}-4\pi\mathbf{M}$ and C is an indeterminate constant. Diffraction by ferromagnetic crystals and magnetic double refraction are calculated for this interaction. Present experimental evidence excludes the value $C=0$. Experimental methods for measuring C are discussed.

I. THE GENERALIZED INTERACTION OPERATOR

It is commonly assumed that the magnetic interaction between neutrons and electrons is described by the interaction Hamiltonian

$$H_{\text{int}}=-\mu\mathbf{s}\cdot\mathbf{B}, \tag{1}$$

where μ is the neutron's magnetic moment, $\mathbf{s}$ the Pauli spin operator acting on the neutron wave function and $\mathbf{B}$ the magnetic field of all electrons. It was pointed out by Bloch,[1] however, that other, more general forms of the interaction Hamiltonian are possible and that the decision should be left to experiment. The purpose of this paper is to examine the experimentally verifiable consequences of the class of Hamiltonians proposed by Bloch, to interpret the existing experimental evidence in this respect, and to suggest experiments which can give a definite decision on the interaction operator.

The interaction of neutrons with ferromagnetic crystals is most likely to supply the desired information. For the case of thermal neutrons, inelastic scattering is small, and the neutron can be described by a wave equation

$$(\nabla^2+k_0{}^2)\psi-(2m/\hbar^2)[V(\mathbf{r})+\langle H_{\text{int}}\rangle_{\text{Av}}]\psi=0, \tag{2}$$

where $\langle H_{\text{int}}\rangle_{\text{Av}}$ is the interaction operator, averaged over the electron wave functions of the ground state, ψ is the Pauli spinor of the neutron, $k_0{}^2=2mE/\hbar^2$ in the usual notation and $V(\mathbf{r})$ the nuclear "quasi-potential."

The magnetic field of the electrons $\mathbf{B}(\mathbf{r})$ is

$$\mathbf{B}(\mathbf{r})=e\sum_{i=1}^{z}\int\varphi_0{}^*(\mathbf{r}_1\cdots\mathbf{r}_z)\frac{\mathbf{r}-\mathbf{r}_i}{|\mathbf{r}-\mathbf{r}_i|^3}\times\boldsymbol{\alpha}_i\varphi_0(\mathbf{r}_1\cdots\mathbf{r}_z)d\tau_1\cdots d\tau_z. \tag{3}$$

In non-relativistic approximation, and in absence of orbital moments, the expectation value of the current $e\boldsymbol{\alpha}=\mathbf{j}$ is

$$\mathbf{j}=c\nabla\times\mathbf{M},\quad \mathbf{M}=\sum_{i=1}^{z}\left[\int\Phi_0{}^*\boldsymbol{\sigma}_i\Phi_0\prod_{n=1}^{z}{}'\,d\tau_n\right]_{\mathbf{r}_i=\mathbf{r}}, \tag{4}$$

where Φ_0 is the Pauli spinor and $\boldsymbol{\sigma}$ the Pauli moment operator. The symbol $\prod'$ means that the integration is carried out with respect to the space and spin coor-

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[1] F. Bloch, Phys. Rev. 51, 994 (1937).