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Low-Field Magnetic Susceptibility of Gallium at Low Temperatures*

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The low-field static susceptibility of high-purity gallium was found to be strongly field and temperature dependent at low temperature. The change of the magnetic induction induced by a small field change was measured by using a superconducting quantum interference device. The observed susceptibility decreased markedly when the temperature was lowered from 4.2 to 1.5 °K; this corresponds to a susceptibility decrease of 7×10^{-4} cgs. A part of the decrease was recovered with an applied magnetic field less than $\frac{1}{2}$ Oe. The results of this static-susceptibility measurement seem to exclude any of the transport-phenomenon-type interpretations to explain the anomalous magnetoresistance previously observed for gallium. The present result strongly suggests an onset of extremely field-sensitive localized diamagnetic centers at low temperature.

I. INTRODUCTION

Transport properties of pure gallium exhibit anomalous behavior at low temperature. They are extremely sensitive to the magnetic field. Newbower and Neighbor reported a strongly field-sensitive magnetoresistance.[1] Previous to their work, Cochran and Shiffman[2] observed that the rf surface reactance of this metal changes sharply as a function of weak external field at low temperature. Boughton and Yaqub[3] found a similar anomaly in the thermal conductivity. Recently, one of the authors[4] conducted a detailed study on the field and the temperature dependence of the surface resistance of this metal with a marginal-oscillator detector. The work by Newbower and Neighbor is a dc measurement; so is the observation by Boughton and Yaqub. The studies in Refs. 2 and 4 are an rf surface impedance measurement. All of these observations are, however, closely related, and it is believed that one and the same mechanism is responsible for these anomalies. Since the rf measurement is a great deal simpler and more sensitive, most extensive information has been obtained using this method.[4]

Although the details of the rf resistivity measurements will be published in a forthcoming paper, the essential properties of the anomaly are summarized as follows:

(i) This is an essentially frequency-independent phenomenon (from dc to at least 100 MHz).

(ii) The effect is independent of sample size.

(iii) The anomaly is not associated with a bulk phase transformation, as was evidenced by a nuclear-quadrupole-resonance study.[5] This was also supported by a specific-heat measurement.[6]

(iv) A very small amount of gas contamination is responsible for this anomaly. A carefully outgassed sample shows no or very weak anomaly.[4]

(v) There is a definite onset temperature T_c for the anomaly. Below T_c the magnitude of the anomaly increases as the temperature decreases. The value for T_c is dependent on the type of the absorbed gas, but independent of the amount of the gas contamination.

(vi) The field H_m which corresponds to the maximum value of dR/dH, R being the resistivity, is almost independent of temperature T, or H_m tends to decrease with decreasing temperature. Therefore, H_m cannot be associated with a critical field such as a critical field H_c in a superconductor. If T_c is associated with a critical temperature for a certain condensation, and *if* H_m be associated with a dissociation field for the condensation, one would expect that H_m would decrease as T increases because a part of the dissociation energy has been provided as thermal energy for $T > 0$. A typical value of H_m is 0.05 Oe. A similar anomalous behavior has been reported for Bi. The influence of gas impurity was confirmed in Ref. 4. A field-sensitive reactance was reported.[7] It is noted that a mirror-smooth surface of the sample is not necessary in order to observe the present anomaly for Ga and Bi. As will be shown later, the surface of the Ga sample used in this experiment is far from mirror smooth.

A strongly field-sensitive surface reactance has been reported for Sn[8] and for K.[9] These metals, however, seem to require a very smooth strain-free surface in order for the anomaly to be observed.[8,9] We confirmed this for K metal. It is quite possible that the effect observed for K and Sn could be due to a completely different origin, although they are similar in appearance.

A few attempts to interpret the anomaly have been tried.[2,3,7,9] Most of the proposed models were based on particular types of transport phenomena, such as a size effect[2,3,7] or a skipping-orbit effect.[9] Since the structure sensitivity of this phenomenon (iv)[4] had not been known, most of the authors attempted to interpret the anomaly as an unusual transport phenomenon inherent to a high-purity metal itself. Instead, it is most likely that there are some kind of localized condensed centers (iii) below T_c (v) which are associated with trapped gas atoms (iv) and that this condensed state is highly sensitive to the magnetic field. A weak field ($\simeq H_m$) changes the state of the localized centers but it is not sufficient to dissociate the condensed state (vi).

The skipping orbits might be responsible for the K and the Sn anomaly, although more extensive study is required to confirm this model.

A dc susceptibility measurement is very important at this stage in order to understand the nature of the postulated centers. Such a strict static measurement involving no transport properties is more straightforward to interpret, whereas all the previous measurements including the surface reactance measurement[2,8] utilize the transport properties.

The measurement, however, requires an extremely sensitive device, since a small change in the susceptibility produced by the minute amount of gas impurity has to be measured in a very weak magnetic field ($\lesssim H_m$).

II. EXPERIMENTAL

A superconducting quantum interference device[10] (SQUID) seems to be the only device which has sufficient sensitivity to satisfy the present requirement. An essential part of the device is a weakly connected superconducting ring. The magnetic flux and the circular current in the ring vary discontinuously and periodically with external field. The discontinuity takes place when the external flux changes by one flux quantum Φ_0, which is known to be $hc/2e$ ($= 2.07 \times 10^{-7}$ G cm^2).

The block diagram for the present apparatus is shown in Fig. 1. The ring, made of niobium, has the same configuration as described in Ref. 10, except that the hole in the ring is $\frac{1}{4}$ in. in diam. An rf coil is inductively coupled to the ring, and it is tuned with a variable capacitance C to a slightly lower frequency than that of an rf oscillator (28 MHz). The same coil is used to generate a low-frequency triangular-sweep field. A triangular-wave generator provides the necessary current. Persistent current in a niobium coil around the ring, which is not shown in the figure, produces a constant noise-free field when needed. A cryogenic device surrounding the ring is described elsewhere.[10]

An rf oscillator in the figure acts as a constant current source for the ring. The induced signal in the ring is amplified and detected as usual. The detected signal is fed back to the coil after being amplified and offsetted in a dc amplifier. The offset level is adjusted so as to suppress the dc level in the feedback signal. The feedback current cancels part of the applied field.

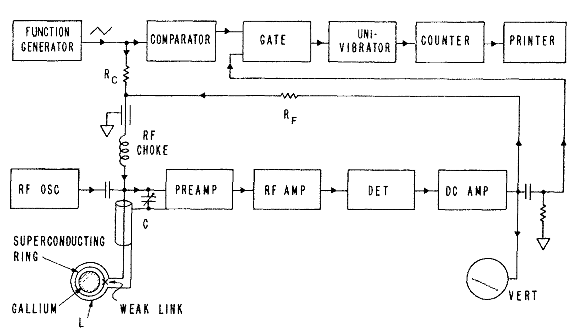

FIG. 1. Block diagram of SQUID.

As the applied field increases, the net field increases until it arrives at the point where the signal without the feedback reaches an extremum value. Then, if the applied field increases further, the feedback current becomes progressively weak; the sign of feedback even becomes positive after the signal crosses zero. As a result, the feedback current suddenly collapses. The feedback current, therefore, exhibits a sawtooth behavior. A typical example of the observed feedback current is shown in Fig. 2.

This new technique has two advantages over the conventional method without the feedback loop as follows:

(i) It is possible to interpolate the value of the applied field between two successive fluxoid jumps. Thereby, one could measure a small fraction of Φ_0, if necessary.

(ii) As is seen in Fig. 2, it provides a simple method of "sign" assignment to the direction of the fluxoid jump. The direction of the signal-level jump at each fluxoid change is either positive or negative depending whether the jump is incremental or decremental.[11]

Because of the noise associated primarily with resistance of the sample in the ring it is unsatisfactory to trigger an electronic counter directly with the sawtooth signal. To avoid such miscounting we differentiated the sawtooth wave to produce a corresponding series of sharp pulses. However, an apparent ringing associated with the edge of the sawtooth wave required the addition of a monostable multivibrator to override the undesirable transient response.

The gate preceding the digital counter is controlled by an analog comparator connected to the magnetic field sweep. The gate is opened for a constant increment in the linear magnetic field, avoiding the transients at the ends of the field sweep. The gate pulse was accurate to 0.02%, but

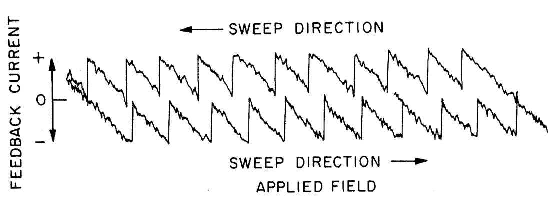

FIG. 2. Sawtooth waves generated by the feedback-type SQUID. The data were recorded on an x-y recorder. The horizontal (x) axis connected to the triangular-wave generator is proportional to the externally applied field. The y axis represents the dc amplifier output. The sweep direction is indicated by the arrows. Each tooth of the observed sawtooth pattern corresponds to the change in the flux by $hc/2e$. The total field sweep is approximately 8 μOe.

the increment in magnetic field may be less precise due to the noise in R_c. The most satisfactory results were obtained using $R_c = 10$ kΩ.

Thermal noise fluctuation generated by the sample loss itself is ultimately the limiting factor in the reproducibility and accuracy of the measurement. These fluctuations produce random magnetic fields which result in a random walk of the phase of the sawtooth wave. Thus the counting frequency has an intrinsic uncertainty which varies as $k_B TR/\Phi_0^2$, where R is the equivalent sample resistance in the uniform decay mode and T is the absolute temperature.[12]

The temperature and the magnetic field dependence of the gallium in the fluxmeter ring were measured as follows: The number of fluxoid jumps for a fixed amount of the external field change was counted and statistically averaged. The averaged count was plotted as a function of temperature and the stationary field provided by the persistent current of the niobium coil.

This count is determined by the sample magnetization, the amount of the external field change, and the cross-sectional area of both the sample and the effective inside area of the fluxmeter ring. The effect of the thermal expansion and the magnetostriction of the sample in the fluxmeter is much smaller than the present experimental error. Another possible effect would be the temperature as well as the field dependence of the superconducting penetration depth, which might change the effective area of the fluxmeter ring. This effect is also negligible in practice.

It is concluded that the T and the H dependence of the sample magnetization is responsible for the observed change in the count as T and H are varied.

Samples were prepared from 99.9999$^+$%-purity metal ingot purchased from the Aluminum Company of America. They were melted in air and casted into cylinders, approximately 5.5 mm in diam and 12 mm long. The mold was made of high-purity graphite. The sample taken out of the mold had a rough surface. The inspection of the surface under a low-power microscope showed that the surface was completely covered with stripes, which were the replica of the drilled inside surface of the mold, and shallow pits. The depth and the size of the pits were of the order of 0.05 and 0.2 mm, respectively. The pitch and the depth of the stripes were approximately 0.05 mm. This surface condition is very unfavorable for the specular reflection of carriers. The rf surface-resistance measurement[4] confirmed that these samples exhibited the anomalous magnetoresistance.

We noticed the possibility[13] that a conventional eddy-current method for resistivity measurement[14] could be improved a great deal, if the decaying field accompanied by the eddy-current decay is measured with the present device instead of a conventional pickup coil. The temperature-dependent resistivity of the samples was indeed observed clearly with this technique. The anomalous field-dependent part of the resistivity was not, however, noticed with the present preliminary setup within the estimated experimental error of 2%.

III. RESULTS AND DISCUSSION

The observed temperature dependence of the fluxoid count is shown in Fig. 3. The count was taken with a fixed field change of approximately 0.49 mOe. The stationary field was kept off during this measurement.

The susceptibility χ of the sample decreases with decreasing temperature. The gallium sample becomes less paramagnetic at lower temperature. The decrease in the susceptibility is estimated as

$$\chi(4.2\ {}^\circ\mathrm{K}) - \chi(1.5\ {}^\circ\mathrm{K}) = 7 \times 10^{-4}\ \mathrm{cgs}.$$

It is noted that the change in the volume susceptibility is two orders of magnitude larger than the Pauli susceptibility.

As a control, the gallium sample was replaced by a copper sample of the same size. No temperature dependence in the fluxoid count was observed. The observed $\chi(T)$ in gallium is much larger than the temperature dependence of the normal susceptibility. This will be interpreted in terms of the proposed model as the onset of diamagnetic localized centers.

The fluxoid count is plotted as a function of external field in Fig. 4. The external field was generated by the persistent current in the superconducting niobium coil. It is noted that the absolute numbers of flux quanta are different from those shown in Fig. 3. This is due to a slight modification of the ring configuration.

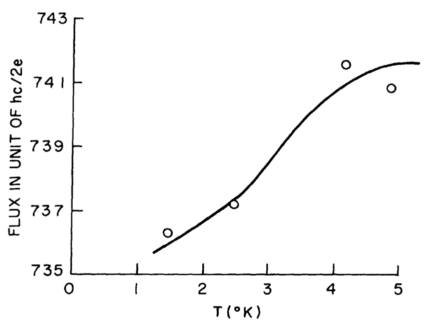

FIG. 3. Magnetic flux count in the Ga sample for a constant amount of field change (approximately 0.49 mOe) plotted as a function of the temperature T. It is shown that the susceptibility of the sample decreases markedly as T is reduced below 5 °K. The experimental error for the two higher and the two lower temperature points are ±1.5 and ±0.5 counts, respectively.

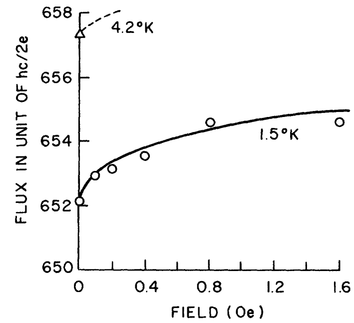

FIG. 4. Field dependence of the flux count. The data were taken at 1.5 °K except for one value at 4.2 °K. The larger experimental error and the smaller field dependence at 4.2 °K prohibited the detailed study of the field dependence at this temperature. The decrease in the susceptibility of the Ga sample when the sample was cooled from 4.2 to 1.5 °K was partially recovered by the weak magnetic field. The experimental error at 1.5 °K is ±0.5 count.

As the field is increased from zero, the susceptibility increases very sharply at first and then it tends to flatten off. The initial rise in χ corresponds to a steep decrease in the resistivity at low field, $H \lesssim H_m$.[4] The temperature was kept at 1.5 °K during this measurement. The signal-to-noise ratio was not sufficient at 4.2 °K to exhibit the detailed field dependence. A single point at 4.2 °K for $H = 0$ is shown in the figure.

The result in this figure shows that the decrease in χ accompanied by cooling from 4.2 to 1.5 °K is partially recovered by the weak magnetic field, but not completely. In the present model this is understood as follows: The localized diamagnetic centers created at T_c increase their diamagnetic condensation as T is reduced. Weak field H ($H_m \lesssim H \lesssim 20H_m$) changes the state of the centers into a less diamagnetic one, but it is not sufficient to dissociate the condensed centers.

The present experimental technique could be improved so that the detailed field dependence could be observed at different temperatures as a function of various types and degree of gas contamination. The present, admittedly crude, measurement has, however, revealed the essential information when combined with the results of the detailed resistivity measurements.[4] As mentioned before the present anomaly is a gas-impurity-induced structure-sensitive effect. The structure sensitivity was noticed in the present measurement also.

The nature of the present measurement can rule out most of the previously proposed interpretations. The matching of the size of cyclotron orbits and the sample dimension causes a field-dependent transport phenomena. A classical-size effect[15] and its modification[16] belong to this group. The present effect is essentially not size dependent. The matching of phonon scattering mean free path $l(T)$ and the sample size or the impurity scattering mean free path l_i could cause some anomalous temperature dependence in resistivity,[17] but it is not sharply field dependent. Besides, it is difficult to explain the well-defined T_c of the present anomaly. T_c is essentially concentration independent. A nonresonant-type skipping-orbit model[18] utilizes the relation between the surface orbit size and the skin depth to interpret the results of the surface-impedance anomaly.[9] The predicted frequency dependence is weak ($\nu^{-1/3}$) but should be observable easily. The surface-resistance anomaly in Ga is frequency independent from dc to at least 100 MHz as stated in the Introduction. The necessity of gas impurity for the present anomaly is not readily understood from this model. The present temperature dependence of χ was measured at the measuring field of only 0.49 mOe. The SQUID head was well shielded against an ambient stray field. The size of the arc of the skipping orbit for $H \simeq 0.5$ mOe is a few cm,[18] which is much larger than the sample diameter and the carrier mean free path. Besides the surface of the present samples hardly permits the carrier to make specular reflection at the surface. Therefore, the surface magnetic state does not exist under these circumstances. Because of the same reason, the surface state associated with a curved surface[19] hardly exists. The large decrease in χ when cooled in zero field can not be explained in terms of the skipping-orbit model.

It would be interesting to study the influence of the surface condition in future, since some part of the observed anomaly in smooth Ga sample could be associated with the surface state. Since the surface-impedance anomaly for K and Sn is reported[8,9] to be extremely sensitive to the surface condition, the surface magnetic state could be responsible for these metals, although they did not find the expected frequency dependence.

One of the nontransport phenomena which has a certain resemblance to the present anomaly is a fluctuating superconductivity. Fluctuating Cooper pairs enhance the diamagnetism and the conductivity just above the superconducting transition temperature.[20–22] The temperature range where the present anomaly is observed is much higher than the critical temperature of normal gallium(1.09 °K). Besides, the structure sensitivity is not easily understood in terms of this model unless one can assume that the clustering gas impurities stabilize the fluctuating Cooper pairs locally.

One of the most celebrated localized condensation phenomena is the Kondo effect,[23] which is believed to be due to the s-d exchange interaction between an impurity d electron and surrounding conduction electrons. The resistivity increases below the Kondo temperature T_K. The localized state is diamagnetic below T_K. The resistivity and the susceptibility are magnetic field dependent, although not as sharply as the present case. The present phenomenon is, however, not related to the paramagnetic impurities. The diamagnetic gases (N_2, H_2, and He) produce the present effect just as effectively as oxygen gas.

If one has to choose one of the "ready-made" phenomena with minimum "alteration" to fit the present effect, the best choice at present seems to be a localized superconductivity, although this particular choice does not exclude or discourage any other theoretician's imaginations. Suppose that the clustered impurity gas atoms trapped at some imperfections such as dislocations create a localized phonon state. It is conceivable that a localized superconducting state could be created via the phonon state. Whatever the interpretation may be, it is known that gallium films evaporated in oxygen atmosphere have a much higher superconducting transition temperature,[24,25] which is approximately in the same temperature range as the present T_c. It is also known that there are a few crystallographic modifications for this metal with the transition temperature in this temperature range.[25]

Although more detailed speculation with more complete literature will be published in a separate paper, the essential argument is presented here. Let us assume the presence of a localized superconductor (LS) at the clustered gas impurities. Assume also that the average diameter of these LS's is of the order of 10 μ.

T_c can be identified as the superconducting temperature of the LS. If this is the case, it is understandable that T_c is independent of gas concentration as long as its average density is low enough and that T_c depends on the type of gas impurity. Probably this LS is a strong superconductor, since the oxygen-grown films are reported to be strong superconductors.[25] Then a McMillan model would be applicable,[26]

$$T_c = \frac{\Theta}{1.45} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) . \quad (1)$$

Here Θ is the Debye temperature of the characteristic phonon frequency. Θ for LS is, in general, different from that for the bulk metal. λ is an electron-phonon coupling constant, which is roughly equivalent to $N(0)V$ in BCS model. μ^* is the coulomb potential. According to McMillan, λ is expressed as

$$\lambda = N(0)\langle \mathcal{J}^2\rangle / M\langle \omega^2 \rangle \quad , \tag{2}$$

where $\langle \mathcal{J}^2 \rangle$ is an average electron matrix element of the change in the crystal potential as one atom is moved. The denominator is the product of the mass of atoms M and the average square of phonon frequencies. Roughly speaking, $M\langle\omega^2\rangle$ is a force constant of the lattice vibration. If λ is the major factor for the enhancement of T_c as is believed to be the case for the oxygen grown film,[25] T_c is predominantly determined by the stiffness $M\langle\omega^2\rangle$, since it is found that $N(0)\langle \mathcal{J}^2\rangle$ is nearly constant for a given series of metals.[26] If this is the case, loosely coupled gas has a small force constant; therefore, large λ and T_c. This is in agreement with the observation that inert-gas-treated samples have the highest T_c.

Let us assume that the penetration depth Λ is larger than the coherent length ξ and that Λ is roughly the same order of magnitude of or larger than the LS size. The flux exclusion due to the LS's is not complete in this case. The degree of the flux exclusion increases with decrease of the temperature. It is expected that the net susceptibility of the sample becomes more diamagnetic at lower temperature. This is in agreement with the tendency shown in Fig. 3. No attempt has been made to compare the observed $\chi\ (T)$ with some of the possible theories, because of the relatively large experimental error at present.

The observed sharp field dependence of the susceptibility can be understood as follows: As the field is increased from zero, the flux would be partially excluded by the LS's at first. When the flux in the LS region reaches Φ_0, a single fluxoid jumps into the LS, if the LS has weak spots.[27] This is most likely the case, because the LS under consideration may not be spatially uniform within the localized region. Since the relation $\Lambda \gg \xi$ has been assumed, a pair potential $\Delta(\vec{r})$ can be nonuniform within the LS region. There may be a few weak spots in $\Delta(\vec{r})$. As the external field is increased further, the flux of the LS increases by Φ_0 every time H becomes equal to $n\Phi_0/S$, until the critical field H_c is reached. Here S is the cross-sectional area for the flux penetration in the LS, and n is the number of flux quanta. The behavior after H_c depends on the type of the superconductor, type I or type II. The speculation about this region, however, is irrelevant to the present problem.

The average susceptibility is, therefore, small near zero field, increases very sharply at $H \simeq \Phi_0/\langle S\rangle\ (\equiv H_M)$ and then increases gradually because the average value of Δ decreases with field. Here $\langle S\rangle$ is the average of S over the LS's. H_M is determined by $\langle S\rangle$ in this model but not by H_c. H_c is of the order of $\Phi_0/(\xi\Lambda)$. H_M for the LS with 10 μ diameter is about 0.2 Oe. As will be shown in a separate paper,

$$H_M \simeq 2H_m \quad . \tag{3}$$

Since H_m (or H_M) is not determined by H_c, H_m can be nearly temperature independent, whereas H_c ought to decrease with increasing temperature. Since the extension of the LS could increase with decreasing temperature, $\langle S\rangle$ tends to increase at low temperature. It is often observed that H_m $(\sim 1/\langle S\rangle)$ decreases at lower temperature.

The structure sensitivity can be understood easily from this model. Several samples prepared under the same condition at the same time show markedly different signal strength, which depends on the subtle nature of the gas-trapping imperfections. The detailed shape of the resistivity curve $R(H)$ is also very structure sensitive. It is not unusual to find a few extra bumps in $R(H)$. This is probably due to the bumps in the distribution of S.

A complicated nonlinearity reported in the literature[2,4,7] with respect to the measuring rf field strength is not surprising if this anomaly is caused by superconductivity.

IV. CONCLUSION

The present results of the static-susceptibility measurement for high-purity gallium strongly suggest that there exist localized diamagnetic centers below T_c, which are associated with a minute amount of gas contamination. The magnitude of flux expulsion due to these centers decreases sharply with an external field of a fraction of one oersted. It is suggested that the present result as well as the related anomalies in resistivity could be explained if one assumes the onset of the localized superconductors, although this contention does not exclude other new models for the present localized condensed state, if any. The transport-phenomenon-type interpretations are, however, not adequate.

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Thermodynamics of the Two-Band Superconductors in the Presence of Nonmagnetic Impurities

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The thermodynamics of the two-band model for the superconducting states of transition metals containing nonmagnetic impurities are developed using the Green's-function technique. The thermodynamic functions of the system are expressed in terms of the densities of state of the s and d electrons. Changes caused by the presence of the impurities of the various functions are obtained. It is shown that in the intraband limit $g_{sd}=0$, the specific heat of transition metals in the superconducting phase is decreased because of the presence of the nonmagnetic impurities.

I. INTRODUCTION

The observed ratios[1] between the jump in the specific heat ΔC and the electronic specific heat of the normal phase at the transition temperature, $\Delta C/\gamma T_c$, for the transition elements are different from those predicted by the BCS theory. Those specific-heat anomalies, along with the absence[2]