greater in D_2O than in H_2O. This is also not observed. The only reasonable mechanism compatible with these experimental results appears to be a cross-relaxation process which occurs *via* spin–spin interaction with another paramagnetic species. The only other known paramagnetic species in 10 *M* hydroxide ices is O^-. We tentatively conclude that O^- is involved in a cross-relaxation process with the trapped electron.

Further paramagnetic relaxation studies are under way. It appears that such studies can yield quite useful insights into the nature of the trapping sites of ions and radicals in solids.

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Kerr-Constant Dispersion for an Electronic Absorption

Sir:

The Kerr constant of a material can be used in the estimation of the anisotropy of the polarizability when measurements are carried out in a region of little or no absorption.[1] If the Kerr constant is measured as a function of frequency in a region of absorption (*i.e.*, the dispersion is determined), then it is possible to assign the polarization of the transition as well as to estimate the properties of the excited state.[2] Kerr-constant dispersion was used in a recent communication[3] to infer the direction of a dipole moment from determinations made at two or three widely scattered frequencies.

We are now reporting the measurement of the dispersion of the Kerr constant throughout an entire absorptive region. The system chosen is the acridine orange–polyglutamic acid complex which has previously been examined by the techniques of optical rotatory dispersion[4] (ORD) and circular dichroism[5] (CD).

The Kerr effect (linear electric birefringence) arises from anisotropies in the electrostatic and electrooptic polarizabilities; the effect is quadratic in the applied field. For the case of a dipolar molecule with the dipole moment lying along one of the principal axes of the molecule (the *z* axis), the Kerr constant (*B*) can be expressed as

$$B = \frac{\pi N}{27n\lambda}(n^2 + 2)^2(\epsilon + 2)^2\frac{\mu_z^2}{45k^2T^2}(2\alpha_z - \alpha_x - \alpha_y) \qquad (1)$$

where N is the number of molecules/unit volume, n and ϵ are the index of refraction and dielectric constant of the medium, λ is the wavelength of the light, and μ_i and α_i are the components of the dipole moment and electrooptic polarizability along the principal axes. From the definition of the polarizability,[6] it can be seen that in the vicinity of an absorption of frequency ν_i, the Kerr constant will vary as $1/(\nu_i - \nu)$. If $2\alpha_z > (\alpha_x + \alpha_y)$, the dispersion is positive and the transition is parallel; a negative dispersion arises from a perpendicular transition. Buckingham and Pople[7] have considered deviations from a linear polarization law (hyperpolarizability); in the vicinity of an absorption, this gives rise to a dispersion that varies as $1/(\nu_i - \nu)^3$ for the axially symmetric case. The width of the absorption will cause a broadening of the dispersion curve with maxima and minima occurring at the half-width frequencies.[2] The polarization of a transition is easily determined by the initial rise or fall of *B* as ν approaches ν_i.

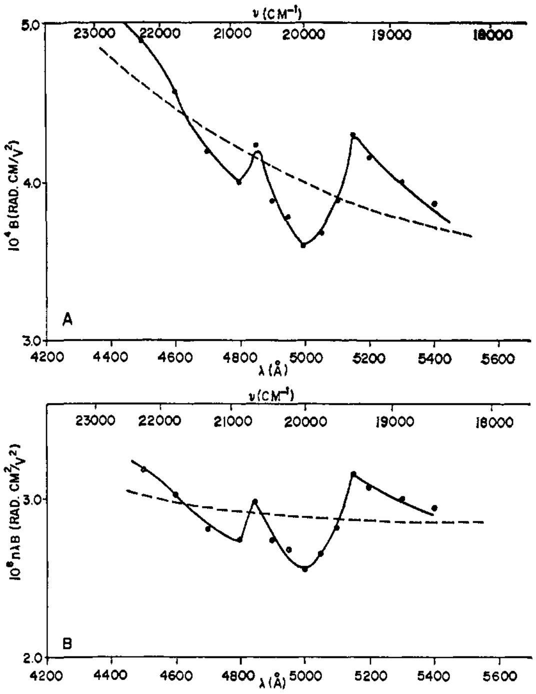

Figure 1. (A) Dispersion of the Kerr constant (*B*) for the AO–PGA complex (solid line) and PGA (dotted line). (B) Dispersion of *nλB* for the AO–PGA complex (solid line) and PGA (dotted line).

The acridine orange (AO)–polyglutamic acid (PGA) complex was formed by mixing the appropriate stock solutions. The dye was zinc free. The solvent used was DMF because of its relatively low conductivity. In this solvent, the polymer is in the helical conformation. The spectrum of the complex in DMF closely resembles that obtained in water; a maximum is found at 4950 A with a shoulder appearing around 4650–4700 A. These absorptions can be assigned to the free protonated dye and aggregated dye, respectively.[8] The Kerr constants were measured by a conventional photoelectric method. The light source was a 1000-w Osram lamp, the appropriate wavelengths being selected by a Bausch and Lomb monochromator; the width of the output beam was about 10 A. Full details of these experiments will be published elsewhere.

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In Figure 1A are shown the results for a solution containing $1.0 \times 10^{-5}\ M$ AO and $2.3 \times 10^{-2}\ M$ PGA. The measured birefringence is the sum of that due to the polymer (large and positive) and that due to the dye (variable). The dispersion curve of the dye is easily seen superimposed on the separately determined dispersion curve of the polymer (dotted line). These curves can be smoothed out by removing the $1/n\lambda$ dependence as shown in the plot in Figure 1B.

The main feature of the dispersion curve is a relatively intense positive curve centered around 5000 A. No assignment can be made at present for the dispersion in the region of dimer absorption (*ca.* 4700 A). More than one transition is probably involved and the experimental data need refinement. Although the center of the strong anomalous dispersion is shifted somewhat to the red relative to the absorption maximum at 4900 A, this same shift is found in both the optical rotatory dispersion[4] and circular dichroism[5] spectra. The shift is not due to electrical dichroism as none could be observed at 5000 A. The reason for this shift is unknown and under active investigation.

Some conclusions can now be drawn concerning the structure of the complex. From this positive dispersion, the transition moment for the long wavelength absorption can be assigned as roughly parallel to the dipole moment in the complex responsible for the orientation in the electrostatic field. The dipole moment in the polymer is very large and directed along the long axis of the helix. The transition moment in the free dye is long-axis oriented[9] and, therefore, the long axis of the bound dye must be approximately parallel to the polymer axis. The direction(s) of the transition moment(s) for the aggregate absorption cannot be identified as yet. It is likely, though, that both perpendicular and parallel polarized transitions are present since the optical rotatory dispersion[4] is normal while a complex circular dichroism is found.[5] The dye is probably bound to the polymer in the form of a left-handed helix as previously suggested;[4] the known tendency of acridine orange to aggregate supports this view. The specification of the orientation of the long axis of the dye molecule as parallel to the polymer axis by this direct measurement corroborates the previous assignment inferred from circular dichroism measurements on partially oriented solutions.[5]

Kerr constant dispersion is in principle a most versatile tool since the Kerr effect is common to all matter and the system need not be asymmetric. Even in systems which are amenable to examination by other techniques, much information of a complementary nature can be obtained. We are currently studying Kerr-effect dispersion in a variety of macromolecular systems.

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Book Reviews

The Solid-State Chemistry of Binary Metal Hydrides. By GEORGE G. LIBOWITZ, Kennecott Copper Corporation, Ledgemont Laboratory. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. xi + 139 pp. 15.5 × 23.5 cm. $7.50.

Here is a short book surveying the solid binary hydrides from a physical–chemical viewpoint, with a bare minimum of descriptive material. Although its brevity makes it vulnerable to criticism for what it leaves out, it also permits a beginner in the field to grasp the fundamentals efficiently. The book has six crisp chapters on classification and bonding, preparation and chemical properties, crystal structures and phase relationships, thermodynamics, electrical and magnetic properties, and nonstoichiometry. The review on hydrides by Gibb (1962) should have been mentioned by more than a reference or two, and the classic work by Smith ("Hydrogen in Metals," 1948) deserved more than a footnote.

Many references, some quite important, to work on hydrides were not mentioned at all. Some of these are: the early work by Pietsch (1933) and the later work by Siegel and others (1960–1964) using atomic hydrogen; Mikheeva and Kost's review of the rare earth hydrides (1960); Goon's paper on lanthanum hydride (1959); the magnetic structures of TbD_2 and HoD_2 by Cox, *et al.* (1963); and Beck's discussion of the Zr–H system (1962). The data on EuH_2 and YbH_2 are presented, but no references. Only a few papers from the vast literature on the Pd–H system are covered. No mention was made of the interaction of certain hydrides with mercury. Except for a brief discussion of the Ni–H system, the author avoided, perhaps wisely, the hotly disputed and controversial hydrides of Fe, Co, and Ni. The proposed structure for BeH_2 (Figure 3-13) could be improved to indicate tetrahedral Be atoms. Most recent work on the tender compound, copper hydride, was ignored, and the structure for it given in Figure 3-12 is incorrect. There are a half a dozen or so errors of the typographical kind, and activation energy is used instead of enthalpy on page 119.

The nonmathematical description of rates of hydride formation in Chapter 2 is uncommonly complete, and helps one retain a large body of observations. The pithy discussion in Chapter 3 of volume changes which occur when metals react with hydrogen is especially lucid. Rare earth hydrides are covered well, although the ionic conductivity of lanthanum hydride (Chapter 5) was not related to the diffusion of hydrogen in the solid as revealed by nmr studies (Chapter 6). When discussing the magnetic properties of lanthanum hydride, unpaired electrons are mentioned; the reader wonders what unpaired electrons. In Chapter 3, the lighter rare earth trihydrides are said to have the bismuth trifluoride-type structure; actually BiF_3 is orthorhombic, not cubic. In the section on actinide hydrides, the mobility of hydrogen in UH_3 was missed (Bigeleisen and Kant, 1954), americium hydride was not included (Westrum, *et al.*, 1951), and the reference to PaH_3 was not given. The various sections on those frightful hydrides of V, Nb, and Ta are the best correlating summaries available.

The chapter on thermodynamics of hydrides goes far to compensate for some of the omissions noted above. The comparison of hydrides and deuterides and their relative dissociation pressures is brief but cogent. The treatment of partial molal quantities is especially clear. On observing that $-\Delta H_{\text{form}}$ for MgH_2 is lower than is the case for other alkaline earth hydrides, the author concludes that this illustrates its partly covalent nature. Yet if this criterion is applied to LiH and CsH, one would conclude that CsH is more covalent, whereas the opposite is true. The section on hysteresis competently summarizes current theories.

Except for some quaint nomenclature, the chapter on nonstoichiometry gives a satisfying account of the energetics of defect solids. The treatment of large deviations from stoichiometric