

conductivity model which predicts that the ac conductivity increases with the minority impurity concentration. It has been suggested³ that interstitial migration at 1.6 K might best be understood by an

athermal migration process; a model⁴ for such a process has been proposed. The present extension of the migration temperature to 0.5 K adds further support to these suggestions.

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Magnetic Susceptibility of Amorphous Semiconductors

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Previously observed paramagnetic contributions to the magnetic susceptibility of As_2S_3 and As_2Se_3 glasses are shown to be due to iron impurities. The density of singly occupied localized states is below 3×10^{16} per cm^3 in ultrapure glasses. Careful measurements of the diamagnetic susceptibility of both the glassy and crystalline phases of several glass-forming semiconductors indicate that the difference in diamagnetism of the phases is small.

I. INTRODUCTION

The magnetic susceptibility (χ) of solids depends in general in a complicated way on the electronic structure, and the comparison of experimental results with theory is usually not straightforward. Nevertheless, studies of magnetic susceptibilities may provide a possible test on the correctness of some models of electronic structures. It is therefore of interest to investigate the magnetic susceptibility of amorphous semiconductors with the aim of obtaining some additional experimental information on a still unresolved problem of the electronic states in amorphous semiconductors. Busch and Vogt¹ observed a difference between the magnetic susceptibilities of amorphous and crystalline Se. At the melting point, χ of the crystalline form changed discontinuously in contrast to that of the amorphous form. Cervinka *et al.*² and Matyáš³ found that χ of CdGe_xAs_2 and related glasses can be separated into a temperature-independent diamagnetic term χ_d and a Curie term χ_C , which has been ascribed to unsatisfied Ge bonds. The paramagnetic contribution may under favorable conditions be observable also in electron spin resonance (ESR), and indeed, Brodsky and Title⁴ observed ESR in nonannealed amorphous Ge, Se, and SiC

films. The signal corresponded to spin concentrations of the order 10^{20} cm^{-3} . These free spins were associated with the dangling bonds at the inner surfaces of voids, and this assignment was later justified by some more observations.

Amorphous materials in which a paramagnetic term was observed are rather poor glass formers and must be produced by a fast quenching of the melt or by vapor deposition. Such materials are likely to contain a large concentration of unsatisfied bonds, and defects of this kind produce paramagnetic contributions to the susceptibility even in crystalline solids. Our aim was to study materials as close as possible to "ideal glasses," that is, glasses in which all chemical bonds are satisfied. We had therefore to choose good glass formers such as As_2S_3 and As_2Se_3 , which can be produced in the amorphous forms even with relatively slow cooling rates.

The question which we asked was whether there are singly occupied states in the gap of an ideal glass, in other words, whether the mere loss of the long-range order produces singly occupied states in the gap. In the original Mott-CFO (Cohen, Fritzsche, and Ovshinsky) theory^{5,6} of the states in the gap, the question of whether the states are doubly or singly occupied is not discussed. States

in the gap are localized over increasingly smaller volumes the deeper in the gap they are.^{7,8} The Coulombic interaction may considerably increase the energy of the second electron in a localized state, and displace its energy level above the Fermi level. Recently, these qualitative ideas were theoretically discussed by Pollak⁹ and Kaplan *et al.*¹⁰ On the basis of these considerations, one expects that a part of the states in the gap should be singly occupied, and should therefore contribute a paramagnetic term to the magnetic susceptibility, which would be observable at low temperatures.

We have not found, as described in detail below, any evidence of such singly occupied states in pure As_2S_3 and As_2Se_3 . The sensitivity of these experiments is about $3 \times 10^{16} \text{ cm}^{-3}$. Bagley *et al.*^{11,12} found similar results in amorphous S and Se.

During our studies, we originally observed^{13,14} a low-temperature paramagnetic contribution that roughly obeyed the Curie law. We found, however, that these "tails" were due to extremely small concentrations of iron in our samples. Also, our measurements¹⁴ on crystalline As_2S_3 , which was melted and quenched *in situ* in a sealed quartz container, showing a large increase of the Curie term in the vitreous material, can be explained, as shown below, by the presence of Fe. The total amount of Fe atoms is, of course, the same in the crystalline and amorphous forms, but the Fe ions are in different states in the two forms.

Finally, our measurements of the temperature-independent diamagnetic part show that the glass is usually more diamagnetic than the corresponding crystalline state. The accuracy of our measurements of both crystals and randomly oriented polycrystalline samples has been improved, and we find that the difference between the crystalline and glass susceptibilities is smaller than reported previously.¹⁵

II. MATERIALS PREPARATION

The samples were prepared from the appropriate elements (S, Se, or As), all of 99.9999% purity. No transition elements were observable by spectrographic analysis in the starting materials, the 1-ppm total impurity level being due to halogens, other chalcogenides, and antimony. The elements were weighed to the correct stoichiometry and sealed in 18-mm-o.d. quartz tubes under a vacuum of less than 10^{-2} Torr; typical samples weighed between 20 and 30 g. The material was reacted by heating to 700 °C in approximately 1 h, and the furnace rocked about the horizontal so that the melt would be thoroughly mixed. The melting points of the starting materials and end products are S, 119 °C; Se, 217 °C; As, 613 °C; As_2S_3 , 315 °C; As_2Se_3 , 368 °C. The boiling point of As_2S_3 is 708 °C,¹⁶ and thus to avoid explosion of

the samples, higher temperatures were not used. Rocking at 700 °C was continued for an interval as short as 1 h or as long as three days, but it was determined that the product was not improved in any way by the longer rocking. After rocking, the furnace was turned to a vertical position so that the melt would be confined to one end of the cylindrical quartz tube. The furnace was then cooled to approximately 450 °C for $\frac{1}{2}$ h, so that bubble formation in the melt was avoided. Rapid quenching of the melts into air or water usually produced samples with a large number of cracks and slower cooling rates still produced glassy products but without cracks. Cooling rates between 2 °C/min and 20 °C/min were used; the higher rates were obtained by shutting the furnace off and blowing cool air through the furnace center. Some of the samples were checked by x-ray powder diffractograms and by differential thermal analysis and all were shown to be glassy with no polycrystalline phases present. The optical quality of the As_2S_3 glasses produced is quite good, the material being transparent in the red even for the largest sample lengths produced (approximately 6 cm). As_2Se_3 is not transparent in the visible, but the samples looked quite homogeneous in an infrared microscope.

III. MAGNETIC MEASUREMENTS

The magnetic susceptibility is measured with an electronic Faraday balance, with samples weighing between 0.2 and 1.0 g. Only recently, however, shaped magnetic pole pieces were added so that the product of magnetic field times the field gradient, was approximately constant over a large volume (to 1% over $2 \times 0.4 \times 0.4$ cm) (see Ref. 17 for a discussion of the technique.) With this change both the precision and absolute accuracy of our measurements improved considerably, and led to a reevaluation of our initial interpretation of the results previously reported.^{13,14}

Small amounts of ferromagnetic contamination can cause large deviations of the measured susceptibility from the true value. This contamination is easily detected, however, since the measured susceptibility is linearly dependent upon the inverse of the applied magnetic field (H).¹⁷ We use only data from those samples shown to have field-independent susceptibilities over the range 1.5–13 kG.

The absolute accuracy of the system was checked with a number of "standards." In cases where the susceptibility is known with high accuracy, we obtained values within $\pm 2\%$ of those published.¹⁸ For example, we obtained for 99.9999% pure single-crystal Ge, $\chi_g = -0.106 \times 10^{-6} \text{ emu/g}$; and for 99.9999% single-crystal Pb, $\chi_g = -0.113 \times 10^{-6} \text{ emu/g}$ (both at room temperature). The

temperature dependence of the susceptibility of the paramagnetic salt chrome alum $[\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ was also measured between 10 and 225 °K. The temperature-dependent part fits an inverse-temperature ($1/T$) law with a coefficient of 3.68×10^{-3} emu °K/g, as compared to the value calculated from ESR measurements of 3.71×10^{-3} emu °K/g.¹⁸ Although the absolute accuracy of the susceptibility measurements is expected to be about 2%, the precision with which *changes* in the susceptibility vs temperature could be observed for a *given sample* is on the order of 0.5%.

IV. EXPERIMENTAL RESULTS

A. Spin Tails in the Susceptibility

In a previous paper, we showed that the magnetic susceptibility (χ_g , in units of emu/g) of amorphous As_2S_3 and As_2Se_3 consisted of two parts, a temperature-independent diamagnetic term and a temperature-dependent Curie-like term. Results from a typical sample are shown in Fig. 1.

With the increased precision our system now affords, we are able to subtract very accurately the diamagnetic part of the susceptibility (χ_d). In Fig. 2 the Curie part (χ_C) vs $1/T$ is shown for a sample of amorphous As_2S_3 in a field of 12.8 kG. χ_C does *not* follow a $1/T$ relation to the lowest temperature of measurement (1.5 °K), but shows a clear deviation at about 6 °K. As a measure of this deviation, the value of χ_C extrapolated from high temperatures (> 6 °K) to 1.5 °K divided by the measured value of χ_C at 1.5 °K, $\chi_C(\text{extrap } 1.5 \text{ °K})/\chi_C(\text{meas } 1.5 \text{ °K})$, is 2.20 ± 0.2 .

There are several mechanisms that could explain this departure of χ_C from a $1/T$ dependence. These include paramagnetic saturation, antiferromagnetic interactions between the paramagnetic moments, and crystal field splitting of the paramagnetic states. Paramagnetic saturation can be

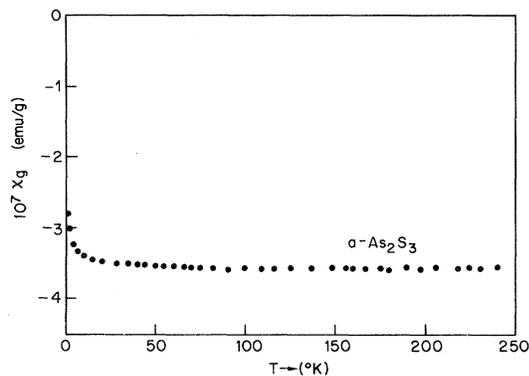


FIG. 1. Magnetic susceptibility χ_g of a nominally pure As_2S_3 glass vs temperature.

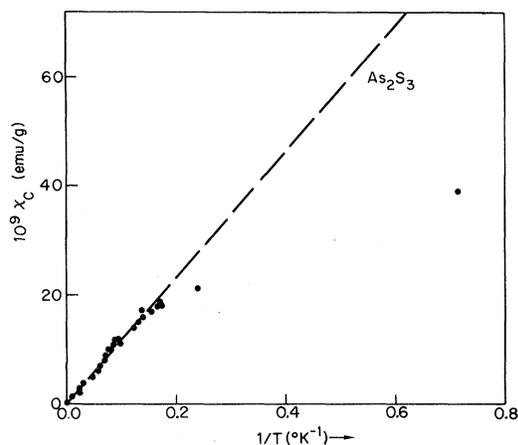


FIG. 2. Temperature-dependent part χ_C of the susceptibility for a nominally pure As_2S_3 glass vs inverse temperature, showing a large deviation at low temperatures from a $1/T$ law.

ruled out as the major cause, since saturation becomes significant only when $H/T \approx 10^4$ G/°K,¹⁹ and saturation does not cause such a sharp break in χ_C vs $1/T$. Exchange interactions cannot be so easily ruled out, even though the density of the postulated singly occupied states would be quite low ($n \sim 10^7$ to $10^{18}/\text{cm}^3$), because the states may be large enough in size (diam > 1000 Å) to allow significant spatial overlap. We shall later eliminate this possibility, however, by showing that the third mechanism is the cause of the deviation.

Crystal field splitting only occurs for paramagnetic centers with a spin greater than $\frac{1}{2}$, since spin- $\frac{1}{2}$ states (Kramers doublets) are not split by a crystal field.²⁰ Since it is expected that the spin of singly occupied localized states would be $\frac{1}{2}$, the existence of this mechanism would imply that the moments are due to impurities, most likely transition metals.

Spectroscopic semiquantitative analysis of 20 different samples of As_2S_x ($2.8 < x < 30$) and As_2Se_3 glasses showed that the only transition-metal impurity present was Fe. Sixteen of these samples showed iron in the 1–10 ppm range and four showed no iron. We believe that the results of three of these four can be understood as explained in the remaining text and the last is probably not a correct analysis. For most of the samples measured, iron impurities at about 3 ppm (assuming Fe^{3+} and $S = \frac{5}{2}$, $g \approx 2$) would easily explain the Curie tail. It is possible, however, that the iron could be in a nonmagnetic state (say, Fe^{2+} , $S = 0$) as in a number of chalcogenide compounds (for example, FeS_2). In order to distinguish between the two possibilities (exchange interactions or Fe impurities), we undertook several experiments.

First, we prepared amorphous As_2S_3 doped intentionally with small amounts of Fe (26 and 120 ppm by weight Fe). The susceptibility again showed a diamagnetic part and a much larger Curie part. Figure 3 shows χ_C vs $1/T$ for a sample containing 120 ppm Fe. Again it is apparent that a deviation in χ_C occurs near 6°K and χ_C (extrap $1.5^\circ\text{K})/\chi_C$ (meas $1.5^\circ\text{K}) = 2.12 \pm 0.03$. These results are the same as those obtained for the nominally undoped As_2S_3 (see Fig. 2). Similar results were obtained for materials doped with 26-ppm Fe. These data made it appear very likely that Fe impurities were causing the Curie tail.

Second, we felt that an explanation of the results of a previously reported experiment was needed to prove conclusively that only impurities were causing the tail. This experiment consisted of first measuring the susceptibility of crystalline As_2S_3 . (Polycrystalline As_2S_3 is very difficult to prepare in the laboratory, but is available as a natural crystal, orpiment.) The crystal was then melted *in situ* to form the glass and remeasured. The results showed that the crystalline material had a slightly temperature-dependent susceptibility up to room temperature but only a small $1/T$ -like upturn at low temperatures. The susceptibility of the glass, however, consisted of the usual temperature-independent part and a Curie part that was considerably larger than that observed in the crystal. Although the source of the temperature dependent background observed in the crystalline material was not understood, some diamagnetic materials are known to show temperature-dependent susceptibilities that are not connected with impurities and, in fact, remain partly unexplained (Ge, In,²¹ and others). It was thought, however, that since the low-temperature tail in the glass was considerably larger than that in the crystal,

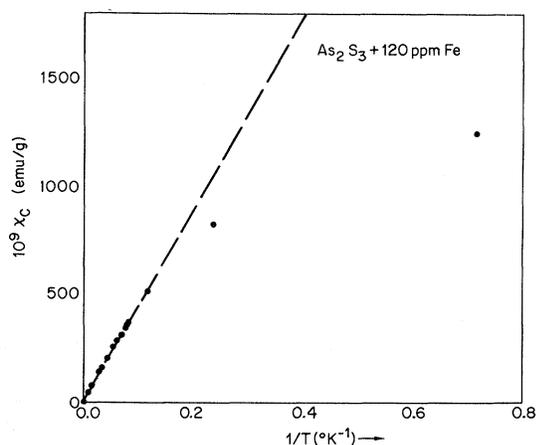


FIG. 3. χ_C vs inverse temperature for As_2S_3 doped with 120 ppm by weight Fe.

the excess Curie susceptibility in the glass must come from singly occupied localized states.

Since As_2S_3 cannot be crystallized in the laboratory, we decided to do the same type of experiment with intentionally Fe-doped As_2Se_3 , which can be prepared in both the polycrystalline and amorphous states. The results for $\text{As}_2\text{Se}_3 + 50$ -ppm Fe are shown in Fig. 4. In the polycrystalline state, the susceptibility shows complex temperature dependence with a small $1/T$ part at low temperature. The amorphous phase shows a much larger Curie part on top of a temperature-independent diamagnetic background. It appears that, in the polycrystalline material, the Fe separates out of the bulk of the material to form an iron-rich phase, probably at crystalline boundaries. This iron-rich (containing a large mole % Fe) phase is antiferromagnetic with a Néel temperature near 20°K . A small fraction of the 50-ppm Fe remains solvent in the bulk As_2Se_3 crystallites producing the small tail at low temperatures. When the glass is formed, the Fe remains completely solvent in the bulk as isolated paramagnetic impurities. Iron apparently has a much higher solubility in As_2Se_3 glass than in the polycrystalline material. This experiment appears to explain both the odd temperature dependence of the susceptibility of orpiment and the increased tail in the As_2S_3 glass as *entirely due to impurities*.

This segregation of impurities to crystalline defects or boundaries probably explains the spectroscopic analysis obtained for natural orpiment crystal. Orpiment was one of the four samples which showed no iron. Only a few milligrams of material is used in the analysis, and it is possible that a portion was used that included no large defects. The susceptibility results of the glass produced from the natural crystal show that the total average iron impurity in the crystals is about 5–10 ppm.

Since the glasses were prepared from 99.9999% pure As, S, or Se, the iron impurities must have been included during preparation. This may have come from dust in the air or have been leached out of the quartz containers in which the glasses were prepared (nominal Fe impurity in "ordinary" quartz tubing is 1–2 ppm).

We attempted to prepare As_2S_3 of very high purity by working under relatively clean conditions, using ultrapure quartz containers ($\text{Fe} \leq 0.2$ ppm), and heating to 700°C for only 1 h. As can be seen in Fig. 5, the Curie part of the susceptibility was considerably reduced. Also shown in Fig. 5 is the susceptibility of a similarly prepared high-purity As_2Se_3 sample.

It cannot be determined whether this small tail in the ultrapure As_2S_3 is still due to iron impurities at approximately a 0.3-ppm level, since the

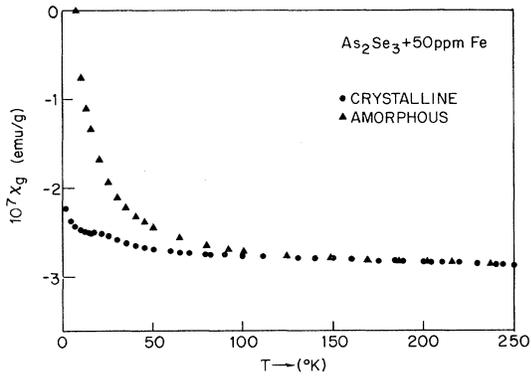


FIG. 4. Susceptibility of As_2Se_3 amorphous and polycrystalline doped with 50-ppm Fe vs temperature.

signal is so small, or to singly occupied localized states. It does allow us, however, to place an upper limit on the density of singly occupied localized states of $3 \times 10^{16} \text{ cm}^{-3}$.

The effects of doping As_2S_3 glasses with noble metals are not fully understood at present but appear also to be related to sample-preparation techniques. We have reported that doping these glasses with small amounts of Cu, Ag, or Au (0.1–1.0 at.%) caused a large reduction of the Curie tail. Since it would appear that these dopants must affect the magnetic moment on the Fe impurities, we prepared several samples of As_2S_3 with both Fe and Cu. Even when there was approximately 100 times as much Cu as Fe, we observed *no reduction* in the iron moment. The Cu does not appreciably affect the contribution of Fe to the Curie tail.

Although we believe that the results obtained with the Fe-doped As_2S_3 samples and the production of As_2S_3 with virtually no Curie tail proves that Fe impurities cause the tail, we feel that a plausible explanation of the previous results¹⁵ of doping with noble metals should be advanced.

These noble-metal results can be explained if several assumptions about the source of the Fe impurities are accepted. These assumptions are supported by a number of circumstantial facts. First we assume that the Fe impurities are leached out of the quartz containers by the molten As_2S_3 at 700 °C or perhaps diffuse through the quartz from the stainless-steel container that surrounds the sample tube. (This container was used to confine the sample in case of explosion or tube breakage.) This assumption is supported by the two following observations. The ultrapure As_2S_3 , showing virtually no Curie tail, was prepared in very high purity quartz tubing, sealed inside a second quartz tube, and held at 700 °C for only 1 h. Also, two of the four samples which showed no iron im-

purities by spectroscopic analysis were very sulfur rich, corresponding to $\text{As}_2\text{S}_{11.3}$ and $\text{As}_2\text{S}_{26.5}$. Since these samples contained such an excess of sulfur, they could only be heated to approximately 500 °C to avoid explosions from the sulfur vapor pressure. At 500 °C one would expect that the diffusion rate of Fe through quartz is considerably reduced from that at 700 °C, and much less Fe would be expected to contaminate the sample. Secondly, we must assume that the noble metals in the melt of As_2S_3 at 700 °C impede the transfer of iron from the quartz to the melt. This would be necessary since the noble metals do not reduce the magnetic moment of the Fe and thus must reduce the initial contamination. This assumption is supported by the fact that As_2S_3 wets so well to quartz that upon cooling and contraction of the melt the quartz tubing is broken by "implosion." When preparing the ultrapure samples, a second quartz tube is sealed around the first tube in order to prevent sample contamination when the first tube shatters on cooling. However, when the Cu is added to the melt, the wetting decreases and the quartz tubes do not break upon cooling of the melt. This reduced wetting may provide a surface barrier to diffusion of iron from the quartz to the melt.

B. Diamagnetic Shifts

Another problem of current interest is the change in diamagnetism observed in materials when they transform between the crystalline and amorphous phase. There are a number of difficulties associated with these measurements, and it is not certain when reading through the literature that all of these have been considered.

First, although the Faraday and Gouy methods are capable of high precision, the absolute accuracy of such data appears to be quite poor in many cases. Contamination by ferromagnetic impurities is quite common but can be easily de-

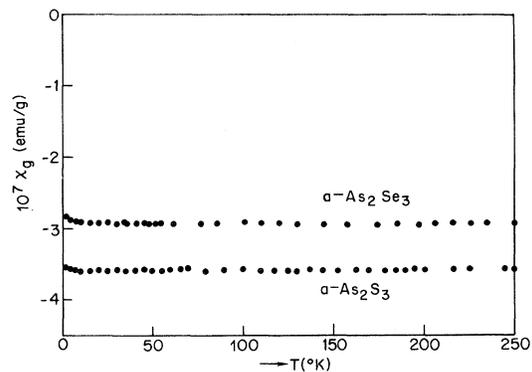


FIG. 5. Magnetic susceptibility of the purest As_2S_3 and As_2Se_3 glasses that we have produced.

tected by a dependence of the measured susceptibility upon the magnetic field. However, some authors fail to make or report such measurements. Calibration of the susceptibility vs well-characterized high-purity standards is not usually reported, so that estimates of the absolute error in the susceptibility cannot be made. To show that this problem is not insignificant, we quote some reported susceptibilities of As_2S_3 glass: $\chi_g = -0.285 \times 10^{-6}$ emu/g,²² -0.336×10^{-6} emu/g,²³ -0.355×10^{-6} emu/g $\pm 2\%$ (this work).

A second problem involves the structure of the crystalline phase. None are cubic and consequently single crystals have two or three principal magnetic susceptibilities. Measurements are usually made of the average susceptibility, where the sample is powdered or polycrystalline, but it is necessary to assure random orientation of the crystallites. Randomness is difficult, if not impossible, to achieve for some of these materials, especially when powdered, since the habit of the crystallites is distinctly two dimensional, as in the case of orpiment. Thus randomness should be assured in a separate way, e. g., by x rays, or each of the principal susceptibilities measured. Also, a number of glass systems, usually the ternary and quaternary systems, phase separate when crystallized. It is not clear in these systems whether to ascribe diamagnetic shifts to the amorphous to the crystalline ($a \rightarrow c$) transition, to the phase separation, or in fact to some combination of both.

Some glass formers are polymorphic in the crystalline phase, and the susceptibility of each polymorph may be different from the other phases. It is apparent, then, that the polymorph must be clearly identified if detailed comparisons are to be made. Sulfur and selenium are examples of glass formers that show this polymorphism. Finally, the crystalline phase of some glass formers shows a marked and complex temperature dependence that cannot be ascribed to impurities. An example of such a material is CdAs_2Ge .² In these cases it is not clear how to subtract out the temperature dependence to obtain an intrinsic change due to the $a \rightarrow c$ transition, or if indeed this separation is possible.

If we avoid glass formers that phase separate upon crystallization and those that show temperature dependent crystalline susceptibility, only a relatively few semiconducting glass formers remain to be studied. The results for five different materials are shown in Table I. Those for S, Se, and CdAs_2 are published in other work, but the absolute accuracy of the CdAs_2 results is not known. The results for As_2S_3 and As_2Se_3 are discussed in more detail below.

As previously noted, As_2S_3 is difficult to crys-

TABLE I. Magnetic susceptibility of five different materials in the polycrystalline and amorphous phases in units of 10^{-6} emu/g.

Material	Magnetic susceptibility		Ref.
	Polycrystalline	Glassy	
S	-0.485	-0.485	11, 12
Se	-0.272	-0.291	11, 12
CdAs_2	-0.258	-0.269	3
As_2S_3	-0.345	-0.355	This work
As_2Se_3	-0.287	-0.292	This work

tallize in the laboratory; consequently, we used the natural crystals, orpiment, for our measurements. Since we could not prepare powders that would be randomly oriented in our quartz measuring tubes, we attempted to measure the principal susceptibilities of the crystal.

As_2S_3 crystallizes in the monoclinic system with $a = 11.46 \text{ \AA}$, $b = 9.57 \text{ \AA}$, $c = 4.22 \text{ \AA}$, and $\beta = 90^\circ 30'$. Since β is very close to 90° , the system is only very slightly distorted from orthorhombic. The atoms are arranged in a distinctly layered structure, and indeed cleavage parallel to the layers (perpendicular to the b axis) is as easy as in mica or graphite. The layers are quite separated from each other and are held together by van der Waals forces. One of the principal magnetic axes is parallel to b and the other two are in the plane of the layer and practically coincident with a and c , since the system is almost orthorhombic.

Our Faraday balance was modified so that single crystals could be held without being able to rotate. Then by orienting the crystal so that the magnetic field is parallel to one of the principal axes, that particular principal susceptibility is measured. This method gives accurate results only if the ratio of the different principal susceptibilities is not too large.²⁴ For our apparatus, anisotropies in the susceptibility as large as a factor of 5 have been accurately measured.

We measured the principal susceptibility perpendicular to the layers, χ_b and the approximate average of the susceptibility parallel to the layers, $\frac{1}{2}(\chi_a + \chi_c)$. The sample was made from several "slabs" of As_2S_3 cut from the same crystal. Each piece was rotated a different amount about the b axis, and then all of them were glued together with their b axes parallel. The weight of the glue was less than $\frac{1}{2}\%$ of that of the sample, but its susceptibility is known and was subtracted from the total. The measurements were made with the magnetic field parallel (to obtain χ_{\parallel}) and perpendicular (χ_{\perp}) to the layers and the average crystalline susceptibility given in Table I is $\frac{1}{3}(\chi_{\perp} + 2\chi_{\parallel})$. χ_{\perp} and χ_{\parallel} differed from each other by only 3%, and thus the anisotropy ratio is not large

and the result is expected to be accurate. Although measurements of the principal susceptibilities of monoclinic crystals by means of torque or oscillation methods are rather difficult (but quite accurate), it would be worth undertaking these measurements as a check on our own. This is especially true since the crystalline and amorphous phase susceptibilities appear to differ by only a small amount.

As₂Se₃ was prepared in polycrystalline ingots by cooling the melt to 280 °C and holding for 24 h, before the final cool to room temperature. The product contained small crystallites of dimensions approximately 0.1 mm on an edge, and that appeared randomly oriented when viewed in a microscope. As a further check on the randomness of the crystallite orientation, several bars were cut from the ingot in different orientations, and χ_g at room temperature for each was found to be the same (actual scatter 1%) at -0.287×10^{-6} emu/g. The measured χ_g for the glassy As₂Se₃ was found to be -0.292×10^{-6} emu/g.

Since the above-measured values for the crystalline and glassy As₂Se₃ differ by 1.7%, which is less than the maximum absolute error on the difference of 4%, a method with smaller absolute error for differences in susceptibility was then used. The method consists of sealing the polycrystalline material in a quartz tube, measuring, making the glass *in situ*, then remeasuring. Since the container and sample remain the same (except for the physical state of the sample), relative shifts on the order of 1% are observable. The shift observed was 1.0%, showing that the difference, if any, in susceptibilities is quite small.

V. CONCLUSIONS

When glasses are prepared in such a way as to avoid contamination with iron impurities, we have shown that the density of intrinsic singly occupied localized states is below 3×10^{16} per cm³. The low-temperature paramagnetic susceptibility of our previously prepared, nominally undoped glasses was shown to be identical in character to that of samples intentionally doped with iron at the 100-ppm level. Iron was also shown to segregate to an iron-rich antiferromagnetic phase in crystalline As₂Se₃ even when the doping level was as low as 50 ppm. This segregation apparently explains the previously reported result that the low-temperature paramagnetic susceptibility observed in As₂S₃ increases upon melting the natural crystals

(orpiment) to form a glass. It is suggested that the iron diffuses out of or through the quartz containers in which the As₂S₃ is prepared.

We find that the increase in diamagnetic susceptibility observed in the amorphous form over the crystalline form is less than 1% for As₂Se₃, and (3 ± 2%) for As₂S₃. This corresponds to other reported values of 7% for Se, 0% for S, and 5% for CdAs₂. These shifts are smaller than those we discussed in a preliminary paper; however, the accuracy of our measurements has since been improved considerably. The shifts are also much smaller than those reported for other amorphous materials that are difficult to prepare in the "glassy" state, such as 300% for Ge.²⁵

VI. COMMENTS

Apparently the mere loss of long-range order, without breaking atomic bonds, does not produce a large number of singly occupied states. It has been shown that, in poor-glass-forming systems, free spins arise from broken bonds but the density of such states is markedly dependent upon the thermal history of the sample.

These experiments do not measure the total density of localized states, since they may be doubly occupied and thus have zero magnetic moment. One may only speculate that the concentration of singly occupied states should be a reasonable fraction of all the states in the gap because of electron-electron repulsion effects. Our results would then indicate that the total concentration of states in the gap in pure ideal glasses is small, in agreement with the large optical transparency of pure glasses below the absorption edge. Recently, it has been suggested that electron-phonon interactions in glass systems may produce atomic displacements that subsequently greatly reduce the density of localized states that might be expected on a Mott-CFO model.²⁶ It also has been pointed out that little, if any, evidence for an observable density of disorder-induced localized states exists in ideal glasses,²⁷ this work being no exception.

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Theory of the Electron Mobility in Inversion Layers on Oxidized Silicon Surface at Room Temperature

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A theoretical calculation of the metal-oxide-semiconductor (MOS) surface mobility at room temperature is presented. It is found that the three-dimensional degenerate-electron-gas model, with specular surface scattering in the MOS inversion layer, fits the experimental data for channel mobility of a typical MOS transistor at high surface electric fields quite well. Calculations based on diffuse surface scattering are also presented and compared to experimental data for the specially treated MOS transistor of Fang and Triebwasser. It is again found that the theory agrees with the data for this transistor. The three-dimensional electron-gas model is justified by means of a calculation of the average thickness of the inversion layer. The theoretical calculations show that the channel mobility should be proportional to $E_z^{-0.4}T^{-1}$, where E_z is the surface electric field and T the temperature, assuming the mean free path to be constant (i. e., lattice scattering).

I. INTRODUCTION

The metal-oxide-semiconductor (MOS) surface mobility has been extensively studied, both experimentally¹⁻⁴ and theoretically.⁵⁻¹⁰ However, the theoretical investigations based either on the three-dimensional electron model⁵⁻⁷ or a two-dimensional quantum-mechanical model⁸⁻¹⁰ have not given good agreement with experimental data. The first paper on the MOS surface mobility was that of Schrieffer,⁵ who followed similar calculations by Fuchs¹¹ and Sondheimer¹² in the calculation of the size effect on the conductivity of thin metallic films. Schrieffer showed the surface mobility of the MOS inversion layer to be inversely propor-

tional to the surface field when he assumed a constant relaxation time and surface field, completely diffuse surface scattering, and a simple energy surface. Several other later papers gave more or less similar results.^{3,6,7} However, recent experimental results show that the mobility of the surface layer decreases more slowly than these results predict.¹⁻⁴ At low temperatures Fowler, Fang, Howard, and Stiles¹³⁻¹⁴ have performed experiments in which they are able to observe Shubnikov-de Haas oscillations in the electron gas at the inverted surface of a *p*-type silicon MOS. The experiment indicates that the motion of the carriers is quantized in the direction perpendicular to the surface. This phenomenon can occur only