excess current which has the resonant behavior of the pair-fluctuation current. As precautions have been taken to minimize the possibility of structural defects, the quantitative discrepancies between experiment and theory are an indication that corrections to the mean-field susceptibility are needed.

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PARAMAGNETIC SUSCEPTIBILITY OF A $2p$ UNPAIRED ELECTRON IN A CRYSTALLINE FIELD

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Paramagnetic susceptibility of the cubic crystal $O_2^+(As^VF_6)^-$ between 4.2 and 300°K reveals a complete quenching of the orbital moment of the $2p_I^4 2p_{II}^3$ configuration of the O_2^+ molecular cation. No ordering of the O_2^+ molecular cations has been detected in the range of measured temperature because of the large interatomic distance O_2^+-O_2^+ of 4.00 Å.

The molecular cation O_2^+ is obtained by ionizing the molecule O_2 subtracting one unpaired outer electron from its $2p$ shell and leaving O_2^+ with only one unpaired antibonding π level. The O_2^+ is thus isoelectronic with the molecule NO which also has only one unpaired electron compared with the two unpaired electrons of O_2 free gas. Hence, O_2^+ and NO are both in the π state. The χ of the NO free-gas molecule has been calculated by Van Vleck[1] and found to be

$$\chi = \frac{N\beta^2}{3kT}\,\frac{4\exp(-x)+(4/x)[1-\exp(1-x)]}{1+\exp(-x)}, \qquad (1)$$

where $x=\Delta/kT$. Taking the interval between $^2\pi_{3/2}$ and $^2\pi_{1/2}$ to be $\Delta = 124\ \mathrm{cm}^{-1}$, a good agreement can be found between the theoretical and experimental χ. Relation (1) predicts that $\chi \to 0$ when $T \to 0$ and n_{eff} is asymptotic at $2\mu_B$. The cubic crystal $O_2^+(As^VF_6)^-$ can be considered as a case where the free-gas molecule of NO is inserted in a crystalline field, and will allow a comparison of the strength of the crystalline field Dq with that of the spin-orbit coupling λ. The only magnetic measurements performed on O_2^+ ion crystals are those[2,3] on its isomorphous $O_2^+(Pt^VF_6)^-$ and $NO^+(Pt^VF_6)^-$ between 80 and 300°K. The molecular cation NO^+ is diamagnetic because it has lost its unpaired electron. By subtracting χ of $NO^+(Pt^VF_6)^-$ from that of $O_2^+(Pt^VF_6)$ it was[3] possible to separate χ of O_2^+ from that of Pt^V and this was found[3] to confirm the χ of the free-gas NO as given by relation (1). The slightly lower χ of O_2^+ was interpreted[3] as stemming from a larger splitting of the two $^2\pi$ molecular orbital states as compared with that of the free NO gas. The Pt^V in the $NO^+(Pt^VF_6)^-$ crystal is in a low spin state with $S=\frac{1}{2}$, rather than the high spin value of $S=\frac{5}{2}$.

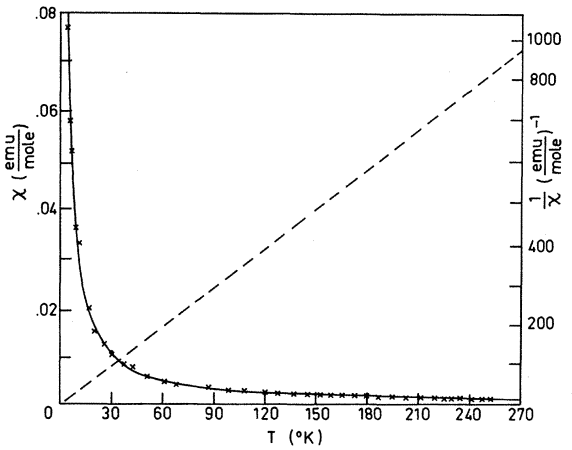

FIG. 1. The molar magnetic susceptibility χ and its inverse χ^{-1} versus temperature T for the fcc crystal $O_2^+(As^VF_6)^-$.

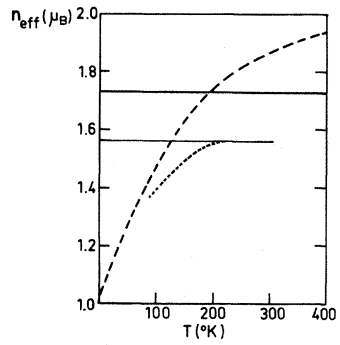

FIG. 2. The effective magnetic moment n_{eff} in μ_B units versus temperature T for $O_2^+(As^VF_6)^-$: solid thin line, our measurements; broken line, Van Vleck's theory (Ref. 1) for NO gas [relation (1)]; dotted line, Bartlett's data (Ref. 3) for O_2^+; solid thick line, spin-only value for $n_{eff}=1.73\mu_B$.

The molar χ of $O_2^+(As^VF_6)^-$ as a function of T (Fig. 1) is obtained with a diamagnetic correction of 70×10^{-6} emu/mole. It follows the Curie-Weiss law with

$$\chi=0.309/(T-0.7), \qquad (2)$$

where the Curie constant C corresponds to $n_{eff}=1.57\mu_B$. This is to be compared with the spin-only value of $S=\frac{1}{2}$ which is established by magnetic resonance[4] and which gives $n_{eff}=1.73\mu_B$. The lower C is probably due to the partial decomposition of about 17% of the freshly prepared but highly reactive sample.

The low value of $\theta=-0.7$°K explains the lack of magnetic spin ordering above 4.2°K, and is interpreted by the large interatomic distance O_2^+-O_2^+ of $\frac{1}{2}a=4.05$ Å.[4] The distance is estimated from the space group $Ia3$ with a fcc unit cell derived[2] for $O_2^+(Pt^VF_6)^-$ which sets the O_2^+ ions on the alternative (nnn) positions against the (000) positions of the Pt^V. The O-O distance (not to be confounded with the O_2^+-O_2^+ distance) inside one O_2^+ ion is 1.13 Å and is directed in the [111] direction of the cubic unit cell. The Pt-Pt distance is estimated to be $\frac{1}{2}a=5.01$ Å.[2] It should be noted that Curie's law is obeyed almost perfectly in $O_2^+(As^VF_6)^-$, whereas there are strong deviations in $NO^+(Pt^VF_6)^-$ and $O_2^+(Pt^VF_6)^-$, suggesting a stronger coupling between the Pt^V-Pt^V or Pt^V-O_2^+ rather than the O_2^+-O_2^+ ions although the latter interatomic distance is smaller.

The only paramagnetic molecular cation found to be magnetically ordered is O_2^- in KO_2.[5] The molecular cation O_2^- has a $2p_I^{4}2p_{II}^{5}$ configuration with one unpaired electron similar to the O_2^+ ion. The crystal KO_2 is antiferromagnetically ordered[5] below 7°K due to a much closer O_2^--O_2^- interatomic distance estimated to be of the order of 2.85 Å. In the paramagnetic state O_2^- has also a spin-only value[6] of $S=\frac{1}{2}$ in KO_2, while in a different structure, NaO_2, the effective magnetic moment[6] is much lower, i.e., only about 70% of that corresponding to $S=\frac{1}{2}$, probably due to partial decomposition.

Our results for χ vs T prove that there is no relation between the free-gas[1] χ of NO and that of O_2^+ in a crystalline field. In the crystal the spin-orbit coupling $\lambda\vec{L}\cdot\vec{S}$ is much smaller than the strength of the crystalline field Dq. Such a result should be expected since λ increases with the period of the periodic table, e.g., from $3d$ to $5d$ and $4f$ ions from 10^{-2} to 10^3 cm^{-1}, so that λ of the $2p$ unpaired electron should be very small, $<10^2$ cm^{-1}. At the same time the crystalline field with $Dq>10^4$ cm^{-1} is strong enough to break down Hund's multiplicity rule and cause low spin states, e.g., in the Pt^V compound which is isomorphous with the $O_2^+(As^VF_6)^-$ compound. The reason that it was originally[3] assumed that O_2^+ behaves in a crystal in a way similar to the free gas NO is explained by the large value of $\theta=-45$°K which has slightly increased the value of n_{eff} at 80 to 180°K from $1.36\mu_B$ to $1.57\mu_B$, leaving it constant at $1.57\mu_B$ between 180-300°K as shown in Fig. 2. According to the Van Vleck theory,[1] relation (1), μ_{eff} is still increasing, even from 180 to 300°K, from $1.71\mu_B$ to $1.86\mu_B$.

The quenching of the orbital moment means that the triplet $L=n-1=1$ of the π state of O_2^+, which is a T of the Γ_4 wave, is split by the trig-

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