

Figure 1. Ultraviolet absorption spectrum for barium naphthalenide complexed with cryptand[222] in THF at 20 °C.¹⁴

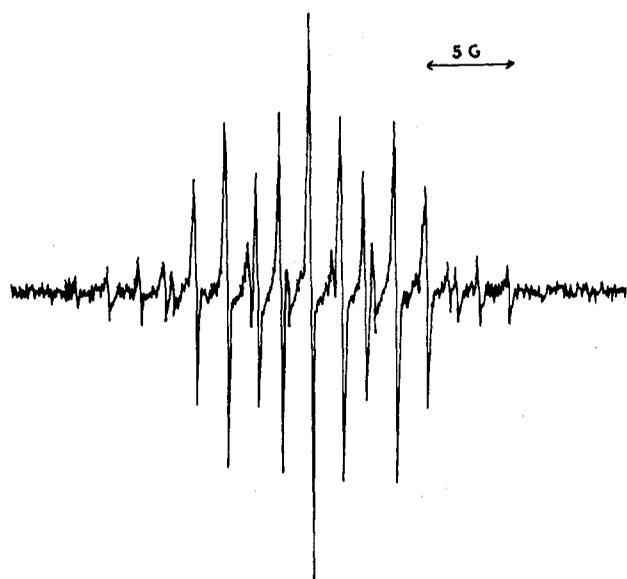


Figure 2. ESR spectrum in THF at 20 °C of barium naphthalenide (1.36×10^{-4} M) complexed with cryptand[222] in the presence of an excess of naphthalene (1.7×10^{-3} M).

coordinating agents.⁷⁻¹¹ We wish, therefore, to report some encouraging preliminary results of studies carried out with barium dinaphthalenide complexed with cryptand[222] ($\text{Ba}^{2+}[222], 2\text{N}^-$). According to the literature, cryptand[222] gives the most stable complex with the barium cation.²

The barium radical anion was prepared in THF over a finely divided barium metal (prepared from an ammonia-barium solution) in the presence of naphthalene and cryptand[222] in an all-glass apparatus under high vacuum ($\sim 10^{-6}$ mmHg) conditions. At room temperature, relatively stable, paramagnetic, green-colored solutions were formed, but at a relatively slow rate.¹²

The UV spectrum of the salt has maxima at 327 and 369 nm identifiable with a fully separated ion pairs¹³ (Figure 1).

Cryptand[222] forms an inclusion type complex where the metal ion is trapped inside the cavity of the ligand. It is not unreasonable to assume a sandwich-type structure for the ($\text{Ba}^{2+}[222], 2\text{N}^-$) radical anion.

The ESR spectrum has been studied (Figure 2). It has the characteristic absorption spectrum of the naphthalenide radical anion (25 lines, $a_\alpha = 4.8$ G and $a_\beta = 1.8$ G). The well-resolved hyperfine pattern indicates a slow rate, on the ESR scale, of the electron exchange reaction between naphthalene negative ion and excess naphthalene.

The suggested sandwich-type structure which would hinder the electron exchange is in agreement with the ESR experiment.

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- (12) THF solutions contained no detectable ammonia contamination according to the Nessler reagent. Analyses of the same solutions for sodium and potassium were made by both emission and absorption flame photometry and gave respectively less than 0.2 and 1.00 ppm. It should also be noted that in the presence of naphthalene and absence of cryptand[222] or vice versa, no UV or ESR spectra were observed.
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- (14) Optical spectra were measured with a Varian Cary 118 C (path length 1.0 cm). The concentration of barium was estimated by an atomic absorption flame photometer (1.36×10^{-4} M). The cryptand concentration was 2.35×10^{-3} M.

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S_2^{2-} as a Point Defect in Monosulfide Oxidation

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Sir: The metal sulfides, in their more oxidized forms, frequently contain covalently bonded diatomic sulfide ions, S_2^{2-} . Pyrite (FeS_2) is a well-known example; and covellite (CuS), oddly enough, contains a high proportion of S_2^{2-} in addition to some sulfur S^{2-} . It seems possible, therefore, that in the initial stages of oxidation (sulfur enrichment) of monosulfides (such as ZnS) in which the valency of the metal is fixed at two, charge balance may be preserved in the face of nonstoichiometry by the formation of S_2^{2-} as a point defect, thus reducing the total charge on the sulfide sublattice. In this note we offer spectroscopic evidence for

TABLE I: New Lines in the Raman Spectrum of ZnS Exposed to High Sulfur Vapor Pressure

Frequency, cm^{-1}		Tentative assignment
165	weak, sharp	Vibration of an S_2 species in a ZnS cage
441	weak, shoulder	A
481	weak, broad	A
492	weak, broad	Induced two-phonon scattering ($W_2 + W_3$) of ZnS
500	strong, sharp	A
557	weak, broad	B
726	medium, sharp	C
738	weak, broad	C
773	strong, sharp	C?

the existence of defects of this kind in oxidized ZnS. If subsequent work confirms and extends the hypothesis it should make a good starting point for a theory of sulfide oxidation; such a theory is sorely needed in many technological fields: mining, flotation, transport, and electrowinning all pose important problems arising from the oxidation of sulfide ores, and their intractability stems primarily from the lack of a sound theoretical basis, particularly with regard to the initial steps.

We chose the technique of laser Raman spectroscopy to search for diatomic sulfur species as point defects in ZnS which had been exposed to a high pressure of sulfur vapor. Natural transparent sphalerite crystal fragments were selected and flats were polished on two adjacent faces. After initial Raman spectra of these crystals had been recorded, they were heated in closed tubes containing sulfur at 650°C for 20 h, at which temperature the sulfur (mainly as S_2) vapor pressure was 11.3 atm. After cooling, the crystals were extracted with benzene in a Soxhlet apparatus for 20 h to remove all traces of free sulfur. The resulting crystals were dark grey; longer heating in sulfur made them quite black and therefore unsuitable for Raman work. Their X-ray diffraction pattern had also changed from that of sphalerite monocrystals to a polycrystalline pattern with the same spacings.

Reobservation of the Raman spectrum disclosed new lines at the frequencies shown in Table I.

These lines are all much weaker than the one- and two-phonon lines of the untreated sphalerite, but they stand out clearly against the background. The intensities and widths are comparative within the set.

Reference to the figure (Figure 1), which is a Clark's rule¹ plot of vibration frequency against internuclear distance on which some of the previously known data on S_2 species are plotted, shows that the new lines labeled A in Table I fall in the S_2^{2-} region (which extends for some distance along the curve); while the line labeled B and those labeled C fall fairly close to the S_2^- and S_2^0 frequencies, respectively. Thus, rather than finding just one line for each species, we have three for S_2^{2-} , one for S_2^- , and another two or possibly three for S_2^0 . It must be noted, however, that these defects may exist in association with each other, or with other defects, and so each may give rise to several lines.

Several other factors will affect the observed frequencies of lines due to an S_2^0 or S_2 group incorporated into a host lattice. The vibrational frequency of the molecule will be changed by interaction with the host lattice; first, by

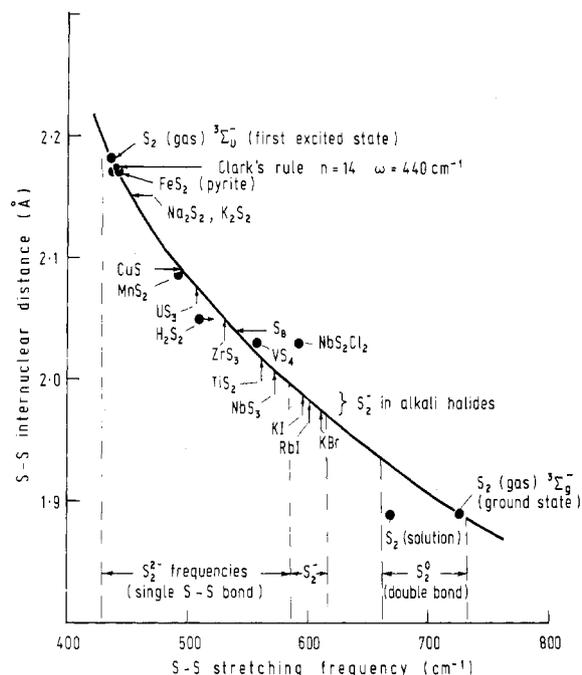


Figure 1. Vibrational frequency vs. bond length for various known S_2 species. Where both parameters are known the point is marked \bullet . If only one is known the point is marked by an arrow to the curve. The curve is drawn using Clark's rule.¹ The data shown are representative of a larger collection.

binding to the host lattice atoms, and secondly by coupling with the vibrational modes of the host lattice. There may also be a coupling (as in the case of OH, see ref 2) between the vibrational mode and the librational mode of the diatomic molecule in the host lattice which will increase the number of lines.

The formation of covalently bonded sulfur species is clearly a hole-trapping process in monosulfide crystals; and it will compete with other hole-traps such as Fe^{2+} when present. In this connection it is interesting that the electron spin resonance signal from iron-containing CdS behaves anomalously as a function of sulfur enrichment.³ Somorjai and Title fired CdS at 900°C in varying pressures of sulfur vapor, and found that the Fe^{3+} signal increased up to $p_{\text{S}_2} = 10$ atm and then decreased to a very low value at $p_{\text{S}_2} = 30$ atm. Their evidence pointed to the existence of a new defect which was not electrically active, in other words, a deep hole trap. Our proposed S_2^{2-} defect exactly fits this description.

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