PHYSICAL REVIEW VOLUME 102, NUMBER 1 APRIL 1, 1956

Magnetic Susceptibility of Carbons and Polycrystalline Graphites. II*

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(Received September 1, 1955)

The change in magnetic susceptibility of carbons of varying crystallite sizes resulting from a shift of the Fermi level has been studied by investigating residue compounds of carbons with bisulfate ions. The susceptibility decreases monotonically with the concentration of the ions and the relative decrease is progressively larger for larger crystallites. As a result, instead of the plateau in susceptibility in the case of untreated carbons extending from diameters of 150 A to sizes greater than 1500 A, one finds a maximum in susceptibility at about 200 A diameter for carbons with a finite (not too small) ion concentration. The temperature dependence of susceptibility for both untreated carbons and residue compounds has also been studied over the temperature range from 80°K to 1300°K. The susceptibilities of the untreated carbons all decrease at higher temperatures and tend towards a temperature-independent limit at low temperatures. For small crystallites, the rapid decrease begins at higher ambient temperature, and the low-temperature limit is smaller. The plateau in susceptibility as a function of crystallite size is present for all ambient temperatures, but the beginning of the plateau shifts somewhat to smaller crystallite size for higher ambient temperatures. A qualitative discussion is given which leads to the conclusion that the Landau-Peierls theory is inadequate to explain all the experimental findings if the simplified band model deduced from other electronic properties of carbons is used.

I. INTRODUCTION

THE diamagnetic susceptibility of carbons and polycrystalline graphites has a very remarkable dependence on crystallite size. The crystallites are composed of parallel graphitic planes stacked, depending on the size, in either an ordered arrangement as in graphite or in a disordered way. The crystallite size will refer throughout this paper to the diameter of the graphitic plane (*a*-direction) and not to the dimension of the crystallite perpendicular to the plane (*c*-direction), since the anisotropic component of susceptibility seems to depend mainly on the former dimension. The single crystals of graphite are very anisotropic; the susceptibility for the field in the direction perpendicular to the graphitic plane being 40 times as large as that for the field parallel to the plane. The room-temperature susceptibility of polycrystalline carbons has been found to be a very slowly increasing function of size up to diameters of about 75 A, with a relatively abrupt increase from -2.0×10^{-6}/g to -7.5×10^{-6}/g over the range of diameters from 75 A to 150 A, and to have an essentially constant value for all diameters above about 150 A.[1] This relation between χ and crystallite size is essentially the same for all carbons irrespective of origin, with the possible exception of slight shifts of the whole curve of perhaps ±10 A in the crystal size.

The susceptibility of small crystallites seems to be explainable on the basis of the closed shell diamagnetism of the nearly full π band.[2] The magnitude of this closed shell susceptibility can be approximately obtained by extrapolation from the known susceptibilities of aromatic molecules of known structure up to 10 benzene rings, assuming the susceptibility to be roughly proportional to the number of benzene rings. An explanation of the susceptibility of very large crystals of graphite was proposed by Ganguli and Krishnan[3] who assumed that the π electrons behave as a two-dimensional free-electron gas with one electron per atom and with a very low degeneracy temperature arising from the extremely high effective mass in the direction perpendicular to the plane. This theory was unacceptable because of serious difficulties in regard to electronic specific heat and paramagnetism. A modification[2] of this theory which takes into account the effective number of electrons and holes and their effective masses removed these objections and gave a value for the susceptibility which is in reasonable agreement with experiment. The explanation of the susceptibilities for the intermediate size range, 75 A to 1000 A seemed to be in a less satisfactory state. The abrupt rise in susceptibility was tentatively ascribed[1] to a combination of two factors controlled by crystallite growth: the shift of the Fermi level towards the corners of the zone (regions of higher curvature of the energy surfaces) as π electrons trapped in surface states are returned to the band, and the change of curvature of the energy surfaces themselves as the energy gap between the π band and the conduction band decreases. However, it was pointed out that while the susceptibility remains constant for crystallites with diameters of 150 A to approximately 1000 A, there are still changes occurring in the number of carriers as indicated by the changes in Hall constant[4] and in the thermoelectric power.[5] An assumption that the number of carriers and their

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[1] H. T. Pinnick, Phys. Rev. 94, 319 (1954). Further designated as Part I.

[2] S. Mrozowski, Phys. Rev. 85, 609 (1952); Phys. Rev. 86, 1056 (1952).

[3] N. Ganguli and K. S. Krishnan, Proc. Roy. Soc. (London) 117, 168 (1941).

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effective masses change in just such a manner as to maintain the susceptibility constant over this large size range, and suddenly, in the narrow size region 75 A to 150 A, change in such a way as to give a very large change in susceptibility, seems to be somewhat forced.

In varying the crystallite size by varying the maximum temperature of heat treatment (T_{ht}) of the carbon, both the energy gap and the number of excess holes due to π electrons trapped on the crystallite boundary are being changed simultaneously. Thus the position of the Fermi level and probably also the curvature of the energy surfaces at the Fermi level are changing[5,6] and it would be very desirable to separate the contribution of these two effects from each other. Donor and acceptor levels cannot be introduced into graphites by the substitutional replacement of carbon atoms by foreign atoms as is customarily done in such semiconductors as silicon and germanium. However, such levels can be introduced into graphites by means of ions located between the graphite layers. Positive ions (e.g., the alkali metals) act as donors while negative ions (e.g., the halogens) act as acceptors. This allows the number of carriers in carbons with different T_{ht} to be changed independently of the possible change in the energy gap and in the shape of the energy surfaces with crystallite growth.

Large crystals of graphite have a pronounced temperature dependence of susceptibility and it might be expected that studies of the temperature dependence of susceptibility as a function of crystallite size would help clarify the relation between the susceptibility and the band structure of carbons and polycrystalline graphites. For example, the low-temperature susceptibility of single crystals of graphite gives information about the possible overlap of the π bands and the conduction band regardless of the details of the model.[7]

While this work was in progress, some results were published by Marchand,[8] who has studied the susceptibility of graphitized carbon blacks with crystallite sizes up to 200 A at temperatures from 78°K to room temperatures. Later these results were extended to ambient temperatures of 1000°C.[9] He found that for crystallite sizes of 200 A the temperature dependence is very similar to that of single crystals, while the susceptibility of very small crystallites is practically independent of temperature. The range of sizes in the investigation reported below includes most of the sizes in Marchand's carbon blacks and covers a wider range from 50 A to 1200 A. The extension to larger sizes is particularly important, since the relations found for these large sizes at high temperatures make possible a prediction of the probable behavior of the susceptibility of smaller sizes at very high temperatures not readily attainable experimentally.

II. EXPERIMENTAL PROCEDURE

The samples which were heat-treated were $\frac{1}{4}$-in. diameter National Carbon Company baked rods of a soft coke base. For these rods, neither the coke particles nor the binder have been heat-treated in the manufacturing process to a temperature higher than about 1250°C. These rods were heat-treated to temperatures of 1200°C, 1400°C, 1600°C, 1800°C, 2000°C, 2200°C, 2400°C, and 2800°C. As many as six rods were treated to each temperature to provide a sufficient number of samples prepared under identical conditions at each T_{ht} to perform experiments both with bisulfate compounds and on temperature dependence. The heat-treatments were carried out in a graphite resistance furnace in a high-purity nitrogen atmosphere, the temperature being measured with an optical pyrometer. Heat-treatment runs lasted from 1–3 hours with a holding time of about 10 minutes at the top temperature.

The choice of bisulfate ions to introduce excess holes into the π band was made because it enables the number of ions introduced to be counted quite readily, as shown by Hennig[10] for the case of polycrystalline graphites. There was an additional advantage in that it has been shown by Kmetko[4] that this technique is also applicable to carbons with T_{ht} as low as 1800°C. The cell used to introduce the ions was similar to that described by Hennig[10] with concentrated sulfuric acid as the electrolyte and a special sintered porous glass disk separating anode and cathode compartments. Bisulfate ions cannot penetrate the small pores of the glass disk, but the hydrogen ions can pass through it easily. Thus, current flows in the cell only when bisulfate ions go into the carbon anode. The current was held constant at 5 ma; the electrical resistance of the rod was ordinarily measured every 20 minutes corresponding to increments of ion concentration of approximately 1.5×10^{-4} ion/atom. The compounds formed by this procedure are the lamellar compounds,[10] which are unstable if the rod is removed from the concentrated sulfuric acid. Experimentally there would be many difficulties involved in measuring the susceptibility of the rods while they were still immersed in the acid. However, if after oxidizing the carbons to a particular ion concentration, the polarity of the cell is reversed, about one-third to one-fourth of the maximum number remain in the carbon no matter how long the current is maintained. The concentration of ions in such a residue compound can be determined from the relative resistance as a function of the ion concentration as obtained during the formation of the lamellar compound since the relative resistance of the lamellar and residue compounds is the same for a given ion concentration.[4,10] These residue compounds are quite stable and no

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[7] S. Mrozowski, J. Chem. Phys. 21, 492 (1953).

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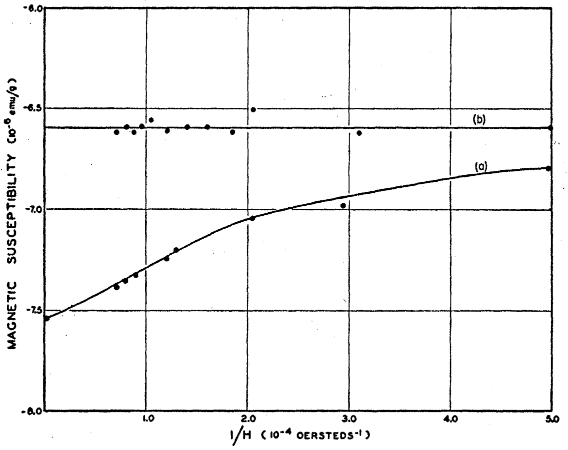

FIG. 1. Mass susceptibility of a carbon heat treated to 2400°C as a function of the inverse magnetic field (a) before and (b) after introduction of bisulfate ions.

further change in ion concentration occurs when the rod is removed from the cell, washed, and dried. For each T_{ht}, three rods were oxidized to maximum levels of 15×10^{-4}, 30×10^{-4}, and 45×10^{-4} ion/atom. After reversing the cell currents this gives residue compounds with ion concentrations of approximately 5×10^{-4}, 10×10^{-4}, and 15×10^{-4} ion/atom. All rods were washed after that in running water for 24 hours and dried for several hours at approximately 125°C. The susceptibility was then measured using the Gouy method as described in Part I. The residue compounds of carbon contain about four molecules of sulfuric acid for every bisulfate ion, giving a considerable increase in weight. The susceptibility was calculated on the basis of the original weight of the carbon rod, however, since the diamagnetic contribution from the sulfuric acid represents a negligibly small correction ($<\frac{1}{2}\%$).

The treatment in the electrolytic cell turned out to be a very efficient way of removing ferromagnetic impurities, being far more effective than prolonged treatment in hot HCl. Figure 1 shows the plot of susceptibility against $1/H$ for a carbon with a T_{ht} of 2400°C; the curve (a) for the untreated carbon showing a pronounced field dependence of susceptibility, but the curve (b) for the residue compound having a susceptibility independent of the field within the experiment error.

In the temperature-dependence studies, the susceptibility was measured at seven temperatures 77°K, 195°K, 300°K, 570°K, 820°K, 1040°K, and 1280°K. The low-temperature measurements were carried out in a cylindrical Dewar flask filled with dry nitrogen to prevent weight changes arising from water vapor condensation. The rods were suspended by means of a chromel-constantan thermocouple (40 gauge) soldered to a brass clamp which gave direct thermal contact to the sample. A tube furnace interchangeable with the Dewar was used for measurements of susceptibility at high temperatures. To avoid oxidation, a nitrogen atmosphere was also used here and in this case the temperature was determined by a thermocouple located near the bottom of the sample. The temperature variation over the six-inch length of the furnace in which the sample was placed was about ±10°C at 575°K. The magnet gap necessary to admit the Dewar and the furnace was about 5 cm and with this pole separation, the maximum field attainable was 6500 gauss. The extrapolation of susceptibility to infinite fields to correct for ferromagnetic impurities is not too reliable for such a low maximum field, but the ferromagnetic corrections were generally small and as a result, the susceptibilities at room temperature agreed within $\pm2\%$ with the room-temperature susceptibilities obtained using a smaller pole separation and maximum field of 11 500 gauss.

III. RESULTS

The room-temperature susceptibilities of the polycrystalline graphites which have been found were all around -7.5×10^{-6}/g, which is very close to the value expected for a random arrangement of crystallites with a susceptibility of -22×10^{-6}/g in the direction of the c-axis and -0.5×10^{-6}/g in the directions parallel to the graphitic planes, the latter values being those reported by Ganguli and Krishnan[3] for large graphite single crystals. In this work the single crystal values were checked by measurements on a sample of specially purified Ceylon graphite. The graphite samples were fabricated from powder without the use of binder by compacting it into rectangular plates at a pressure of 20 000 lb/in.[2] The compression tends to align the small particles with their c-axis parallel to the applied pressure and although the alignment was not complete, the anisotropy in susceptibility was about 4 to 1. The susceptibility of a rectangular rod cut out from such a

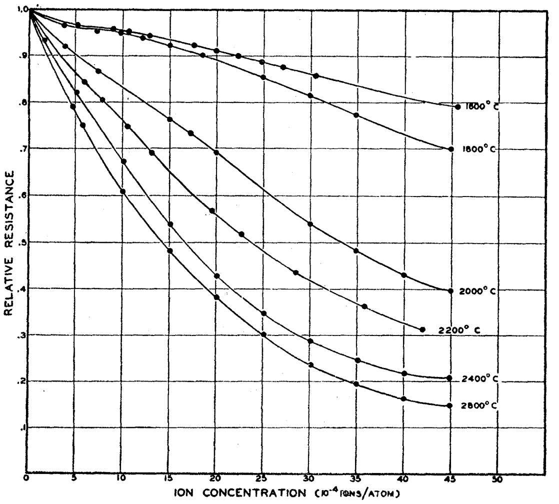

FIG. 2. Relative resistance of carbons as a function of concentration of introduced bisulfate ions.

plate was measured in two perpendicular directions, both of which were perpendicular to the axis of the rod. Three determinations were made and representative values of the susceptibilities in one of these were -16.3×10^{-6}/g for the direction parallel to axis of compression and -4.3×10^{-6}/g for the direction perpendicular to the axis of compression. The sum of the susceptibilities in three perpendicular directions assuming that susceptibility is the same in any direction perpendicular to the direction of the compressing force was $-25.0\times10^{-6}/\text{g}\pm0.3\times10^{-6}$/g. If the susceptibility in the *a*-direction is taken as -0.5×10^{-6}/g, then the anisotropic component for a single crystal in the *c*-direction is -23.5×10^{-6}/g, a higher value than that reported by Ganguli and Krishnan[3] (-21.5×10^{-6}/g) by about 10%.

The relative resistance curves for carbons with various T_{ht} are plotted in Fig. 2 as a function of the number of ions/atom introduced during the oxidizing cycle of the chemical treatment. From these curves, the residual ion concentration was determined by measuring the relative resistance of the rods after the cell current had been reversed until no more ions could be driven out electrolytically. The curves, although similar to those of Kmetko,[4] show somewhat greater change in relative resistance for a given ion concentration as T_{ht} is increased. The similarity provided a qualitative check on the residue concentrations computed from relative resistance curves. The susceptibility of the untreated rods and of the three residue compounds for each T_{ht} were measured at room temperature. Using these values, a plot of susceptibility as a function of ion concentration for each set of rods with a particular T_{ht} was obtained (Fig. 3). The figure shows that the change in susceptibility is qualitatively the same as the change in relative resistance; that is, the higher the T_{ht}, the greater the decrease in susceptibility for a given ion concentration. The range of ion concentrations for the residue compounds of carbons with a T_{ht} of 1600°C only extends to 1×10^{-4} ion/atom. These rods behaved differently from rods of higher T_{ht} in that they retained almost half the maximum ion concentration regardless of how long the cell was run with reversed polarity, but when the rod was washed in water, practically all the residue ions were washed out.

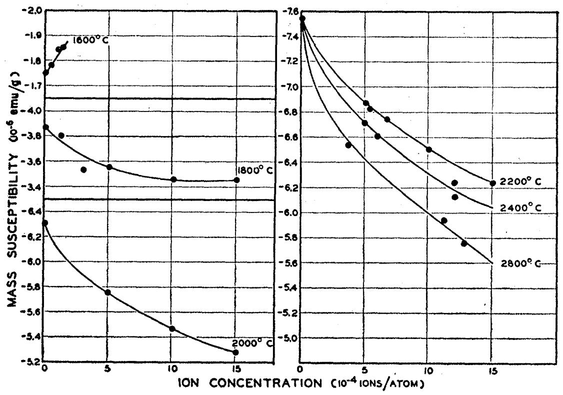

FIG. 3. Mass susceptibility of bisulfate residue compounds of carbons with varying heat treatment as a function of ion concentration.

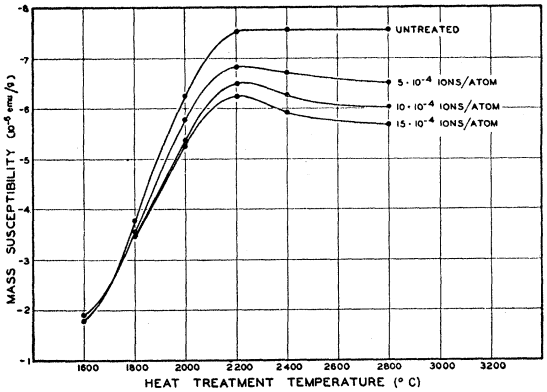

FIG. 4. Mass susceptibility of bisulfate residue compounds carbons as a function of crystallite diameters.

In order to present more clearly the effect of changing the Fermi level in carbons of different T_{ht}, values of susceptibility at three ion concentrations, 5×10^{-4}, 10×10^{-4}, and 15×10^{-4} ion/atom have been determined by interpolation using smooth curves drawn through the experimental points in Fig. 3. These values were used to construct in Fig. 4 a plot of susceptibility as a function of crystallite size for the untreated rods and for rods containing these three ion concentrations. Since the susceptibility of the untreated rods is constant for sizes larger than 150 A and since the susceptibility is more sensitive to the introduction of ions as the size increases, the curves of susceptibility *vs* size for all the residue compounds have a maximum near 200 A and this maximum becomes more pronounced as the ion concentration is increased.

The results of the temperature-dependence measurements on the untreated rods are summarized in Fig. 5 where the curves of χ *vs* T_{ht} are plotted for each temperature at which measurements were made. The general shape of the curves is similar for all ambient temperatures, but the limiting value of susceptibility for large crystallite sizes is smaller as the ambient temperature is increased. The shape of the curves makes it difficult to determine the T_{ht} at which the limiting value of the susceptibility is reached but it is readily visible from the figure that it is shifting towards lower T_{ht} as the ambient temperature is increased. Roughly estimated, it shifts from $T_{ht}\approx2400$°C at 77°K to $T_{ht}\approx2200$°C at 1280°K. The rate of shift of 200° in T_{ht} per 1200°C increase in ambient temperature is roughly the same as the rate of shift in the peak of the Hall constant as measured recently by Mrozowski and Chaberski.[11]

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[11] S. Mrozowski and A. Chaberski, Phys. Rev. **94**, 1427 (1954).

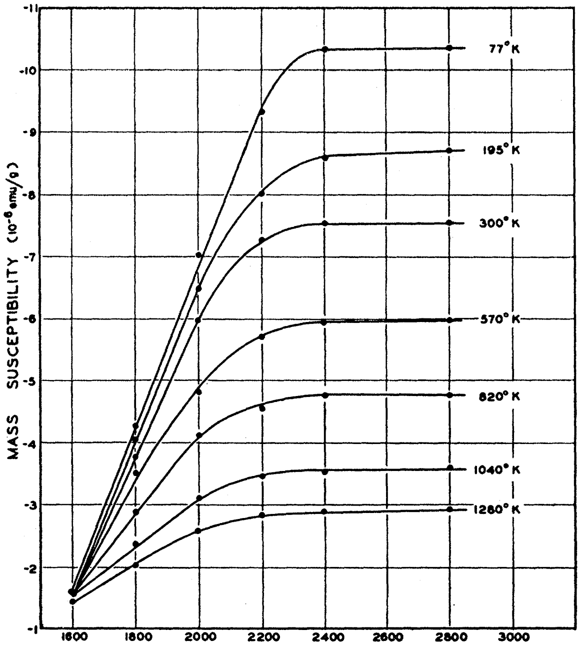

Fig. 5. Mass susceptibility of carbons as a function of heat treatment for seven ambient temperatures.

The susceptibilities for carbons with a T_{ht} of 2400°C and greater are about identical with that of single crystals with the anisotropic component reduced by a factor of approximately three to take into account the nearly random orientation of the microcrystals in the polycrystalline material, (Fig. 6). The susceptibility of carbons in the range of T_{ht} from 1600°C to 2400°C for which the large increase in susceptibility occurs approaches a temperature independent value at low temperatures and this value is smaller for lower T_{ht}. For lower T_{ht} the susceptibility falls off with increasing temperature in much the same way as for carbons of higher T_{ht}, but the beginning of the decrease is more sudden and starts at somewhat higher temperature.

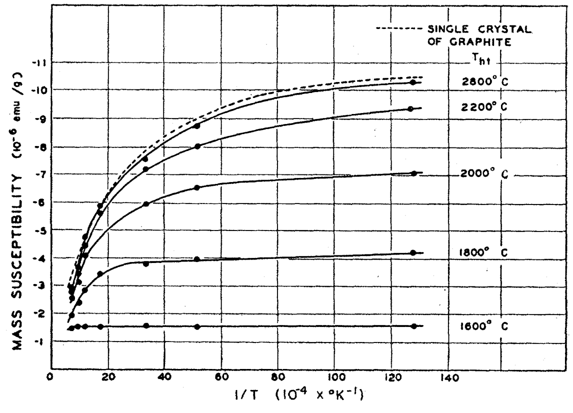

Fig. 6. Mass susceptibility of differently heat-treated carbons as a function of inverse absolute temperature.

This illustrates essentially the same effect as the shift of the beginning of the plateau is susceptibility *vs* T_{ht} described above only presented in a different fashion. All the curves (Fig. 6) seem to have a tendency to join the single crystal curve at sufficiently high temperatures. The susceptibility of carbons with a T_{ht} of 1600°C or less is practically independent of temperature.

The variation of susceptibility of carbon bisulfate compounds was also investigated as a function of temperature. The susceptibilities for three ion concentrations obtained by interpolation are given in Table I for three ambient temperatures. One can see that the decrease in susceptibility with increase in ion concentration is relatively even more pronounced at low temperatures. The measurements were not extended above room temperature since fumes came out from the bisulfate compounds when they were heated. After cooling to room temperature, both the susceptibilities and electrical resistivities correspondingly increased, indicating a partial decomposition of the compound. This driving out of ions has been studied by heating one bisulfate sample for each heat-treatment to a series of consecutively increasing temperatures. The results for the susceptibility are collected in Table II. It is evident that most of the bisulfate ions are being expelled by heating to temperatures below 800°C. As the result of driving out of ions, the electrical resistance increases considerably above the original value; this being due to breaking off of small pieces of the material (loss in weight of the sample) and probably also to formation of internal fissures.

Table I. Magnetic susceptibility of bisulfate compounds in -10^{-6} emu/g.[a]

Temperature of heat treatment	Ambient temperature	Ions/atom 0	5×10^{-4}	10×10^{-4}	15×10^{-4}
1800°C	300°K	3.8	3.7	3.6	3.6
1800°C	195°K	4.0	3.8	3.7	3.6
1800°C	77°K	4.3	3.9	3.7	3.6
2000°C	300°K	6.0	5.6	5.1	5.0
2000°C	195°K	6.6	6.2	5.8	5.0
2000°C	77°K	7.1	6.8	6.2	5.3
2200°C	300°K	7.2	6.6	6.1	5.8
2200°C	195°K	8.2	7.8	7.3	6.4
2200°C	77°K	9.3	8.9	8 1	7.0
2400°C	300°K	7.5	6.9	6.2	5.6
2400°C	195°K	8.6	8.1	7.2	6.3
2400°C	77°K	10.3	9.5	8.5	7.1
2800°C	300°K	7.6	6.9	6.2	5.4
2800°C	195°K	8.8	8.0	7.2	6.2
2800°C	77°K	10.3	9.2	8.3	6.9

[a] The values for the susceptibility given in this table were obtained one year after the original oxidation of the samples. Small changes occurred during this interval, as can be seen by comparison with Fig. 3.

IV. DISCUSSION

In the region below $T_{ht}=1700$°C, it was impossible to introduce a significant concentration of bisulfate ions so that the influence on the susceptibility of changing the hole concentration could not be studied.

TABLE II. Magnetic susceptibility of bisulfate compounds in -10^6 emu/g.

T_{ht}	No. of ions per carbon atom	Untreated carbon	With introduced ions	After keeping ionized sample 4 hr at 300°C	After keeping ionized sample $\frac{1}{2}$ hr at 800°C	After keeping ionized sample $\frac{1}{2}$ hr in 1400°C	After keeping ionized sample $\frac{1}{2}$ hr at 2100°C
1800°C	17.2×10^{-4}	3.8	3.6	3.5	3.7	3.8	...
2000°C	12.5×10^{-4}	6.0	5.0	5.2	5.8	5.9	...
2200°C	15.3×10^{-4}	7.3	5.8	6.0	7.2	7.2	7.4
2400°C	18.7×10^{-4}	7.5	5.1	5.1	7.3	7.4	7.4
2800°C	15.5×10^{-4}	7.6	5.4	5.5	7.6	7.5	7.6

However, the fact that the susceptibility is practically temperature-independent supports the conclusion that the susceptibility in this region is due mostly to closed-shell diamagnetism. The closed-shell diamagnetism would be expected to be temperature-independent since the energy distribution of these electrons would not be affected by changes in temperature. The tendency of all the curves of T_{ht} higher than 1600°C to join the single-crystal curve at high temperatures implies that the susceptibility for $T_{ht}=1600$°C and lower might become temperature-dependent at high enough temperatures, but this temperature would be so high that the T_{ht} of the carbon would be changed. Thus such temperatures can never be attained experimentally. If, however, this would be possible, the top of the Fermi distribution would be spread out over such a large energy range that even the closed shells would become excited, details of the band structure would tend to be obliterated, and all curves would tend toward a common temperature dependence.

It seems that the increasing change in susceptibility as a function of ion concentration could be explained on the basis on the shift in Fermi level (observed for carbons in the region of T_{ht} from 1800°C up to 2800°C) to regions of lower curvature assuming the same band structure for carbons of all T_{ht}. Carbons heat-treated to 2800°C have very large crystallite diameters and therefore relatively few holes left in the π band due to electrons trapped at the peripheral sites. Near the zone corner the density of states is quite small, so that for a particular ion concentration the Fermi level will be shifted more than for a carbon with lower T_{ht} in which the Fermi level is initially lower because of the larger number of π electrons which are trapped at the boundaries of crystallites. However, if the only result of increasing T_{ht} in the region 2200°C–2800°C were to raise the Fermi level as a result of the return of trapped electrons to the π band, then, as was pointed out in the introduction, in order to explain the plateau in susceptibility over this range of T_{ht}, one would have to assume that the effect of the decrease in the effective number of carriers is exactly compensated by the increase in curvature of the energy surface at the Fermi level. Such a model would require that the susceptibility of a carbon with a T_{ht} of 2800°C, for example, remain constant when bisulfate ions are introduced until the Fermi level is lowered to the same point below the top of the π band as it is in a carbon with a T_{ht} of 2200°C (at the end of the plateau). This is obviously not the case since the 2800°C carbon actually shows the largest change in susceptibility for a given ion concentration. Therefore, in order to explain both the presence of the plateau and the influence of acceptors, it seems necessary to assume that the curvature of the energy surfaces at a definite depth in the π band changes with crystallite size, or more generally that the dependence of energy E on k changes inside of the Brillouin zone. Thus one is led to the suggestion originally made by Mrozowski[2] concerning the change of curvature of the energy surfaces near the corner of the zone as the energy gap between the π band and the conduction band changes with crystallite size. To explain both the plateau and the results of the ion experiments, the direction of the change as the energy gap becomes larger would have to be towards greater curvature at a particular value of k below the top of the π band, compared to the curvature at that point in the π band of a very large crystal.

The rapid change in susceptibility with T_{ht} from 1700°C to 2200°C is consistent with this general scheme of the change in curvature of the energy surfaces near the top of the band since the change of sign of Hall effect near a T_{ht} of 1700°C shows that in this range of T_{ht} the Fermi surface is near the inflection curve where $\partial^2E/\partial k^2=0$. Here the curvature is zero, but due to the symmetry of the zone, the inflection curve is not far from the top of the π band. Therefore, the curvature must increase relatively rapidly with increasing k in the neighborhood of the inflection point so that as the Fermi level is raised by a relatively small amount with increasing T_{ht}, the susceptibility must also increase rapidly.

The room-temperature susceptibility and the change in the susceptibility as a function of ion concentration can be qualitatively understood, therefore, on the basis of the previous explanation involving both a shift of Fermi level with change in T_{ht} and a corresponding change in the E *vs* k relation as the energy gap changes with increasing size. However, the assumption of increasing curvature with decreasing crystallite size and increasing gap does not seem reasonable. Furthermore, the temperature dependence of susceptibility is such that the susceptibility as a function of T_{ht} is constant at large T_{ht}'s for all ambient temperatures from 80°K up to 1300°K. The shift of the beginning of the susceptibility plateau towards lower T_{ht} for higher ambient temperatures (similar to the shifts in the peaks of the thermoelectric power[5] and Hall effect[11] is undoubtedly due to the thermal excitation of electrons over a correspondingly larger gap. The Fermi level for a carbon with a given T_{ht} shifts as the ambient temperature changes, causing a change in the average curvature or effective mass of the carriers. In order to explain the existence of the plateau of susceptibility *vs* T_{ht} for all ambient temperatures, it would be necessary, then, to assume that the change in susceptibility resulting from the shift of the Fermi level with temperature is just balanced by the change in the number of carriers resulting from thermal excitation into the conduction band. While this assumption is acceptable on qualitative grounds, it seems highly improbable that such an exact cancellation of these factors could occur over the observed wide ranges of temperature and T_{ht}. The difficulties seem to be of a basic nature and probably some modifications in the general theory of diamagnetism will be required in order to explain all the experimental findings.

The problem of the simultaneous explanation of the susceptibility plateau and of the change in susceptibility of bisulfate compounds must be considered to be in an unsatisfactory state. A part of this difficulty might be due to the interpretation of the addition of bisulfate ions as affecting the number of carriers in the π band only. It may be that the band structure of the bisulfate compounds is different from that of untreated carbon of the same T_{ht} and some additional scattering effects are present.

ACKNOWLEDGMENTS

The authors would like to express their thanks to Professor S. Mrozowski, who suggested this problem, for his continued advice and encouragement throughout the course of this work. The x-ray spectrometer was obtained with the assistance of a grant from the Research Corporation.

PHYSICAL REVIEW VOLUME 102, NUMBER 1 APRIL 1, 1956

Dislocations, Relaxations, and Anelasticity of Crystal Quartz

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(Received December 8, 1955)

By careful grinding and etching, contouring and mounting in a vacuum, very small internal friction coefficients Q^{-1} are found in *AT* shear vibrating crystals. Various tests show that the internal friction corresponds to that of the quartz itself. The internal friction at room temperature increases proportionally to the frequency up to 100 Mc/sec indicating the presence of relaxations. These have been investigated by measuring the internal friction at very low temperatures down to 1.5°K and two relaxations were found. One having a time constant of 10^{-13} second appears to be connected with a distorted lattice due to impurities while the other having a time constant of 7.7×10^{-10} second is thought to be connected with dislocation loops. Using equations developed previously for metals the indicated number of dislocations is $\bar{N}\approx10^3/\text{cm}^2$, the average loop length about 1.8×10^{-3} cm and the ratio of Peierls force to shear modulus about 5×10^{-8}. Confirmation of these values is given by the time constant 7.7×10^{-10} second and the change in frequency as a function of amplitude. A long-time aging effect is thought to be due to closer pinning of dislocations by impurity atoms. It is suggested that an improved frequency standard, free from aging, can be obtained by holding the temperature of the crystal at liquid helium temperature.

I. INTRODUCTION

During the course of development of high-Q, high-frequency crystal units for primary frequency standards,[1] it has become increasingly evident that the maximum Q obtainable for *AT*-cut crystal units at ordinary temperatures is an inverse function of frequency, ranging from 10×10^6 at 1 Mc/sec to 0.1×10^6 at 100 Mc/sec.

Techniques have been developed which virtually eliminate energy loss through the supporting structure at the edge of the quartz plate, and studies have since been carried out which show that all other sources of energy loss can be made insignificant in comparison with the energy loss caused by the anelasticity of quartz.

The resulting curve of maximum Q *vs* frequency suggests a relaxation process. To verify the existence of such a relaxation, measurements of internal friction of single crystals have been made from 1.5°K to 300°K and in the 5 to 80 Mc/sec frequency region. Two relaxations are found having activation energies and angular frequency constants equal, respectively, to

$$\begin{aligned}\gamma_1&=1.3\times10^9/\text{sec};\quad H=155\text{ cal/mole}=6.7\times10^{-3}\text{ ev},\\ \gamma_2&=10^{13}/\text{sec};\quad H=1300\text{ cal/mole}=0.056\text{ ev}.\end{aligned}\tag{1}$$

The first process can be shown to be due to dislocations in the crystal quartz, while the second process appears to be the result of impurities in the crystal.

II. EXPERIMENTAL EVIDENCE FOR Q VARYING INVERSELY PROPORTIONAL TO THE FREQUENCY AT ROOM TEMPERATURE

AT-cut quartz plates are excited electrically by centrally located electrodes and supported by wires fastened at the edge. The frequency of oscillation is a

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[1] A. W. Warner, Proc. Inst. Radio Engrs. 40, 1030–1033 (1952).