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Effect of Disorder on the Temperature-Independent Magnetic Susceptibility of Se and Ge[†*]

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Observations are reported of the room-temperature specific diamagnetic susceptibility of both the polycrystalline (χ_c) and amorphous (χ_a) forms of Se and Ge using a new type of rotating-sample magnetometer. Measurements performed on 99.9999% pure Se yielded a ratio $\chi_a/\chi_c = 1.0 \pm 0.05$. For Ge a ratio $\chi_a/\chi_c = 2.7 \pm 0.3$ was obtained. Although an enhanced diamagnetism has been observed in the disordered modification of several materials, the ratio for Ge is the largest yet reported. The amorphous Ge was prepared by evaporating a 3-μ-thick film onto a Pyrex substrate at room temperature. The enhanced diamagnetism of the *a*-Ge was observed to be independent of annealing below crystallization.

I. INTRODUCTION

There has been an increasing interest in the magnetic properties of amorphous (*a*-type) semiconductors over the past several years. This has resulted, in large part, from initial reports of disorder-produced changes in the magnetic susceptibility of several semiconductors. Of particular interest has been the observation of a disorder-produced increase in the temperature-independent diamagnetic component of the susceptibility. This diamagnetic enhancement was originally reported to occur in such diverse materials as Se,[1] As_2Se_3, As_2S3,[2] $CdAs_2$,[3] and $CdGeAs_2$[4] and, for a time, semed to be a general phenomenon associated with the amorphous state. Recent work has, however, indicated that earlier measurements were in error and many of the previously reported materials are now believed to show no diamagnetic enhancement. This paper reports new measurements on *a*-Se and *a*-Ge,[5] summarizes the present state of the problem, and discusses suggested theoretical approaches to understanding this phenomenon.

The materials *a*-Ge and *a*-Se were chosen for two reasons. First, they are each somewhat representative of the two broad classes of covalently bonded noncrystalline semiconductors. Se represents the class of "lone-pair" semiconductors or those materials in which group-VI elements are present in twofold coordination, and Ge represents the class of tetrahedrally coordinated semiconductors. Second, both are elemental and hence available in high-purity forms in which stoichiometric problems are obviated. Because of this high purity, the Curie contribution resulting from impurities carrying unpaired spins will be negligible at room temperature, and thus the temperature-independent component of the susceptibility can be measured directly.

II. EXPERIMENT

The room-temperature specific magnetic susceptibility of the samples was measured with a rotating-sample magnetometer described in another publication.[6] The basic operation of the instrument is illustrated in Fig. 1. Two samples contained in fused-silica sample tubes are spun rapidly by a rotating-sample holder in a static magnetic field. The motion of the samples past a stationary pickup coil causes a periodic change in the magnetic flux threading in the coil. This change in flux induces an emf in the coil in the form of a pulse train where successive pulses are due to, alternately, sample one and sample two. After electronically selecting and integrating the pulses due to one or the other sample, one obtains at the output of the instrument a voltage level proportional to the total magnetic moment of the selected

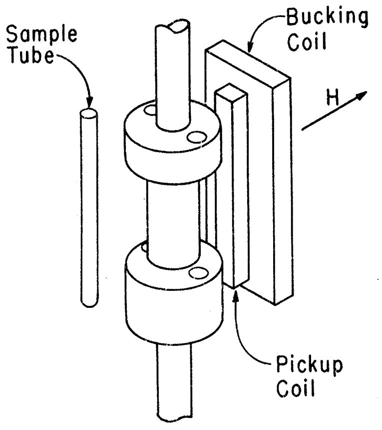

FIG. 1. Rotating-sample magnetometer: Rotating-sample holder and pickup-coil geometry. A sample tube is shown removed from the holder.

sample.

The ratio of voltages obtained when one first selects one sample and then the other can then be related to the ratio of the magnetic susceptibilities of the two samples. If one of the samples in the holder is chosen to be a calibration standard, one obtains a measurement of χ for the other sample. In this way we are able to measure specific magnetic susceptibility with a relative error of ± 2%.

The Se samples were prepared by placing 1 g of 99.9999% pure polycrystalline Se into the fused-silica sample tubes. The tubes were then flushed with Ar, evacuated to 10^{-4} Torr, and sealed. The Se was vitrified by heating the prepared samples to 300 °C for 30 min, followed by a rapid quench in a room-temperature water bath. A magnetic-susceptibility measurement was made immediately following the quench. The Se was then crystallized into its stable trigonal modification by heating the sample tube to 195 °C for 6 h. After allowing the sample to cool slowly to room temperature, the magnetic susceptibility was again measured. The ratio of the specific magnetic susceptibility of the amorphous phase to that of the crystalline phase thus obtained was $\chi_a/\chi_c = 1.00 \pm 0.05$. This value is at variance with the value 1.16 ± 0.04 previously reported by Busch and Vogt,[7] but is consistent with recent measurements by Bagley *et al.*[8] and White and Koehler.[9]

Amorphous Ge differs from *a*-Se in several respects. First, it is not a true glass in the sense that it cannot be obtained by rapid quenching from the melt. Accordingly, it is necessary to initially prepare the *a*-Ge as an evaporated thin film and then to transfer it from its substrate to the sample tube. Second, previous measurements have shown that, unlike *a*-Se, many of the optical and electrical properties of *a*-Ge are strongly dependent on the thermal history of the material. Therefore, one expects the ratio χ_a/χ_c to be properly defined only if one also specifies the annealing history of the amorphous sample. For this reason a series of measurements was made as the sample was annealed at successively higher temperatures.

Crystalline Ge ($\rho \approx 40$ Ω cm at 300 K) was electron-beam evaporated from a graphite crucible at a pressure $< 10^{-6}$ Torr onto a large Pyrex substrate located 25 cm from the crucible. Thermocouples on the Ge side of the substrate allowed the film temperature to be monitored during evaporation. In order to keep the film temperature below 75 °C, the Ge was deposited in a series of short evaporation runs. The deposition rate was ≈500 Å/min. After ≈3 μ of *a*-Ge had been deposited, the substrate was removed from the evaporation chamber and the *a*-Ge was scraped off with a Pyrex microscope slide. This procedure produced 600 mg of *a*-Ge in the form of small flakes, typically of dimensions 0.1×0.3 cm. A small quantity of the material thus obtained revealed no evidence of crystallinity when examined by x-ray powder diffraction.

The *a*-Ge sample was prepared by placing this scraped material into a fused-silica tube using the procedure for the Se sample.

The results of the annealing experiment appear in Fig. 2. The points in Fig. 2 represent the value of χ measured after a 6-h anneal at each temperature.

There are two interesting aspects to this curve. First, one notices that the magnetic susceptibility of the unannealed amorphous phase is a factor of 2.75 more diamagnetic than the crystalline. This value of χ_a/χ_c is the largest diamagnetic enhancement factor reported for any amorphous semiconductor. Second, and perhaps most striking, is that this enhanced diamagnetism is independent of annealing to within our experimental uncertainty up to temperatures of ≈ 350 °C, where crystallization occurs. An examination of the crystallized material revealed that the original dimensions of the Ge flakes were unchanged through the annealing process.

This lack of annealing dependence is in strong contrast to the behavior of optical, electrical, and mechanical properties of the material, many of which—for example, resistivity, position of the fundamental absorption edge, porosity to water vapor, and so forth—show strong annealing dependence.[10] This suggests that the temperature-independent diamagnetic susceptibility provides a probe of the effect of disorder on the electronic states of this system which is unaffected by the presence of cracks or voids. Although unpaired-spin densities of 10^{20} spin/cm^3 were observed in ESR measurements[11] performed on an identically

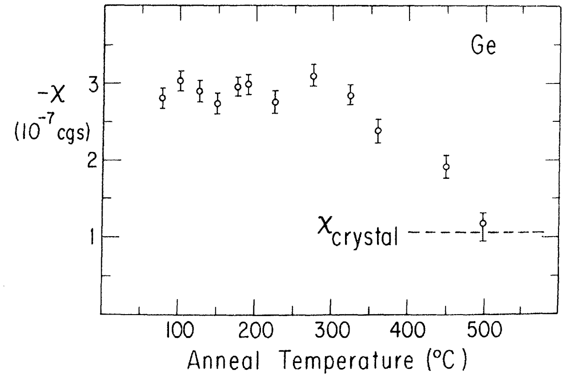

FIG. 2. Annealing dependence of the room-temperature specific magnetic susceptibility of *a*-Ge. Each point represents the value measured after a 6-h anneal at the indicated temperature. Crystallization is complete at 500 °C.

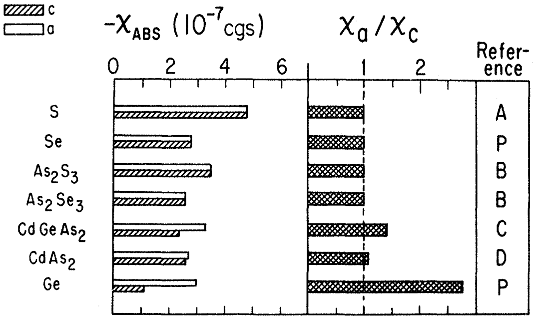

FIG. 3. Room-temperature specific magnetic susceptibility of the amorphous and crystalline modifications of several semiconductors. In the left-hand column, crystalline and amorphous values are indicated by shaded and unshaded bars, respectively. In the right-hand column, bars indicate the ratio χ_a/χ_c. (A) B. G. Bagley, F. J. DiSalvo, and J. V. Waszcak, Bull. Am. Phys. Soc. 16, 1409 (1971); (B) F. J. DiSalvo, Phys. Rev. B 6, 4574 (1972); (C) L. Červinka, A. Hrubý, M. Matyáš, T. Simček, J. Škácha, L. Štourač, P. Hösche, J. Tauc, and V. Vorlíček, J. Non-Cryst. Solids 4, 258 (1970); (D) M. Matyáš, Phys. Status Solidi 43, K63 (1971); (P) Present work.

prepared sample of *a*-Ge, the spin contribution to the magnetic susceptibility of the material in this temperature region is smaller than the uncertainty in the measurement. One therefore expects that the observed annealing dependence of this unpaired-spin density will not be detectable in the magnetic-susceptibility measurement.

III. DISCUSSION

Figure 3 shows a table of measurements of the room-temperature magnetic susceptibility of several amorphous semiconductors and their crystalline counterparts. It is interesting to note that among the "lone-pair" semiconductors As_2S_3, As_2Se_3, Se, and S, there exists either a very small change in χ or none at all as the material goes from the ordered to the disordered state. The tetrahedral and quasitetrahedral materials $CdAs_2$, $CdGeAs_2$, and Ge, on the other hand, display a wide variation in values of χ_a/χ_c.

Recently, White and Anderson[12] have suggested two mechanisms which might be responsible for the phenomenon of diamagnetic enhancement. One is an extra diamagnetic contribution from the disorder-created localized valence states, which have become spatially large by lying in energy near the mobility edge. This contribution has the form of the classical Langevin expression for atomic diamagnetism:

$$\chi_{\text{loc}} = -(Ne^2/6mc^2)\,\langle r^2\rangle \ , \qquad (1)$$

where N is now the volume density of localized states and $\langle r^2\rangle$ is an appropriate average of the square of the radius of the states. The second mechanism arises from a reduction in the paramagnetic interband contribution. This contribution, present in both the crystal and amorphous states, is of the form

$$\chi_{vv} = \mu_B^2 \sum_k \sum_{k'} \frac{|\langle k'_1|\vec{\mathrm{L}}|k0\rangle|^2}{\epsilon_{k'1}-\epsilon_{k0}} \ , \qquad (2)$$

where the band indices 0 and 1 refer to the valence and conduction band, respectively. White and Anderson argue that, assuming that the matrix elements of the angular-momentum operator are unchanged as the material is disordered, a change in χ_{vv} can occur as a result of differences in the manner in which the energy denominator is summed in the crystalline and amorphous case. In the crystalline case, k conservation causes the sum over energy denominators to become

$$\sum_k \frac{1}{\epsilon_{k1}-\epsilon_{k0}} \ , \qquad (3)$$

while in the amorphous case the sum remains

$$\frac{1}{N}\sum_k \sum_{k'} \frac{1}{\epsilon_{k'1}-\epsilon_{k0}} \ . \qquad (4)$$

It is argued that if the gap minimum of the material occurs in a restricted region of k space, the amorphous average will give a smaller value than the crystalline and thus cause an increase in the over-all diamagnetism of the disordered phase.

It is further argued that the existence of this second mechanism can be inferred from the experimental observation that the index of refraction measured at energies below the band gap in many amorphous materials is considerably smaller than the crystalline value. Since ϵ and hence the refractive index can be written in the form of a sum of matrix elements of the electric-dipole operator over the same energy-difference denominator, it is argued that differences in the manner in which the energy denominator is averaged in this expression can result in a reduction of the refractive index in a way analogous to the reduction of the paramagnetic interband term.

One notices in the literature, however, that this disorder-produced reduction in refractive index n is large only in the chalcogenide amorphous semiconductors which, we have seen, show little or no diamagnetic enhancement. The tetrahedrally coordinated materials exhibit either a small change in n or no change at all. As an example, values of the infrared refractive index of amorphous and crystalline Ge and Se are presented in Table I. As a way of explaining this lack of correlation, it has been suggested recently[16] that the reduced refractive index observed in the glassy form of the chalcogenide materials can be explained to a large extent simply on the basis of the density change which

TABLE I. Refractive index n and average refractive index $\langle n\rangle$ for amorphous (a) and crystalline (c) Se and Ge.

Material	n	$\langle n\rangle$	Reference
c-Se	($\perp$) 2.78 ± 0.02 ($\parallel$) 3.58 ± 0.02	3.05 ± 0.06	13
a-Se	2.44 ± 0.003	2.44 ± 0.003	14
c-Ge	4.01	4.01	15
a-Ge	4.05 ± 0.1	4.05 ± 0.1	15

occurs when these materials are disordered. As an example, we will consider Se.

Crystalline Se is composed of large molecular units (helical chains in the trigonal modification and eight-membered rings in the monoclinic modification) in which the bonding is primarily covalent. These units are then bound to one another by van der Waals forces. If one assumes that, as the material is disordered, the covalent bonding is unchanged to first order, then one expects that the observed density change results largely from changes in the van der Waals binding. On the basis of these assumptions, one would expect a decrease in refractive index to occur simply as a result of the decrease in density, independent of the presence or absence of long-range order.

To make the argument quantitative, let us assume that the refractive index of Se is described by the Lorenz–Lorentz relation

$$(n^2-1)/(n^2+2)=\tfrac{4}{3}\pi N\alpha \;, \qquad (5)$$

where N is the volume density of molecular units and α is the average molecular polarizability, which is assumed to be independent of density. It is, of course, impossible to justify the use of Eq. (5) on a first-principles basis, since its derivation assumes the existence of a local-field correction of the form

$$E_{\text{loc}}=E_{\text{app}}+\tfrac{4}{3}\pi P \;. \qquad (6)$$

This expression is strictly valid only for cubic or isotropic systems of van der Waals bound molecules. There is, however, convincing experimental evidence for the validity of Eq. (5) in describing the relationship between refractive index and density in many chalcogenide materials. Kastner[17] has shown, for instance, that Eq. (5) predicts the change in refractive index with pressure in several chalcogenide materials with fair accuracy. In the case of Se, the prediction is in error by only 4%. Perhaps more astonishing, Hilton *et al.*[18] have shown that Eq. (5) predicts the refractive index of 28 chalcogenide glasses with an average error of ±4.1% when one simply estimates α by a weighted average of the polarizabilities of the individual constituents of the glass which are, in turn, approximated by a constant times the cube of the elemental radius of the constituent.

Substituting refractive-index values of Se from Table I into Eq. (5) and taking N to be the number of Se atoms per unit volume, one obtains the polarizability for the crystalline material $\alpha_c = 4.8 \pm 0.4\times 10^{-24}$ cm^3 and the polarizability for the amorphous material $\alpha_a = 4.54 \pm 0.03\times 10^{-24}$ cm^3. One sees that the two values are within experimental error of one another. Calculations for As_2S_2 and As_2Se_3 give similarly good agreement. For both of these materials α_a and α_c agree to within 5%. Barring the possibility of fortuitous agreement, this stands as *a posteriori* justification for the assumption that the covalent bonds are largely unchanged in these materials as a result of the density change, and further confirms the observation that Eq. (5) provides a good prediction for the refractive index. Finally, it indicates that the reduced refractive index in the amorphous phase of the chalcogenide glasses can be accounted for in a way that makes no use of the degree of long-range order of the material. Thus, it is clear that evidence for the operation of the mechanism described in Eq. (2) in the chalcogenide semiconductors can be obtained from refractive-index measurements only if one first takes into account the large effect of the change in density which occurs on vitrification.

Let us consider now the mechanism described by Eq. (1). In this mechanism an excess diamagnetism arises in disordered materials from the spatially large localized states lying near the valence-band mobility edge. For these states the expectation value of the operator r^2 will be large, and thus White and Anderson argue that the diamagnetic contribution from these states plus the extended valence-band states will exceed the diamagnetic contribution from the extended states in the valence band of the undisordered material. It has been pointed out,[19] however, that unless disorder produces significant mixing of the unperturbed valence-band states with higher-lying states, the value of the over-all valence-band diamagnetic contribution will be unchanged. This is a consequence of the principle of spectroscopic stability which states that quantities which can be expressed in the form

$$Q=\sum_k \langle k|F|k\rangle \qquad (7)$$

are invariant under unitary transformations to a new basis set where F is an observable and the sum is over all of the states of a complete basis set. If, as one might expect, the localized states nearest the valence band can be constructed from linear combinations of the unperturbed valence-band states, then one expects no excess diamagnetic contribution from these spatially large states. Localized states further into the gap may involve an admixture of states from higher bands and thus yield an extra contribution to the diamagnetism. Such deep states, however, probably have a small density and are rather localized, causing their contribution to the over-all diamagnetism of the material to be small.

In the light of the lack of evidence for the operation of the mechanism of Eq. (2) and the theoretical argument against the operation of Eq. (1), one is not surprised that the chalcogenide materials show no diamagnetic enhancement. It is, however, difficult to understand the diamagnetic enhancement observed in some of the tetrahedrally coordinated materials, particularly a-Ge. Perhaps in these materials there is enough interband mixing in the creation of localized states to render the argument against the operation of the "large-localized-state" mechanism invalid. On the other hand, there may be other diamagnetic enhancement processes. For example, the matrix elements in the interband term [Eq. (2)] may be strongly affected by disorder in these materials, resulting in a decreased paramagnetic contribution from this term. In the case of a-Ge, previous experience with these films and their notorious dependence on preparation conditions should also cause one to be cautious in immediately ascribing an observed characteristic of the film to disorder alone. It is important to determine initially whether the enhanced diamagnetism observed in a-Ge is a genuine effect of disorder as indicated by the annealing study or somehow associated with voids and other mechanical nonuniformities present in the film.

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