onal field acting on the O_2^+ molecular cation into a widely separated singlet and a doublet of the order of 10^4 cm^{-1}, which make a very small contribution to g_{eff} and to ϵL, where ϵ is the infinitely small unquenched orbital contribution to χ. This is confirmed by EPR measurements[4] which show $g_{eff} = 1.998$.

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OPTICAL AND MAGNETIC INVESTIGATIONS OF THE LOCALIZED STATES IN SEMICONDUCTING GLASSES

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We measured optical absorption and magnetic susceptibility of amorphous As_2S_3 as a function of temperature. An exponential variation of absorption constant with photon energy was found in the range $0.09 < \alpha < 0.5$ cm^{-1}. A Curie term in the susceptibility was shown to be characteristic of disorder in the vitreous material. A model relating the weak absorption tail to the susceptibility requires highly localized states having an exponential energy distribution in the gap.

Localized states in the energy gap have been predicted by theory as a typical property of highly disordered materials,[1] and their concentration in chalcogenide glasses was assumed to be as high as 10^{19} cm^{-3}. The exponential optical absorption edge observed in these glasses for the absorption constant in the range of $0.5 < \alpha < 10^3$ cm^{-1} was tentatively attributed to these states.[2] However, more recently it has been suggested[3,4] that this part of the absorption curve might better be interpreted as due to interband transitions with the absorption edge broadened by internal electric fields.[4] Below this exponential edge an optical absorption extending into the infrared region has been noticed previously.[5,6] We report here detailed results for this region in vitreous As_2S_3, and we have also obtained qualitatively similar results for vitreous As_2Se_3. In addition, we measured the temperature dependence of the magnetic susceptibility, particularly at low temperatures, on the same samples. We show that the results from these two different types of measurement can be interpreted in terms of localized states near the band edge, and new information about their properties is obtained.

The absorption curve of vitreous As_2S_3 can be divided into three regions.[4] Two have been described by Kosek and Tauc[7]: one above $\alpha \approx 10^3$ cm^{-1} where $\alpha \sim (\hbar\omega - E_g)^2$, and E_g is the optical gap, and the other for $0.5 < \alpha < 10^3$ cm^{-1} where $\alpha \sim \exp(\hbar\omega/E_c)$, with $E_c \approx 0.05$ eV. In the third region which we report here is a tail at $\alpha < 0.5$ cm^{-1} in which $\alpha \sim \exp(\hbar\omega/E_t)$ with $E_t = 0.3$ eV.

Figure 1 shows the absorption curves at various temperatures with the new results in the lower part of the diagram. The results for the tail at low α values have been very carefully determined using a Cary model 14 spectrometer on samples up to 2 cm thick with very good optical finishing techniques in order to avoid errors from nonparallel faces and surface roughness. The reflection losses were calculated from published refractive index data,[8] and checked against transmission values for different thicknesses. The weak absorption remaining after these factors were eliminated was shown to be intrinsic to the vitreous As_2S_3 rather than due to light scattering or ionic impurity absorption, by direct measurement of light scattering at various wavelengths, and by repeating the original measurements on samples prepared from highly purified starting materials. The results were practically the same for commercial samples (Servofrax) containing about 500 ppm total impurity ions and for laboratory batches containing less than 10 ppm total impurities. The measured light scattering value
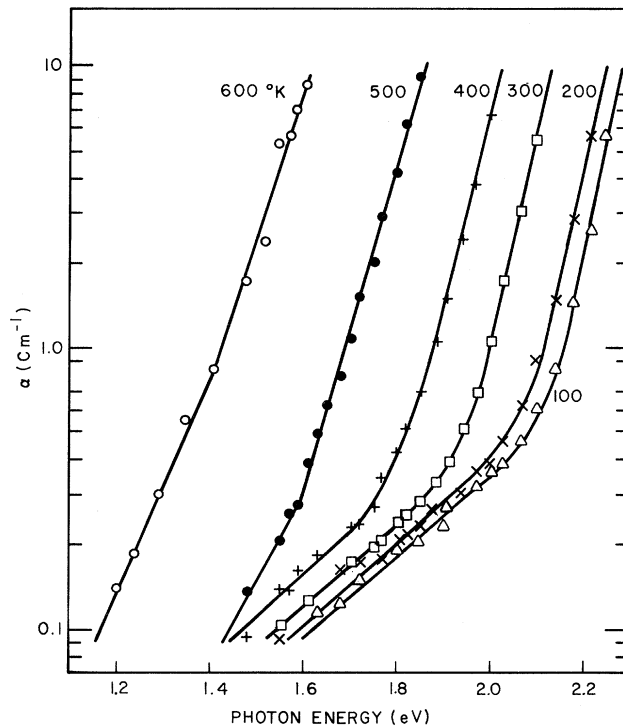
FIG. 1. Absorption constant versus photon energy in vitreous As_2S_3 at various temperatures.

FIG. 2. Magnetic susceptibility (emu/g) as a function of temperature for crystalline (c) and amorphous (a) As_2S_3.

corresponded to an apparent absorption level less than $\alpha = 0.04$ cm^{-1} for the samples used, indicating that this was not the origin of the weak absorption tail.

The magnetic susceptibility measurements were made by the Faraday method in the temperature range from 1.6 to 300°K. Our results for vitreous As_2S_3 and for crystalline samples (orpiment) are shown in Fig. 2. The susceptibility of the amorphous material has a temperature-independent part on which is superimposed a Curie term which becomes apparent below 80°K.[9] This term corresponds to a concentration of 6×10^{17} free spins per cm^3. This concentration of spins is not accounted for by foreign ions because analysis shows that the impurity level is too low, and because of the following experiment. We measured the susceptibility of crystalline As_2S_3 in a sealed silica ampoule, and of the vitreous As_2S_3 sample produced by melting the orpiment in situ. The resulting susceptibility curves were the same as those shown in Fig. 2. In contrast to the amorphous As_2S_3, the crystalline material shows a temperature-dependent part over the whole temperature range. The insert of Fig. 2 indicates that the Curie term in crystalline material, if present at all, is at least one order of
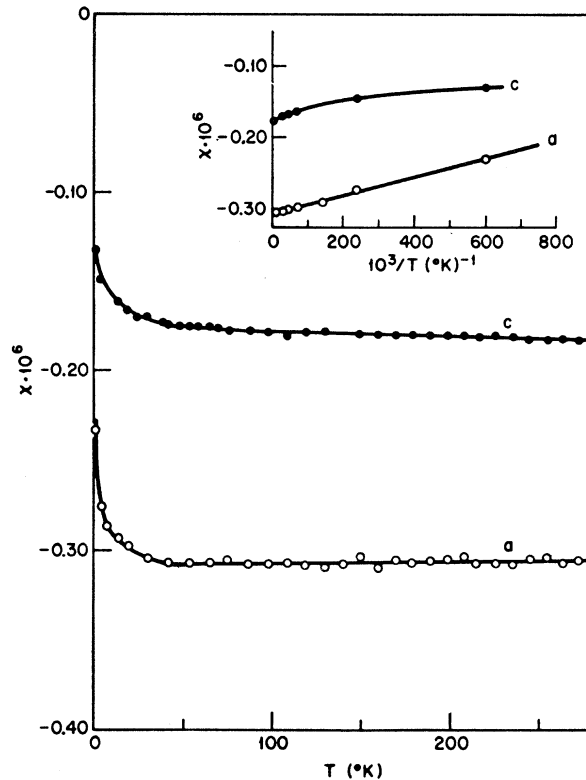
magnitude less than in the vitreous material, and therefore the Curie term in the vitreous material represents an intrinsic property due to the disorder.

The different temperature dependence of the optical absorption tail ($\alpha < 0.5$ cm^{-1}) and the exponential edge ($0.5 < \alpha < 10^3$ cm^{-1}) and their different behavior when the material passes through the softening point ($\approx 470°K$) imply that the two parts of the absorption arise from different mechanisms. We suggest a model in which localized states in the energy gap near the top of the valence band give rise to the Curie term of the magnetic susceptibility, and transitions from those localized states into the conduction band states are responsible for the optical absorption tail.[10] No quantitative theory has been worked out to describe the wave functions of such localized states. We can make a rough estimate by constructing them as linear combinations of the valence-band wave functions in the corresponding crystal in a part $B_0 = (2\pi)^3/V_0$ of the Brillouin zone[11] where V_0 is the volume over which the wave function is localized. The ab-

sorption constant is approximately[12]

$$\alpha(\omega) = \frac{\pi^2 e^2 \hbar}{mc} \frac{f}{n} \int_{E_g - \hbar\omega}^{\infty} V_0(E_i) N(E_i)$$

$$\times g(\hbar\omega - E_g + E_i) dE_i, \qquad (1)$$

where E_g is the optical energy gap (2.32 eV at 300°K from Ref. 7); $N(E_i)$ is the energy distribution of the concentration of localized states, whose energy E_i is measured from the top of the valence band; f is the oscillator strength for transitions between the valence band and the conduction band, which is of the order 1; n is the index of refraction (2.6 in our case); $g(E)$ is the conduction-band state density which we take equal to the free-electron density in the whole band. We obtain an exponential dependence of α on $\hbar\omega$ if $V_0(E_i) N(E_i)$ is dominated by an exponential function of E_i. Comparing Eq. (1) with the experimental results we find that we cannot reconcile the high concentration of states found from the magnetic measurements with the values found for α unless we assume that $V_0(E_i)$ is of the order of the atomic volume. The methods used for the deduction of Eq. (1) are not applicable if $V_0 < (2\pi)^3/B$ (B is the volume of the Brillouin zone), but we assume that Eq. (1) may be used for a plausible estimate even for smaller V_0. $V_0(E_i)$ decreases with E_i but it cannot become smaller than the atomic volume. We take $V_0(E_i) = V_0$ = const, and assume $N(E_i) = NE_t^{-1} \exp(-E_i/E_t)$ where N is the total concentration of localized states and E_t is constant. Then

$$\alpha(\omega) = \frac{\pi^{5/2} e^2 \hbar}{2mc} \frac{f}{n} g(E_t) V_0 N$$

$$\times \exp[-(E_g - \hbar\omega)/E_t]. \qquad (2)$$

The temperature dependence of $\alpha(\omega)$ in the tail is related by this formula to that of the optical gap E_g. The dependence of E_g can be experimentally determined from the temperature shift of the edge where $\alpha \sim (\hbar\omega - E_g)^2$ ($\alpha \approx 10^4$ cm^{-1}). We measured the temperature shift of the absorption curve at $\alpha = 2$ cm^{-1} (Fig. 1), which, according to Ref. 7, is about 40% larger than that of E_g. For all temperatures below the softening point we obtained a good agreement between the experimental values and the values calculated from Eq. (2) when $fV_0 N = 2 \times 10^{-5}$. In Table I the experimental and calculated values with this assumption are compared.

From the value of $N = 6 \times 10^{17}$ cm^{-3} deduced from the susceptibility, and taking $f = 1$ and $V_0 N$

Table I. Temperature dependence of α at $\hbar\omega = 1.8$ eV.

T (°K)	α_{meas} (cm^{-1})	α_{calc} (cm^{-1})
100	0.18	0.17
200	0.20	0.19
300	0.23	0.23
400	0.31	0.31

$= 2 \times 10^{-5}$ as above, we find the localization volume to be about 30 Å^3. It is reasonable to expect that such highly localized states would be singly occupied and give rise to the Curie term of the magnetic susceptibility.

The suggested model can thus consistently explain the magnetic and optical results in terms of disorder-produced localized states. In pure vitreous As$_2$S$_3$ these states were found to be localized over atomic dimensions and their density distribution was estimated to be $N(E_i) \approx 2 \times 10^{18} \exp(-E_i/0.3 \text{ eV})$ cm^{-3} eV^{-1} where E_i is measured from the top of the valence band.

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CRYSTAL FIELDS IN RARE-EARTH METALLIC COMPOUNDS

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Neutron crystal-field spectroscopy has been carried out in a series of praseodymium monochalcogenides and monopnictides; the results illustrate the power of inelastic neutron scattering techniques in such problems. It is found that all of the crystal-field levels in all compounds studied can be quantitatively accounted for by use of a simple point-charge model.

The magnetic properties of rare-earth metals and metallic compounds are profoundly influenced by the crystal field.[1] However, because of the difficulty of doing unambiguous experiments there is at the present time only very limited experimental information available on the crystal field itself.[2] In addition, most of the existing theories for its microscopic origins are speculative in nature.[3] This is in sharp contrast to the situation in insulators, where the energy-level schemes of rare-earth ions over many J multiplets are accurately known in a wide variety of materials.[4] Furthermore, it has proven possible to calculate these splittings from first principles to much better than an order of magnitude.[5] The reason for the lack of empirical information in metals is, of course, the difficulty in doing photon spectroscopy in metallic systems. However, these difficulties can be circumvented by using thermal neutrons instead of photons as the probe, and indeed, a crystal-field transition has been

observed with neutrons recently in the metal CeAs by Rainford et al.[6] In this Letter we report inelastic neutron-scattering measurements on a series of rare-earth metallic compounds. These confirm that neutrons may indeed be effectively used for rare-earth crystal-field spectroscopy in the far infrared provided only that the exchange field is somewhat smaller than the crystal field. In addition, in the materials we have studied we find that an effective point-charge model[7] is surprisingly accurate in predicting both the magnitudes and the systematics of the Stark splittings. This latter result is not understood at all.

We consider first the neutron-scattering aspects of the problem. In general, the scattering cross section for a system possessing both spin and orbital angular momentum is quite complicated. However, if we are operating within a given J multiplet and if, in addition, we limit ourselves to small momentum transfers, then the cross section for a single ion simplifies to[8]

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{1.91e^2}{2mc^2}\right)^2 \frac{k_f}{k_i} f^2(Q) \sum_{nm} \rho_n |\langle n|J_\perp|m\rangle|^2 \delta\left(\frac{E_n - E_m}{\hbar} - \omega\right), \tag{1}$$

where $|n\rangle$, $|m\rangle$ are states belonging to a given J multiplet; $J_\perp$ is the component of the total angular momentum operator perpendicular to the scattering vector $\vec{Q}$; and the remaining symbols have their usual meaning.[8] The effect of increasing the momentum transfer $|\vec{Q}|$ is to decrease the magnetic-dipole transition intensities via the form factor $f(\vec{Q})$ and also to make allowed magnetic octupole and pos-