

and a loss on quenching are clearly indicated. The optical-absorption data in the range from 200–900 m μ was taken on a Beckmann DK-2 Spectrophotometer, and indicated the presence of V^{+++} in each sample. However, no conclusive evidence can be seen that the V^{+++} concentration diminished when annealed in air. In fact, in some cases the optical absorption due apparently to V^{+++} increased at the same time the resonance signal of V^{++} increased. This would indicate that yet a different valence state of vanadium is present in the crystal. The significant increase in V^{++} EPR signal on annealing would seem to rule out local strains as the strongest local distortion mechanism.

If the presence of these other valence states is responsible for the distortion, the mechanism is likely

to be the presence of interstitial oxygen needed for charge compensation. The ionic radii of triply or quadruply ionized vanadium ions suggest that they may be more favorable in MgO than doubly ionized and may even be so after inclusion of the necessary interstitial oxygen.¹² The black color of the 0.5% sample suggests the formation of V_2O_3 or VO_2 complexes in the lattice, but no further evidence of this is available at present.

ACKNOWLEDGMENTS

The authors are grateful to Professor Graeme Baker for help with the optical data and to Dr. R. A. Lefever for helpful discussion.

¹² See, for example, Linus Pauling, *The Nature of the Chemical Bond*, (Cornell University Press, Ithaca, New York, 1960), p. 518.

Paramagnetic-Resonance Spectra of S_2^- in Alkali Halides*

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(Received 13 March 1967)

The impurity ion S_2^- has been introduced into six alkali-halide crystals: NaI, KCl, KBr, KI, RbBr, and RbI. The center is characterized by extreme g anisotropy; in KBr, for example, the principal g factors were 3.5037, 0.8434, and 0.8388. The first of these corresponds to the S-S bond direction which, in all crystals studied, was parallel to the $\langle 110 \rangle$ directions of the crystal. The direction of minimum g factor was associated with the direction of the molecular π orbital occupied by the unpaired electron. This direction was $\langle 110 \rangle$ for S_2^- in KCl, RbBr, and RbI, but $\langle 100 \rangle$ for S_2^- in NaI, KBr, and KI. Sulfur enriched in the isotope S^{33} was used to investigate the S^{33} hyperfine interaction. The largest S^{33} hyperfine interaction occurred when H_0 was parallel to the S-S bond direction, and not, as might have been expected, when H_0 was parallel to the direction of the π function. This was due to the dominant contribution from the $L \cdot I$ term in the hyperfine Hamiltonian. Hyperfine structure due to lattice nuclei could not be resolved but gave rise to the highly anisotropic linewidths of the resonances.

INTRODUCTION

IT was established some years ago¹ that the characteristic fluorescent emission exhibited by alkali-halide crystals containing hydroxide ion impurity was due to the presence of O_2^- . This identification was based on the band structure of the emission spectrum, the band interval of 1000 cm^{-1} being associated with transitions into various vibrational levels of the ground state of the diatomic molecule. Moreover, crystals exhibiting this fluorescence showed electron-paramagnetic-resonance (EPR) spectra² which were also consistent with the presence of O_2^- .

More recently an analogous fluorescence has been detected in crystals of KCl and KBr grown from the melt in an atmosphere of sulfur vapor.³ The vibrational

interval of 580 cm^{-1} suggested that in this case S_2^- ions might be present in the crystals. This was later confirmed by the detection of the EPR spectrum of S_2^- in the KBr crystals.⁴

The purpose of the present experiments was to introduce S_2^- into as many alkali halides as possible, with a view to using the paramagnetic resonance technique to detect and characterize the impurity, comparing the results with those obtained for O_2^- .

EXPERIMENTAL

Commercially available (Harshaw, Semi-Elements) ultrapure alkali-halide crystals were used. In order to introduce the S_2^- impurity into the samples, small crystals (typically $5 \times 2 \times 10$ mm³) were placed, with a small amount of sulfur, in quartz ampoules, which were sealed off after evacuation. The ampoules were then heated in a furnace for 100–200 hours at a temperature close to the melting point of the crystal. In the case of KCl, KBr, and RbBr the temperature was 20° below

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¹ J. Rolfe, F. R. Lipsett, and W. J. King, *Phys. Rev.* **123**, 447 (1961).

² W. Känzig and M. H. Cohen, *Phys. Rev. Letters* **3**, 509 (1959).

³ J. H. Schulman and R. D. Kirk, *Solid State Commun.* **2**, 105 (1964).

⁴ J. R. Morton, *J. Chem. Phys.* **43**, 3418 (1965).

the melting point; for crystals of NaI, KI, and RbI, 50° below the melting point was adequate. It did not prove possible to introduce S_2^- into NaCl, NaBr, or RbCl even by heating in sulfur for over 200 h at 10° below the melting point.

Some of the alkali-halide crystals exposed to sulfur vapor became highly colored, but there was no evidence that the coloration was due to S_2^- . Thus the pink color in KCl and KBr crystals⁵ may be due to S_2^- ; KI and RbI turned green and NaI yellow. Both KI and RbI exposed to sulfur were found to contain a second paramagnetic center (not identified), but in NaI only S_2^- could be detected.

The EPR spectra of S_2^- were examined at 4°K. The liquid-helium Dewar vessel was similar to that described by Hornig and Hyde,⁶ being made of Pyrex glass but having a quartz finger which carried the helium into the microwave cavity. The alkali-halide

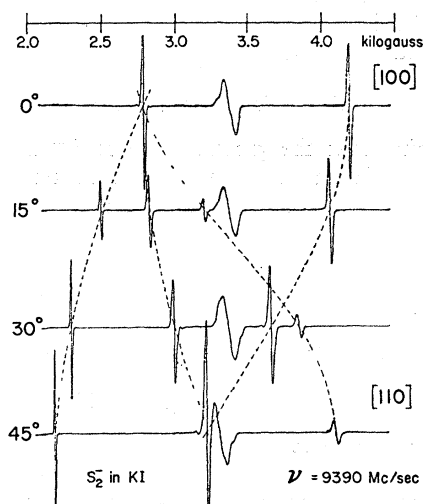


FIG. 1. Paramagnetic resonance spectra of S_2^- in KI at 4°K. (The broad resonance near 3.4 kG has not been identified).

samples were placed in open-ended, thin-walled quartz tubes attached to a 2-mm quartz rod. The rod was connected to a small goniometer so that the crystal could be rotated about a vertical axis for alignment purposes, final adjustments being made by rotating the magnet or tilting the Dewar vessel. Exact alignment of the crystal so that H_0 was parallel to $\langle 100 \rangle$ or $\langle 110 \rangle$, for example, was carried out by observing the coalescence of certain lines in the spectrum (see Fig. 1). The accuracy of this alignment procedure varied from crystal to crystal, of course, due to the varying linewidths encountered. In the potassium salts, alignment accuracy of $\pm 0.1^\circ$ was possible, but in the rubidium and sodium salts only $\pm 0.5^\circ$ could be obtained by this technique.

A Varian V-4502-15 spectrometer was used. The

⁵ J. Schneider, B. Dischler, and A. Rauber, Phys. Status Solidi 13, 141 (1966).

⁶ A. W. Hornig and J. S. Hyde, Mol. Phys. 6, 33 (1963).

TABLE I. g factors of S_2^- resonances for H_0 parallel to $\langle 100 \rangle$ and $\langle 110 \rangle$ in various alkali halides.

	Magnetic field parallel to				
	$\langle 100 \rangle$	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$	$g_{90'}$
	g_{45}	g_{90}	g_0	g_{60}	$g_{90'}$
		(g_{yy})	(g_{zz})		(g_{zz})
KCl	2.5163 ^a	0.9500	3.4303	1.9015	0.9484
RbBr	2.3783	1.7571	2.8936	2.0960	1.7448
RbI	2.5482	1.2968	3.3595	^b	1.2895
		(g_{xx})	(g_{xx})		(g_{yy})
NaI	2.1267	1.9942	2.2303	2.0608	2.0178 ^c
KBr	2.5468	0.8388	3.5037	1.8955	0.8434
KI	2.4560	1.6254	3.0629	2.0827	1.6369

^a All entries ± 0.0004 .

^b Overlapped by a resonance of another center.

^c Overlapped, calculated from g_{45} and g_0 .

magnetic field of the V-3603 12-in. rotating magnet was controlled by a "Fieldial" Hall-effect regulator, and measured with the aid of a Varian F-8A NMR fluxmeter. A Hewlett-Packard 540B transfer oscillator was used to measure the microwave frequency. The frequencies of the transfer oscillator and the NMR fluxmeter were measured with a Computer Measurements Company 707B frequency counter.

In Fig. 1 the spectrum of S_2^- is reproduced for four orientations of the crystal (KI) in the magnetic field. The S_2^- resonances are seen to be highly anisotropic with respect to the magnetic field direction. In all crystals studied the minimum field for resonance was obtained when H_0 was parallel to $\langle 110 \rangle$, demonstrating that the S-S bonds were parallel to one of the six $\langle 110 \rangle$ directions in the crystal. Thus, for a random orientation of the crystal in the magnetic field six resonances were apparent. However, for certain orientations, particularly H_0 parallel to $\langle 100 \rangle$ or $\langle 110 \rangle$, two or more lines coalesced. For example, with H_0 parallel to $\langle 100 \rangle$, only two resonances were observed (Fig. 1): (a) a fourfold resonance of S_2^- ions inclined 45° to H_0 and designated g_{45} in Table I, and (b) a twofold resonance of S_2^- ions at right angles to H_0 and designated g_{90} . Similarly, for H_0 parallel to $\langle 110 \rangle$ three resonances were observed (Fig. 1): (a) a non-

TABLE II. Maximum-slope linewidths of S_2^- in alkali halides (gauss).^a

	ΔH_{xx}	ΔH_{yy}	ΔH_{zz}
KCl	41	28	5.0
RbBr	124	80	43
RbI	105	91	33
NaI	54	85	33
KBr	50	90	3.8
KI	19	35	7.5

^a Errors: $\pm 5\%$.

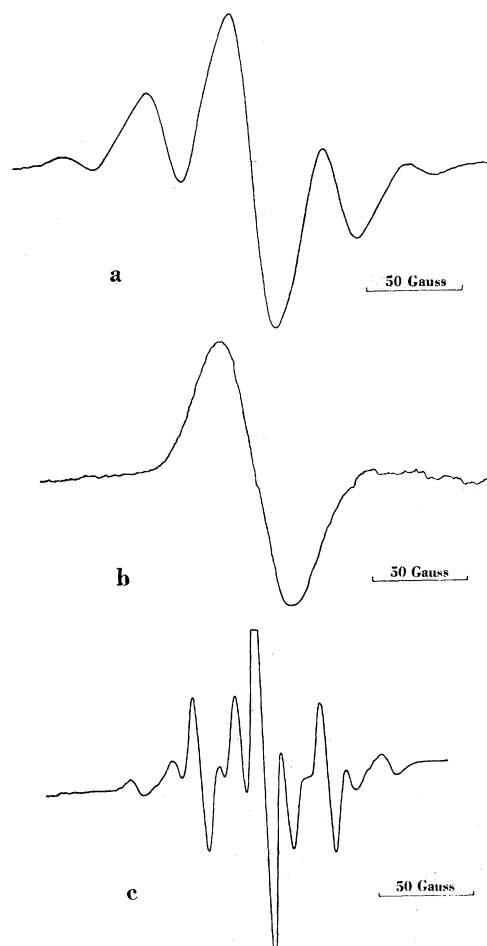


FIG. 2. Paramagnetic resonances of S_2^- in KI obtained using sulfur enriched to 48.6% in the isotope S^{33} ($I = \frac{3}{2}$): (a) H_0 parallel to x , (b) H_0 parallel to y , and (c) H_0 parallel to z .

degenerate resonance from S_2^- ions lying parallel to H_0 (g_0), (b) a fourfold resonance g_{60} , and (c) a non-degenerate resonance g_{90}' . These five g factors are listed in Table I; the values of g_0 , g_{90} , and g_{90}' are principal values of the g tensor, and are also designated g_{zz} , g_{yy} , and g_{xx} .

The maximum-slope linewidth ΔH was also measured and in Table II values of ΔH_{xx} , ΔH_{yy} , and ΔH_{zz} are listed.

Sulfur enriched to 48.6% in the isotope S^{33} was purchased from Oak Ridge National Laboratory, and used in order to determine the S^{33} hyperfine interaction in S_2^- .

DISCUSSION

Identification as S_2^-

There can be no doubt that the specie under examination is S_2^- . Sulfur enriched in the isotope S^{33} has already been used to identify the center in KBr,⁷ and

⁷ J. R. Morton, J. Phys. Chem. **71**, 89 (1967).

in Fig. 2 the resonances of S_2^- in KI corresponding to g_{xx} , g_{yy} , and g_{zz} are shown, the hyperfine structure being clearly seen in the top and bottom spectra. Since S^{33} has a spin $I = \frac{3}{2}$, $(S^{33}S^{32})^-$ gives rise to a four-line contribution to the spectrum, and $(S_2^{33})^-$ gives rise to a manifold of seven lines of relative intensity 1:2:3:4:3:2:1. The values of the S^{33} hyperfine interaction for H_0 parallel to z are listed in Table III. Figure 3 is a diagram of the S_2^- impurity occupying a halide-ion vacancy. The sulfur $3p_x$ functions which together constitute the dominant contribution to the molecular orbital are also indicated. The equivalence of the two S nuclei, which is clearly shown by the S^{33} hyperfine interaction, and the analogy with O_2^- support the proposed model. The decreasing difficulty in introducing the S_2^- impurity into the series KCl, KBr, KI (and similarly RbCl, RbBr, RbI) also suggests that the S_2^- replaces only one halide ion. Had the S_2^- ions been associated with a trivacancy, as is S_3^- ,⁵ one would expect the impurity to enter different crystals with almost equal facility.

Analysis of the g Factor

Assuming that the ground state of S_2^- is ${}^2\Pi_{3/2}$, the principal g factors can be written in terms of the parameters λ/Δ , l , and λ/E (Ref. 2):

$$g_{xx} = g_e(1 + \lambda^2/\Delta^2)^{-1/2} - (\lambda/E)[1 - (1 + \Delta^2/\lambda^2)^{-1/2} - (1 + \lambda^2/\Delta^2)^{-1/2}], \quad (1)$$

$$g_{yy} = g_e(1 + \lambda^2/\Delta^2)^{-1/2} - (\lambda/E)[(1 + \Delta^2/\lambda^2)^{-1/2} - (1 + \lambda^2/\Delta^2)^{-1/2} - 1], \quad (2)$$

$$g_{zz} = g_e + 2l(1 + \Delta^2/\lambda^2)^{-1/2}. \quad (3)$$

⁸ In these equations, z is the S-S bond direction, x is the direction of the p functions, and y is the mutually perpendicular direction; g_e is the free-spin g factor 2.0023, and l is the effective g factor for the orbital contribution to the magnetic moment (in the free ion $l = 1$); λ and Δ are the spin-orbit coupling and crystal-field-splitting parameters, respectively, and E is the energy separating the ${}^2\Pi_g$ ground state and the ${}^2\Sigma_g$ state connected to it by the spin-orbit interaction.

The values of g_{xx} , g_{yy} , and g_{zz} are determined by the parameters λ/Δ and λ/E . Since $E \gg \Delta$, the dominant factor is the magnitude of λ/Δ , and λ/E gives rise to a small difference between g_{xx} and g_{yy} . From Eqs. (2)

TABLE III. S^{33} hyperfine interaction (Mc/sec) in S_2^- for H_0 parallel to the bond.^a

	KCl	KBr	KI	RbI
t_{zz}	137	145	93	105
Error	± 2	± 2	± 3	± 5

^a t_{xx} and t_{yy} not resolved except for KI ($t_{xx} = 64 \pm 5$ Mc/sec).

and (3) it may be shown that

$$g_{yy} - g_{xx} = (2\lambda/E) [1 - (1 + \Delta^2/\lambda^2)^{-1/2}], \quad (4)$$

so that, if $\lambda > 0$, the direction of the p function is associated with the smallest principal g factor, since $[1 - (1 + \Delta^2/\lambda^2)^{-1/2}]$ is positive for all values of λ/Δ .

From Table I it may be seen that g_{90} is the smallest principal g factor of S_2^- in NaI, KBr, and KI, whereas g_{90}' is the smallest for S_2^- in KCl, RbBr, and RbI. It is therefore concluded that in NaI, KBr, and KI the p functions of S_2^- are parallel to $\langle 100 \rangle$ but in KCl, RbBr, and RbI they are parallel to $\langle 110 \rangle$. The situation may be compared with that of O_2^- in the alkali halides. The p functions of O_2^- were shown to be parallel to $\langle 100 \rangle$ only in the case of the sodium salts²; in potassium and rubidium salts the p functions were parallel to $\langle 110 \rangle$.

In Table IV the computed values of λ/Δ , l , and λ/E for S_2^- in the six alkali halides are listed. Equations (1) and (2) were solved graphically to obtain λ/Δ and λ/E , and then Eq. (3) yielded the parameter l . The dominant parameter determining the g anisotropy is λ/Δ , and it will be seen from Table IV that there is wide variation in its value. The values of λ/Δ for O_2^- in KCl, KBr, and KI are 0.23, 0.28, and 0.26, respectively.⁸ It will be seen that between S_2^- and O_2^- , there is a difference both in the magnitude of λ/Δ and in its variation from matrix to matrix.

The S^{33} Hyperfine Interaction

The S^{33} hyperfine interaction in S_2^- was measured in KCl, KBr, KI, and RbI. In all crystals the direction of the largest splitting was z , the S-S bond direction, whereas one might have expected, as in the case⁸ of O_2^- , the direction of the p function (x) to correspond to the largest hyperfine splitting.

According to Abragam and Pryce,⁹ the nuclear hyperfine structure can be expressed in terms of the following Hamiltonian:

$$H = \gamma_e \gamma_n \left[\frac{3(\mathbf{I} \cdot \mathbf{r})(\mathbf{r} \cdot \mathbf{S})}{r^5} - \frac{\mathbf{S} \cdot \mathbf{I}}{r^3} + \frac{\mathbf{L} \cdot \mathbf{I}}{r^3} + \frac{8}{3} \pi \delta(\mathbf{r}) \mathbf{S} \cdot \mathbf{I} \right]. \quad (5)$$

TABLE IV. Spectroscopic parameters of S_2^- in alkali halides.

Alkali halide	λ/Δ	l	λ/E
NaI ^a	~0.10	~1.2	~0.013
KCl	1.94	0.80	0.072
KBr	2.19	0.83	0.025
KI	0.73	0.90	0.014
RbBr	0.57	0.90	0.012
RbI	1.20	0.88	0.016

^a More accurate data could not be obtained because of poor resolution in the spectra.

⁸ H. R. Zeller and W. Känzig, *Helv. Phys. Acta* (to be published).

⁹ A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A205**, 135 (1951).

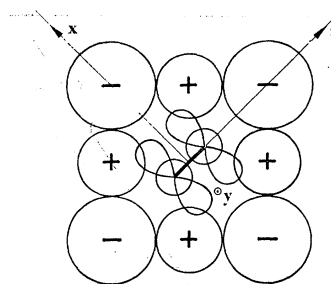


FIG. 3. Orientation of S_2^- impurities in the alkali-halide matrix. The x axis defines the direction of the p functions and corresponds to S_2^- in KCl, RbBr, and RbI. In NaI, KBr, and KI x and y are interchanged.

The first two terms in this expression correspond to the dipolar interaction between the electronic and nuclear spins. The third term represents the contribution to the hyperfine interaction resulting from the orbital motion of the electron. The last term describes the Fermi contact interaction.

In order to calculate the matrix elements of (5), an appropriate wave function for the ground state of S_2^- must be assumed. In their recent work on O_2^- , Zeller *et al.*^{8,10} derive expressions for the t_{ii} using a many-electron wave function to describe the ground state of O_2^- . Zeller's equation for t_{zz} is

$$t_{zz} = \gamma_e \gamma_n \left[(8\pi/3) \psi^2(0) + (\Delta g_{zz}/2l) \langle r^{-3} \rangle_l - \frac{1}{5} \langle r^{-3} \rangle_s \right], \quad (6)$$

where $\langle r^{-3} \rangle_l$ and $\langle r^{-3} \rangle_s$ represent the average of r^{-3} over the orbital-moment and spin-moment densities, respectively. The equations for t_{xx} and t_{yy} are not reproduced here, since, in the case of S_2^- , the experimental values could not be determined.

If it is assumed that $\langle r^{-3} \rangle_l = \langle r^{-3} \rangle_s = \langle r^{-3} \rangle$, Eq. (6) becomes

$$t_{zz} = \gamma_e \gamma_n \left[(8\pi/3) \psi^2(0) + \gamma_e \gamma_n \langle r^{-3} \rangle \left[(\Delta g_{zz}/2l) - \frac{1}{5} \right] \right]. \quad (7)$$

In the absence of values of t_{xx} and t_{yy} for S_2^- , the validity of the above assumption cannot be tested, but in the case of O_2^- , the difference between $\langle r^{-3} \rangle_l$ and $\langle r^{-3} \rangle_s$ was found to be approximately 15%. In Eq. (7), the first term is the Fermi "contact" contribution, arising from the spin polarization of atomic s or molecular σ orbitals. The last term is the contribution from the normal dipolar interaction, and the second term arises from the $\mathbf{L} \cdot \mathbf{I}$ term in the Hamiltonian. The very large values of Δg_{zz} which have been determined for S_2^- cause the second term in (7) to be the dominant contribution to t_{zz} .

If $\langle r^{-3} \rangle$ is a purely molecular parameter, there should be a linear relationship between t_{zz} and $(\Delta g_{zz}/2l) - \frac{1}{5}$, the value of $\langle r^{-3} \rangle$ determining the slope. This graph is shown in Fig. 4. The deviation from linearity has to be attributed to the size of the S_2^- ion, i.e., an adequate description of it in terms of sulfur orbitals only may be

¹⁰ R. T. Shuey and H. R. Zeller, *Helv. Phys. Acta* (to be published).

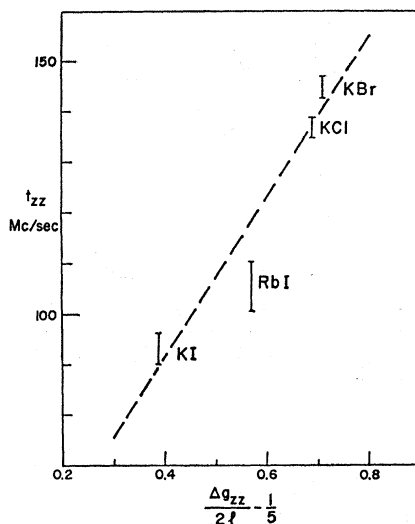


FIG. 4. Graph of t_{zz} versus $(\Delta g_{zz}/2I) - \frac{1}{5}$ for S_2^- in KCl, KBr, KI, and RbI.

impossible. Renormalization factors different for each lattice may have to be introduced into the expression for t_{zz} , since for S_2^- in KCl and RbI x is parallel to $\langle 110 \rangle$, but in KBr and KI x is parallel to $\langle 100 \rangle$. Unfortunately no hyperfine splitting from the alkali or halide ions could be resolved and so the involvement of the lattice ions cannot be estimated.

An estimate of $\langle r^{-3} \rangle$ for S_2^- could only be obtained by drawing a straight line through the four points in Fig. 4. Although the RbI: S_2^- measurement was the least accurate, its central position on the graph suggested that any error in or correction to its position would not appreciably affect the slope of the "least-squares" straight line. This slope was determined, and found to be $\gamma_e \gamma_n \langle r^{-3} \rangle = 160$ Mc/sec, corresponding to a value of $\langle r^{-3} \rangle$ for sulfur in S_2^- of 2.6×10^{25} cm $^{-3}$. The major contribution to the molecular orbital occupied by the unpaired electron will be that of the sulfur $3p$ atomic orbitals. Therefore, this estimate of $\langle r^{-3} \rangle$ should be approximately equal to $\langle r^{-3} \rangle_{3p}$ for sulfur. The

Hartree-Fock wave function of Watson and Freeman¹¹ yields a value of $\langle r^{-3} \rangle_{3p}$ for sulfur of 3.25×10^{25} cm $^{-3}$, and a recent computation¹² from Herman and Skillman's wave function¹³ gave 4.14×10^{25} cm $^{-3}$. Reasonably good correlation between the experimental data and theoretical estimates can thus be said to be obtained.

The Linewidth

It will be apparent from Table II that the linewidths of the S_2^- resonances were highly anisotropic, and that the linewidth was also dependent on the host matrix.

In the case of O_2^- it was found^{8,10} that when x was parallel to $\langle 110 \rangle$ (K and Rb salts), ΔH decreased with increasing lattice constant, but when x was parallel to $\langle 100 \rangle$ (Na salts), ΔH increased with increasing lattice constant. Since the halogen nuclear moments increase along the series Cl, Br, I, it was suggested that the linewidth of the O_2^- resonances was due to unresolved hyperfine interaction with metal ions in the K and Rb salts, but with halide ions in the Na salts. It is probable that a similar situation exists in the case of S_2^- . For example, going from RbBr to RbI (x parallel to $\langle 110 \rangle$), the S_2^- linewidths tend to decrease (ΔH_{yy} is anomalous), suggesting an alkali-metal hyperfine interaction, as in O_2^- . However, it does not seem possible to draw any conclusions from the data on S_2^- in NaI, KBr, and KI (x parallel to $\langle 100 \rangle$). Going from KBr to KI, ΔH_{zz} increases, as might be expected, but ΔH_{xx} and ΔH_{yy} decrease.

ACKNOWLEDGMENTS

The authors are grateful to Professor W. Känzig and Dr. H. R. Zeller for a copy of their article (Ref. 8) on O_2^- ,⁸ for permission to refer to it in advance of publication and for helpful correspondence; and to Dr. J. Rolfe for the gift of some alkali-halide crystals.

¹¹ R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 521 (1961).

¹² C. M. Hurd and P. Coodin, *Phys. Chem. Solids.* **28**, 523 (1967).

¹³ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).