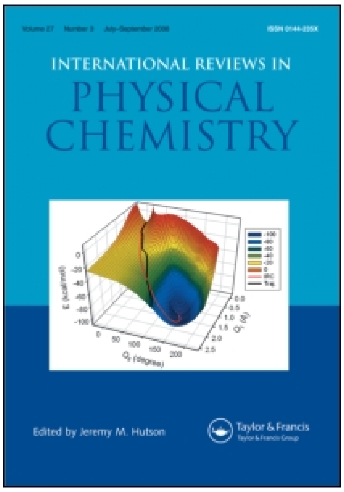

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Pressure Tuning of Electronic Energy Levels

H. G. Drickamer[a]
[a] School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, IL, USA

To cite this Article Drickamer, H. G.(1982) 'Pressure Tuning of Electronic Energy Levels', International Reviews in Physical Chemistry, 2: 3, 171 — 196
To link to this Article: DOI: 10.1080/01442358209353334
URL: http://dx.doi.org/10.1080/01442358209353334

International Reviews in Physical Chemistry (1982), *2* (171–196)

PRESSURE TUNING OF ELECTRONIC ENERGY LEVELS

H. G. DRICKAMER

School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, IL 61801, USA

ABSTRACT

Over the past three decades it has been demonstrated that pressure is a very useful tool for investigating electronic phenomena in condensed systems. Compression results in different degrees of perturbation of different types of orbitals. This 'pressure tuning' can induce electronic transitions to new ground states. It can also be used for critical tests of theories or to uncover hitherto unforeseen correlations involving electronic properties.

We discuss three types of electronic transitions: insulator–conductor transitions with emphasis on iodine; transitions between photochromic, thermochromic, and piezochromic ground states; and changes of spin state of magnetic ions. Tests of theories include Bethe's R^{-5} rule for magnetic ions, Van Vleck's prediction of spin pairing, the Förster-Dexter theory of energy transfer in phosphors, theories of emission efficiency in doped zincblende phosphors, and energy transfer between excited states of electron donor–acceptor complexes. Finally, as a challenge to further theoretical work, we demonstrate a relationship between the rate of phosphor emission k_r and the low-frequency dielectric constant ε.

INTRODUCTION

Over the past 30 years pressure has proven to be a powerful and versatile tool for understanding electronic phenomena in condensed systems. Basically, pressure decreases interatomic (or intermolecular) distance and increases the overlap among adjacent electronic orbitals. Different types of orbitals differ in their radial and angular characteristics and thus are perturbed in different degrees by the compression. It is this 'pressure tuning' which provides the basis for high-pressure studies of electronic phenomena. One of the more spectacular consequences of pressure tuning is, for many systems, to provide a new ground state for the system with different electrical, magnetic, optical or chemical properties. One of the major consequences of high-pressure research over the past three decades has been to demonstrate that electronic transitions are ubiquitous phenomena (Drickamer and Frank, 1973), just as Bridgman earlier demonstrated that structural phase transitions are common. In addition to inducing electronic transitions, high-pressure studies have provided critical tests of theories which could not be so readily verified by ambient-pressure work, and, upon occasion, have yielded relationships not anticipated by theory and have thus provided a challenge to theorists.

This brief overview can provide only a sampling of the wide variety of studies which have been made. We discuss first insulator–conductor transitions with emphasis on iodine as a model for other molecular crystals, then we consider conversions among the various states of thermochromic and photochromic materials. The third type of electronic transition we discuss involves changes in spin state of magnetic ions—a topic which includes tests of ligand field theory and Van Vleck's theory of spin states. This discussion forms a bridge to experiments primarily designed to investigate theories, which include a definitive test of the Förster-Dexter theory of energy transfer in phosphors and an analysis of luminescent efficiency of zincblende-structure phosphors. We conclude with brief discussions of dual emission from electron donor-acceptor (EDA) complexes and of a recently observed relationship between the radiative rate of emission from phosphors and the low-frequency dielectric constant of the medium. This last observation provides a challenge for future theoretical work.

INSULATOR–CONDUCTOR TRANSITIONS: IODINE

From the early days of solid-state physics (e.g. Seitz, 1940) the insulator–conductor transition has been a problem of fundamental interest. In the early 1960s insulator–conductor transitions were observed in molecular crystals such as I_2, Se, As, and some organic materials, in ionic compounds like the thallous halides, as well as in Si, Ge, GaAs, GaSb, InP, InAs, InSb, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, etc, all having the zincblende or related structures (*see* Drickamer, 1965 and references therein). A few more such transitions have been observed since, but much of the more recent effort has been directed towards a more detailed understanding of the insulator-conductor transition.

Insulators may become metals or semimetals due to band broadening and overlap with no discontinuity in resistance or change of structure, as illustrated in the treatises of Seitz (1940) and Slater (1965). They may transform to metals or narrow-gap semiconductors with a large discontinuity in resistance and a change in crystal structure as occurs in materials with the diamond or zincblende structure. Recently Van Vechten (1973) and Yin and Cohen (1980) have been able to predict reasonably well from theoretical considerations the pressures at which the insulator-conductor transition occurs in diamond and zincblende type crystals. The insulator-metal transition may also occur with a discontinuity in resistance and volume but with no change in structure, as predicted by Mott (1961 and references therein) and as McWhan and Remieka (1970 and references therein) have shown for transition-metal oxides. In rare earth chalcogenides insulator–metal transitions occur over a range of pressures with a discontinuity in compressibility but not in volume, as shown by Jayaraman *et al.* (1975a and b).

We confine our detailed discussion here to the behavior of iodine because it is the most thoroughly studied of the elements and is used as a prototype for other diatomic molecular crystals.

The earliest studies bearing on the insulator-conductor properties of iodine were measurements of the shift of the optical absorption edge by Suchan *et al.* (1959) and of the resistance and temperature coefficient of resistance by Balchan and Drickamer (1961) and by Riggleman and Drickamer (1962, 1963). (In the following discussion all pressures are corrected to a modern scale.) The resistance decreased rapidly with increasing pressure, with a decreasing slope above 130–170 kilobars depending on crystal orientation. Resistivities are difficult to estimate, but in the 180–190 kilobar region they are of the order of a few hundred $\mu\Omega$ cm which is certainly in the metallic range. The optical absorption edge shifted rapidly to lower energy with pressure. For an intrinsic semiconductor the temperature coefficient of resistivity is related to the optical gap by the equation

$$R = R_0 \exp\left(\frac{-E_g}{2RT}\right) \tag{1}$$

In *Figure 1* we show a plot of E_g as obtained optically and from the temperature coefficient of resistance. The agreement is remarkably good, and the gap extrapolates to zero in the range 130–170 kilobars depending on crystal orientation. *Figure 2* exhibits the temperature coefficient of resistance at a pressure of the order of 190 kilobars. The behavior is typical of a metal. Lynch and Drickamer (1966) attempted x-ray measurements and pointed out that there were two possibilities; either the disappearance of the gap due to band broadening provides a diatomic metal (or semimetal), or the conducting material is atomic iodine. Their data did not permit unequivocal selection between these alternatives.

Recently there has been considerable experimental activity on iodine at high pressure. Dunn and Bundy (1980) made resistance measurements of higher precision over a larger range of temperature and pressure than the early work. They found no sign of superconductivity. There has been extensive x-ray work (Shimomura *et al.*, 1978; Takemura *et al.*, 1979, 1980, 1982). These studies have been most revealing. In the region between ~160–205 kilobars, iodine is a diatomic metal (or semimetal). Near 205 kilobars there is a small but definite volume change and iodine becomes a monatomic metal, while still retaining the orthorhombic structure. *Figure 3* shows the projections on the basal plane as obtained by the Japanese group at one atmosphere, at 198 kilobars just before the diatomic→monatomic transition, and at 300 kilobars where iodine is a monatomic metal. From the changes in the axial ratios it can be estimated that the structure will change from orthorhombic to tetragonal by ~450 kilobars, and to face-centered cubic at some considerably higher pressure. Reflectivity measurements by Syassen *et al.* (1981) on the monatomic metallic phase indicate that it is probably a *p* band metal.

These iodine studies are intrinsically of interest as they represent the most complete

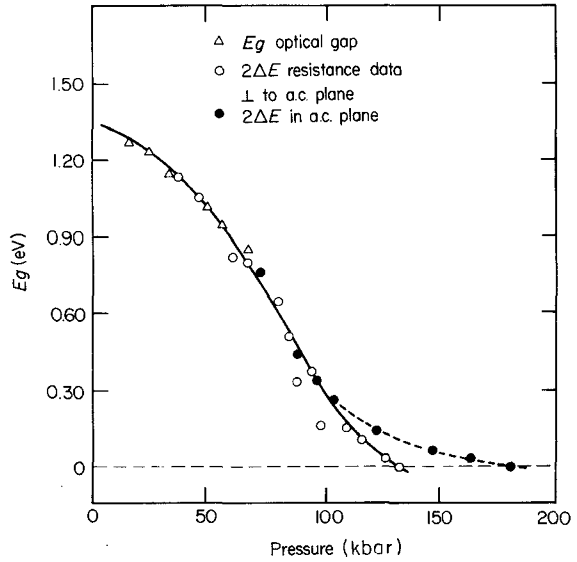

FIG. 1. Optical energy gap (E_g) and $2\Delta E$ (where ΔE is activation energy for electrical conductivity) vs pressure for iodine.

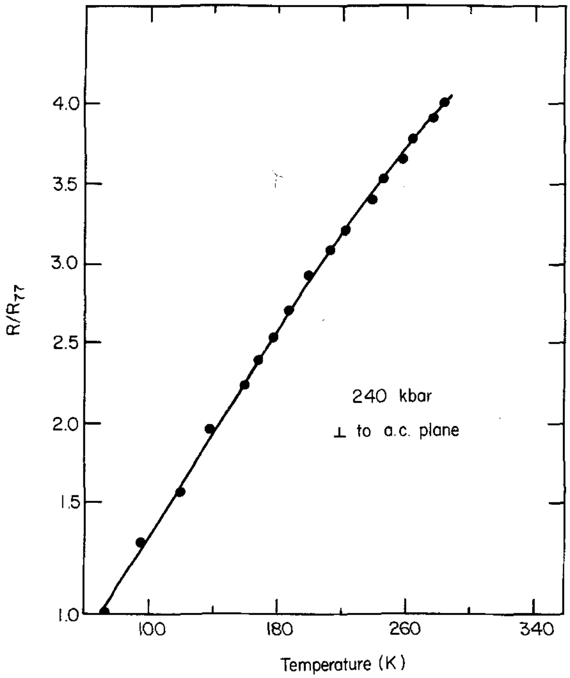

FIG. 2. Resistance vs temperature for iodine at 180–190 kilobars.

study of an insulator–metal transition for any element and illustrate the stages by which a diatomic insulator may become a monatomic metal. In addition, iodine has served as a prototype for theoretical analyses of the approach to the metallic state for diatomic molecular crystals, in particular for hydrogen. The monatomic metallic state of hydrogen has been the subject of much speculation for a variety of reasons. A number of recent theoretical analyses (McMahan *et al.*, 1977; Friedli and Ashcroft, 1977; Chakravarty *et al.*, 1981) have used the observed behavior of iodine as a basis for calculations on hydrogen. It is estimated that hydrogen will become a diatomic conductor at ~2–2.5 megabars and a monatomic metal at ~3.5 megabars, although the latter estimate may vary from 2.5–5.5 megabars depending on the precise equation of state of molecular hydrogen and the degree of correlation used for calculations on the metallic state (Van Straaten *et al.*, 1982).

These pressures are beyond what can be achieved statically now or in the foreseeable future, but experimental and theoretical work on solid bromine, and perhaps chlorine, could considerably improve understanding of the insulator–conductor transition.

THERMOCHROMIC AND PHOTOCHROMIC ANILS

There is a broad class of materials, both organic and inorganic, in which an electron can be transferred either by heating or by optical excitation to a metastable state with a different absorption spectrum (Brown, 1971). These compounds are called thermochromic if the transfer mechanism is thermal, and photochromic if it is optical. The anils constitute a group of compounds where different derivatives or crystal structures can exhibit either of these phenomena. In general, derivatives or structures which are

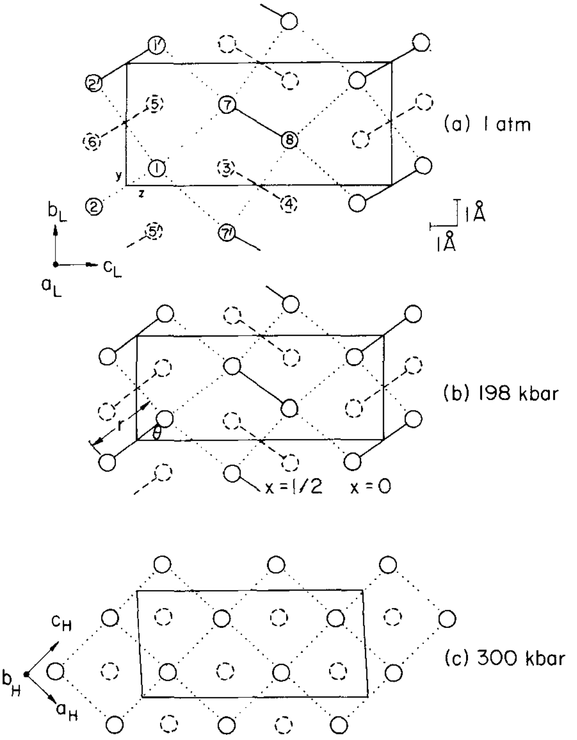

FIG. 3. Projection of atomic positions for iodine on the basal plane at (a) one atmosphere, (b) 198 kbar, and (c) 300 kbar. The solid rectangle represents the basal plane of the orthorhombic unit cell (from Takemura *et al.*, 1982).

thermochromic are not photochromic. We discuss here salicylideneaniline (SA) which is photochromic and the 5-bromo derivative (5BrSA) which is thermochromic. The various possible structures appear in *Figure 4*. The thermochromic yield is generally only a few percent even at elevated temperatures, but photochromic yields may be 50% or more at low temperature. Our discussion refers entirely to the crystalline solids.

As shown in *Figure 4*, there are three possible molecular arrangements.

1. The normal ground state is the enol form (A).
2. The cis-keto form (C) is the thermochromic product and the structure which fluoresces.
3. The trans-keto form (B) is the photochromic product.

The solid horizontal lines represent energy levels at one atmosphere. The straight vertical lines represent optical transitions, while the wavy lines represent thermal processes. The dotted lines describe the situation at high pressure. As indicated in the figure, only the cis-keto (C) structure emits fluorescence.

For these materials two types of pressure tuning are of interest.

1. One can displace the excited states of each species with respect to the corresponding ground states.
2. Pressure can tune the energies of the three ground states with respect to each other.

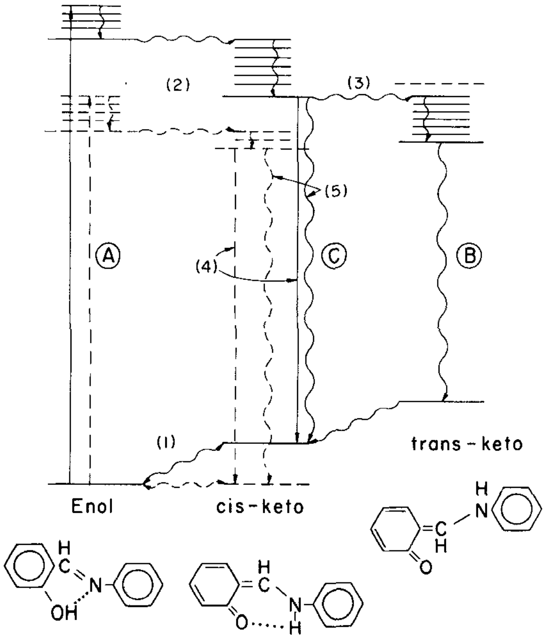

FIG. 4. Structures and energy levels for thermochromic (C) and photochromic (B) anils at one atmosphere and high pressure.

As we shall demonstrate, the factor which determines whether a given structure is photochromic or thermochromic is the relative location of the ground and excited states of the (C) form *vis-à-vis* those of the (A) and (B) forms.

If the ground state of (C) is too high with respect to (A) one cannot reach it thermally, nor will it be occupied when the ground state of (B) reverts to (A). At the same time the excited state of (C) is then so high that it is bypassed in the transfer between excited states so one observes only the (A) and (B) form—i.e. one has a photochromic material. On the other hand, if the ground and excited states of (C) are sufficiently low, *vis-à-vis* (A), thermal transfer from (A) to (C) in the ground state becomes possible. At the same time, the excited state of (C) is low enough to trap any excitation transferred from (A) and one observes only states (A) and (C), i.e. one has a thermochromic material. As we demonstrate, with pressure tuning one can transform the photochromic material into a thermochromic one, and one can, in fact, make the metastable cis-keto (C) state the stable ground state of the molecule at high pressure. High-pressure studies have been made by Hockert and Drickamer (1977a and b).

From *Figure 5* we see that absorption peaks which correspond to the enol (A) and cis-keto (C) structures, as well as the fluorescence peak, shift to lower energy by 2500 to 3200 cm^{-1} (0.3–0.4 V) in 100 kilobars, so the enol (A) and cis-keto (C) excited states are stabilized significantly with respect to their ground states. The photochromic (trans-keto) peak (B) shows little or no shift with pressure.

We consider first the behavior of the thermochromic compound (5BrSA). At room temperature and one atmosphere there is at most a trace of thermochromic product, but with increasing pressure at 296 K the intensity of the thermochromic peak increases rapidly and it constitutes 80% of the spectrum at 80 kilobars as shown in *Figure 6*, so the cis-keto ground state is stabilized *vis-à-vis* the enol ground state by

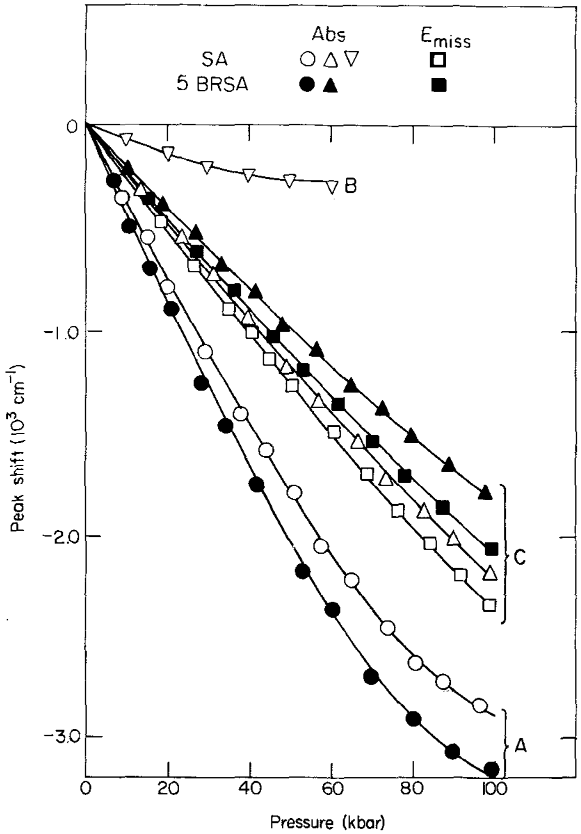

FIG. 5. Shift of absorption and emission peaks in anils.

pressure. We call this process piezochromism. From the areas under the peaks at steady state we extract the equilibrium constant (*Figure* 7). From the relationship

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = \frac{-\Delta V^\circ}{RT} \tag{2}$$

we establish that the volume change in transforming from the enol to the cis-keto form is 0.7% of the one-atmosphere enol volume.

A series of isobars (*Figure 8*) permits us to establish ΔH° as a function of pressure. The results are shown in *Figure 9*. The line represents a plot of $p\Delta V^\circ$ normalized at one atmosphere. The agreement between the temperature and pressure data is excellent.

The emission intensity from 5BrSA decreases by a factor of 50–60 in 100 kilobars. This is associated with the large red shift of the emission peak. It has been clearly demonstrated (Mitchell *et al.*, 1977; Tyner and Drickamer, 1977) that a shift of the emission peak to lower energy is accompanied by an increase in k_{nr}, the non-radiative rate to the ground state, because of increased overlap between excited- and ground-state vibrational levels.

We turn now to the photochromic compounds (SA). At one atmosphere there is no sign of the thermochromic peak, even at the most elevated temperatures. However, with increasing pressure at room temperature a modest but quite measurable amount

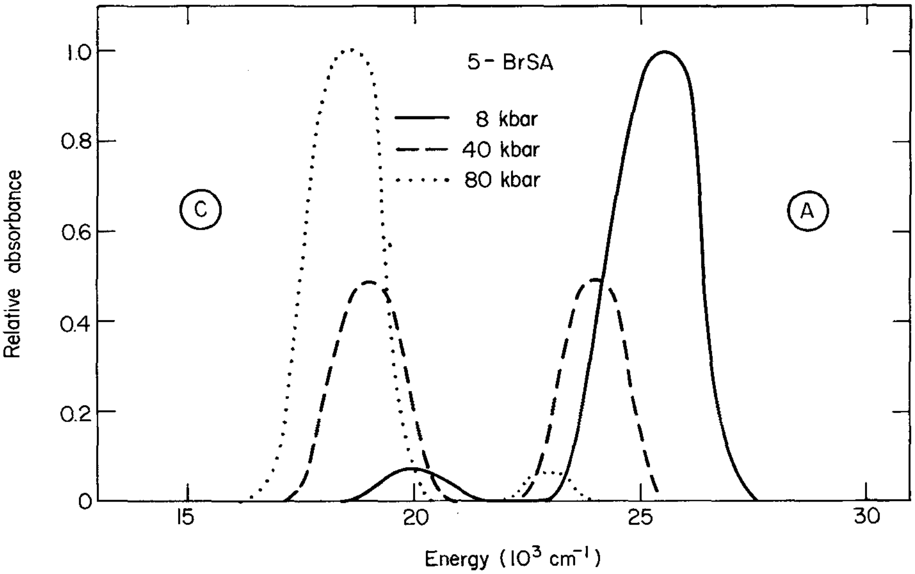

FIG. 6. Absorption bands A and C for 5BrSA at various pressures.

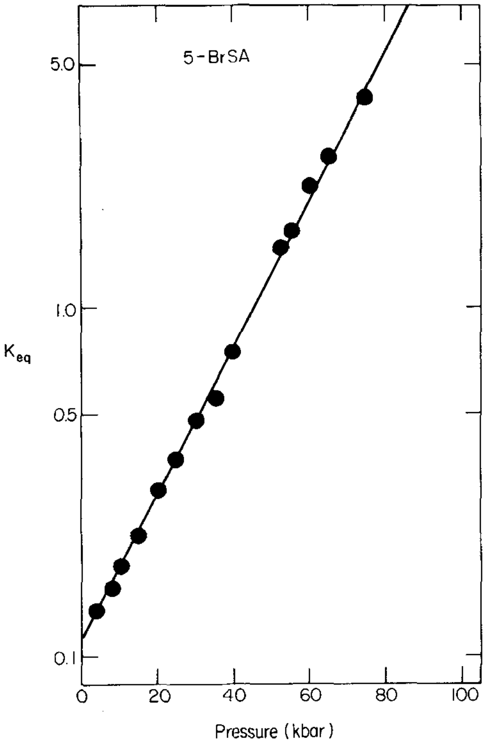

FIG. 7. ln K_{eq} vs pressure (5BrSA).

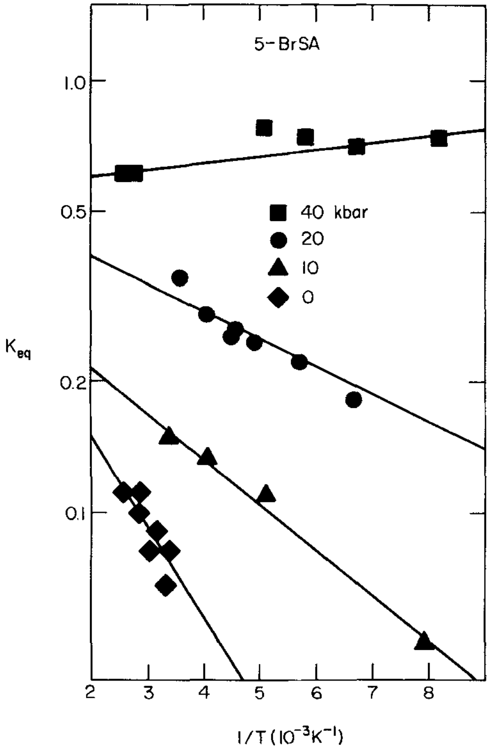

FIG. 8. ln K_{eq} vs $1/T$ at various pressures (5BrSA).

of the thermochromic (piezochromic) peak appears—about 10% yield at 90 kilobars (*see Figure 10*). Evidently the cis-keto ground state is stabilized significantly with pressure, even in the SA structure.

In *Figure 11* we exhibit the photochromic yield about one hour's irradiation as a function of pressure at three temperatures. It should be emphasized that these results represent rates, not equilibrium yields. The rate of formation of the photochromic state decreases with increasing pressure at all temperatures. From *Figure 4* we see that at high pressure the excited state of the cis-keto form lies below the excited state of the trans-keto form. Evidently the mechanism of formation of the photochromic state is:

enol(ground)→enol(ex)→
cis-keto(ex)→trans-keto(ex)→
trans-keto(ground).

Pressure inhibits the rate of the second last step.

Finally, in *Figure 12* we exhibit the fluorescence yield for SA as a function of pressure. It should be kept in mind that the emission occurs from the excited cis-keto state (C). The inhibition of the cis-keto (ex)→trans-keto (ex) step by pressure permits the increase in fluorescence yield by a factor of over 20 in 70 kilobars. At the highest pressures the increase in k_{nr} discussed above more than compensates, so that there is a drop in emission efficiency.

These results illustrate rather well the use of pressure tuning to sort out the steps in a

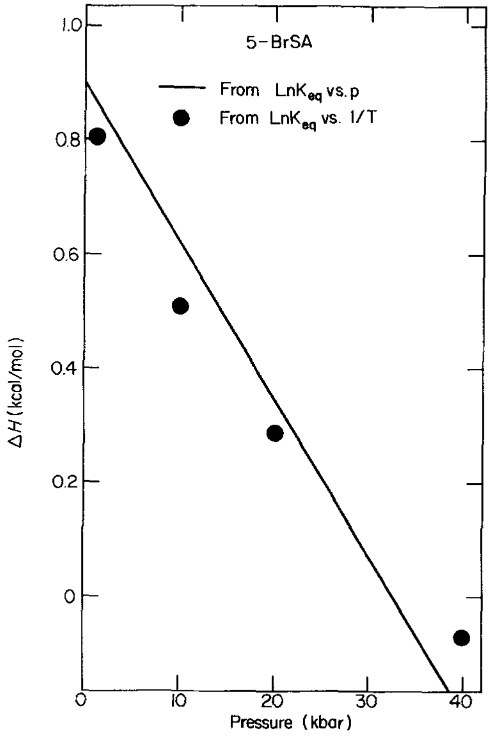

FIG. 9. ΔH and pΔV vs pressure (5BrSA).

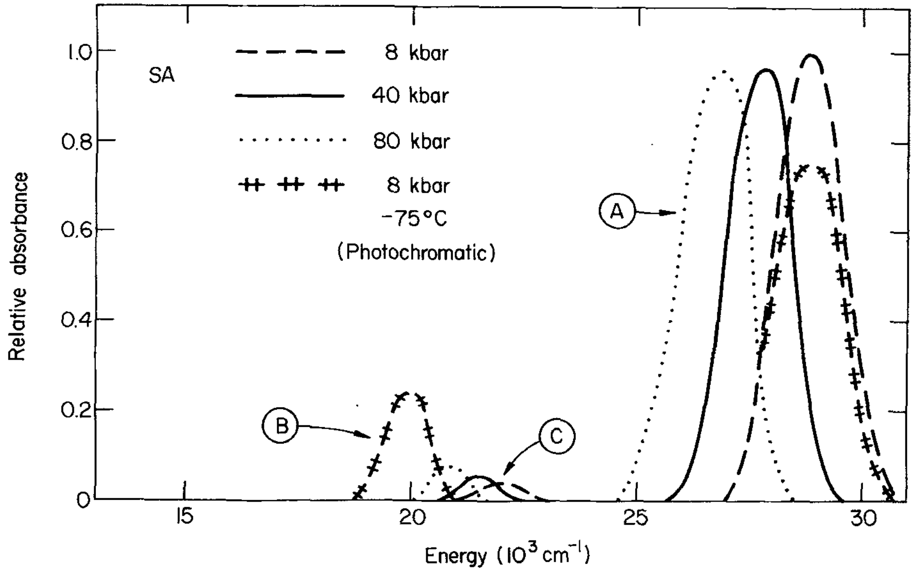

FIG. 10. Absorption spectra at various pressures (SA).

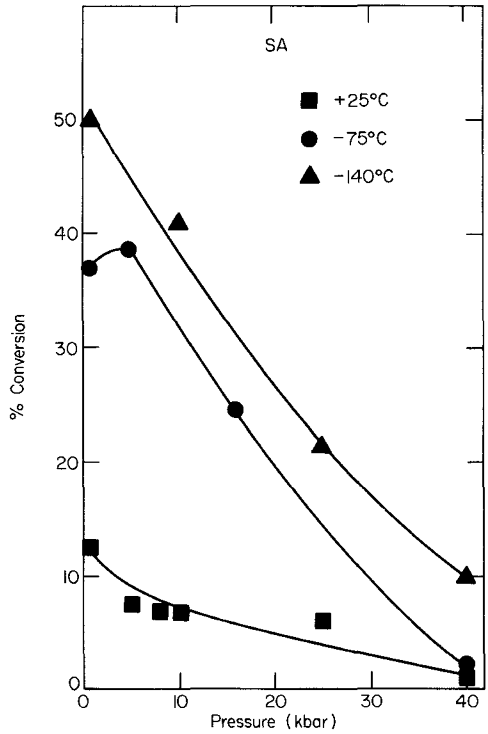

FIG. 11. Photochromic yield vs pressure (SA).

group of interacting processes and to transform a material from one ground state to another one having quite different characteristics.

LIGAND FIELD THEORY AND SPIN STATES

The basic theory involving the energies of the electrons of transition-metal (magnetic) ions in the field of surrounding ions or molecules was developed by Bethe (1929) and Van Vleck (1932, 1935a). In refined form it is now a standard part of undergraduate and graduate texts. The degeneracy of the d orbitals is partially removed by the field of the ligands. The type of splitting depends on the symmetry of the ligands; the magnitude of the splitting is established by the strength of the ligand field. In the limit of point-charge ions, Bethe showed that the field (10 Dq) should vary as R^{-5} where R is the ligand-metal ion distance. High-pressure optical measurements have provided the basic tests of this theory (Drickamer, 1965 and references therein). A number of standard texts exhibit plots of 10 Dq vs R^{-5} for various transition-metal ions in Al_2O_3 or MgO, showing reasonable agreement with the simple theory. These results are, however, subject to the caveat that the relation between the bulk compressibility and the compressibility near the impurity ion is unknown. Probably the best test of the theory is given by a combination of optical and x-ray measurements on NiO (Drickamer and Frank, 1973 and references therein). As shown in *Figure 13*, the change in the ligand field is slightly but measurably greater than predicted by the R^{-5} law. Of course other

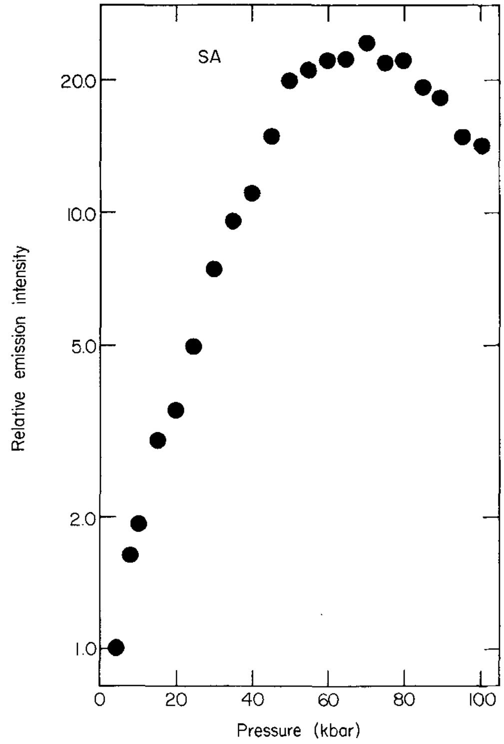

FIG. 12. Fluorescence emission yield vs pressure (SA).

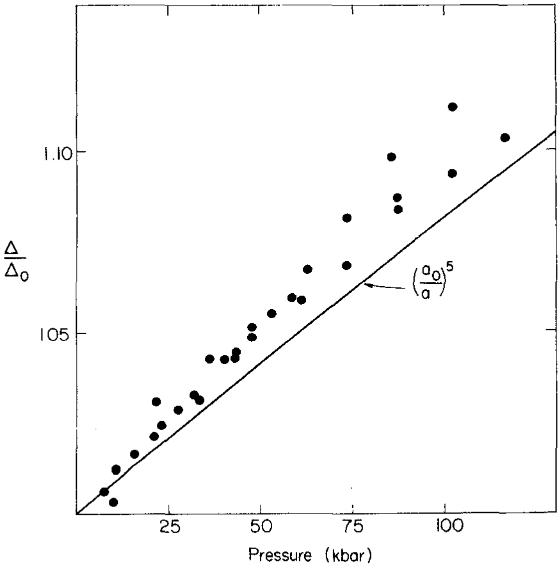

FIG. 13. Change of 10 Dq and R^{-5} vs pressure (NiO).

ligands may be approximated more or less well as point charges, but it is probable that similar cancelling factors would occur for many of them.

The normal ground state of a transition-metal ion is that of maximum multiplicity as predicted by Hund's rule. Van Vleck (1935b) predicted that as the ligand field increases, at some point it would become energetically economical to pair the spins. Indeed low-spin compounds are observed. However, it is only from pressure measurements that one can observe the transformation from high to low spin for a given compound.

Fe(II) in FeS_2 (pyrite) is low spin at all pressures. MnS_2 has the same cubic crystal structure as FeS_2 but with a somewhat larger lattice parameter. Fe(II) as a dilute substitutional impurity in MnS_2 is high spin, as demonstrated by the Mössbauer spectrum. As shown in *Figure 14a* and *14b*, Bargeron *et al.* (1971) demonstrated that by 65 kilobars there was about 50% low spin Fe(II) present, and by 100 kilobars all of the Fe(II) is low spin. In a magnetically concentrated system with completely hydrostatic pressure, the transition could well be first order. This is, in any case, the most clearcut test available of Van Vleck's prediction.

In this section we have demonstrated an electronic transition in Fe(II) with magnetic consequences as well as tests of two theories concerning magnetic ions. Thus it forms a connecting link between the two previous sections on electronic transitions and the following three sections involving tests of theories.

ENERGY TRANSFER

Energy transfer in phosphors is a topic of widespread interest. Consider a medium (crystal or solution) containing two phosphors which absorb and emit in somewhat different regions of the spectrum. Under some circumstances one can excite one of these phosphors with a definite probability that the excitation can be transferred to the second phosphor by a radiationless process so that both phosphors may emit. This process is important in such diverse areas as fluorescent lighting, the excitation of rare earth lasers, and organic photochemistry including photosynthesis, so it is of interest in physics, chemistry, biology, and materials design. If the concentration of phosphors is dilute the transfer will be by a dipole-dipole process like a van der Waals' interaction. This situation was first discussed by Förster (1948) whose analysis was refined by Dexter (1953).

The probability per unit time of transfer between donor and acceptor is given by

$$P_{DA} = \frac{\alpha}{n^4}\left(\frac{1}{\tau_D}\right)\frac{1}{R_{DA}^6}\int \frac{f_D(E)F_A(E)}{E^4}\,dE \tag{3}$$

$$= \frac{R_{DD}^6}{R_{DA}^6} \tag{3a}$$

P_{DA} is then averaged over values of R_{DA} (Dexter, 1953). Here α contains only constants, and the integral is an overlap integral between donor emission and acceptor absorption peaks; τ_D is the donor emission lifetime and n the refractive index of the medium. R_{DD} is the effective donor-acceptor distance such that there is an equal probability that the donor will fluoresce or transfer its energy to the acceptor. The transfer efficiency is given by

$$\psi = \frac{P_{DA}\tau_D}{1 + P_{DA}\tau_D} \tag{4}$$

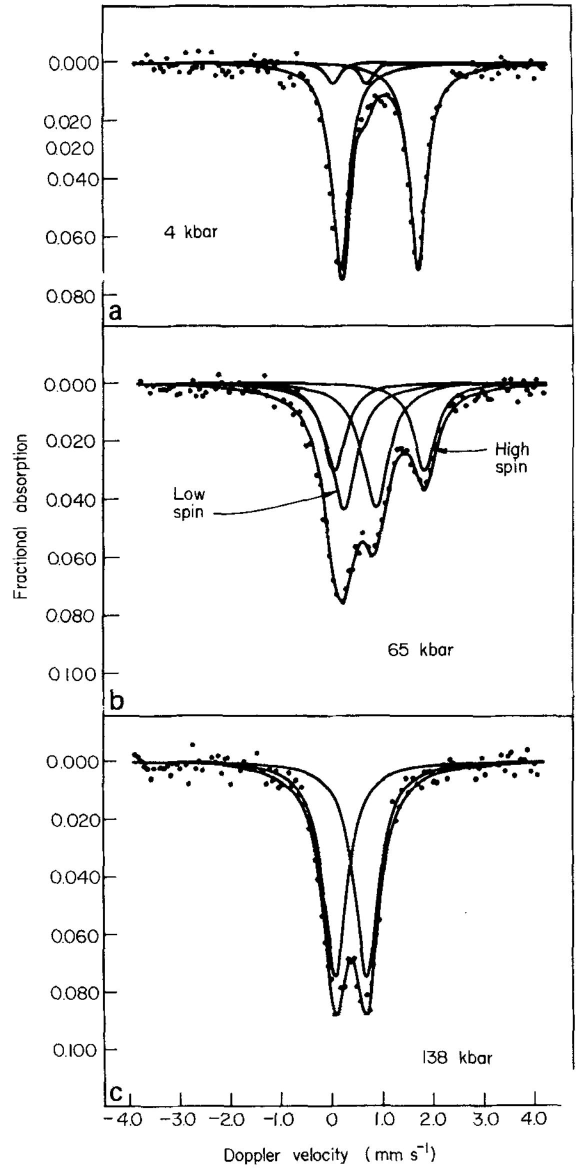

FIG. 14. Mössbauer spectrum of Fe(II) in MnS_2: 4 kilobars (a), 65 kilobars (b) and 138 kilobars (c).

This can be determined experimentally by measuring the relative areas under the donor and acceptor emission peaks in the mixed crystal. On the other hand, all of the quantities on the right hand side of Eq. (3) can be determined for the pure medium or for the medium singly doped with donor or acceptor ions or molecules. A comparison between the relative areas under the donor and acceptor peaks and the calculated efficiency is one test of the theory.

A second test depends on measuring the intensity of emission as a function of time.

The theory gives this intensity for sensitized luminescence by the relation

$$I_D(t)=I_0\left[\exp\left(-\frac{t}{\tau_D}\right)\right]\left[\exp\left(-\beta R_{DD}^3\left(\frac{t}{\tau_D}\right)^{1/2}\right]\right] \qquad (5)$$

The first bracket gives the lifetime of the donor as a single dopant. The second bracket represents the intensity lost by dipole-dipole transfer to the acceptor. β represents a combination of coefficients independent of pressure. From a comparison of intensity vs time measurements on the singly and doubly doped medium, R_{DD} can be calculated and thus P_{DA} and the efficiency ψ established.

This theory has been widely used, but most of the tests of the theory have been based on varying R_{DA} by changing the concentration. The use of pressure permits a variation of R_{DA} through the compressibility of the medium, and through a variation of the refractive index. The largest potential effect of pressure is, however, in changing the overlap integral. We present results obtained by Bieg and Drickamer (1977) for a system KCl:Ag:Tl where there are no important secondary effects and where there is a large change in the overlap integral with pressure. As can be seen schematically in *Figure 15*, the Ag^+ ion absorbs at high energy (~220 nm) and, at low pressure, the overlap with the Tl^+ absorption, and the consequent Tl^+ emission, is small. By 18 kilobars the overlap and the Tl^+ emission have increased considerably. The calculated efficiency of transfer (Eq. (4)) increases from 7% to 28% in 18 kilobars.

In *Figure 16* we compare the calculated efficiency (the solid line) with that extracted

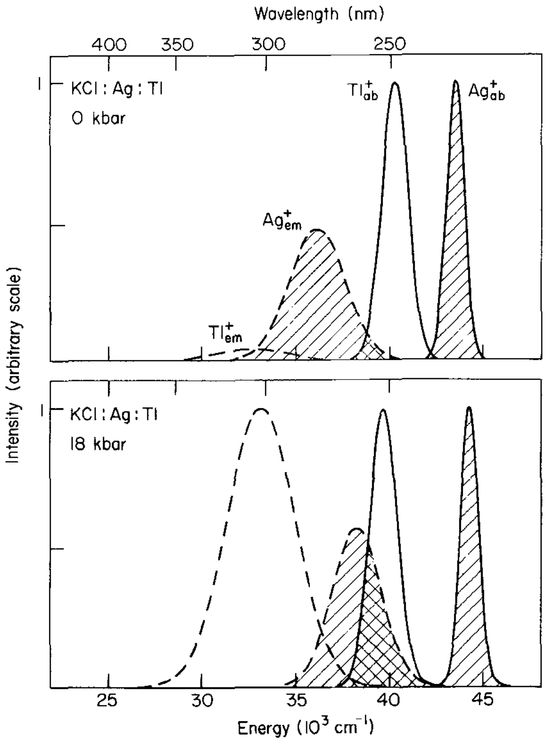

FIG. 15. Schematic representation of spectra for KCl:Ag:Tl at low and high pressures.

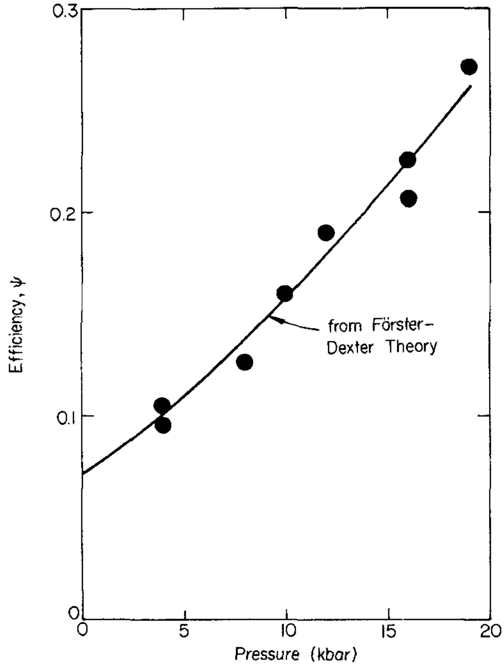

FIG. 16. KCl:Ag:Tl energy transfer efficiency as obtained from sensitizer emission decay.

from measuring the time-dependent emission intensity of the donor (Ag^+) in KCl:Ag:Tl compared with that in KCl:Ag, using Eq. (5) to obtain R_{DD} and then calculating ψ from Eq. (4). The agreement between theory and experiment is excellent.

As discussed above, it is also possible to test the theory by measuring the relative intensity of donor and acceptor emission compared with values calculated from Eq. (3). In taking this path it is necessary to make a correction for absorption by the acceptor of photons emitted by the donor and consequent emission from the acceptor (the cascade effect). This correction has been worked out by Dexter (1953) and depends on the crystal thickness. Experiments were performed with crystals 0.75 mm thick and with 'thin' crystals 0.20 mm thick to be sure the correction was done adequately. As we see in *Figure 17*, although there is some scatter due to the number of corrections, the agreement with theory is again excellent.

The efficiency can also be varied by changing temperature at constant pressure. The primary effect of lowering the temperature is to decrease the peak width and thus to modify the overlap. This effect is most important in regions of small overlap. In *Figure 18* we compare the measured and calculated efficiencies as a function of temperature at two pressures. The agreement is very good.

These results constitute an excellent illustration of the use of pressure to perform a critical test of a theory important in a wide variety of atmospheric pressure applications.

ZINCBLENDE EMISSION

Crystals having the zincblende structure, with appropriate dopants, are utilized commercially in television screens, light-emitting diodes and a variety of other applications.

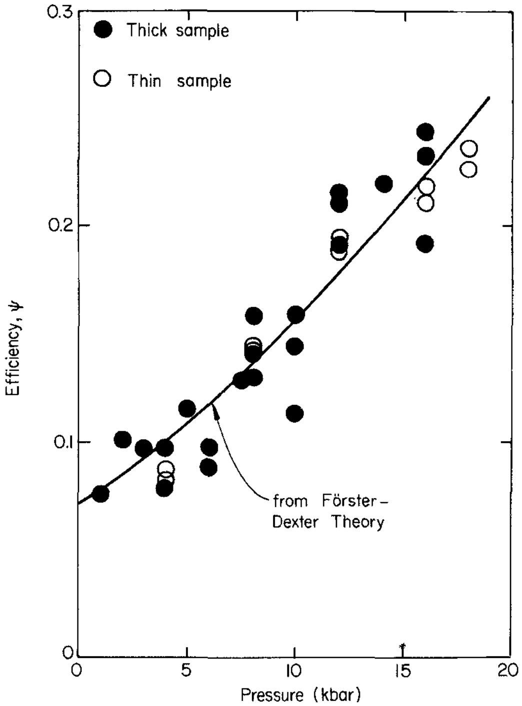

FIG. 17. KCl:Ag:Tl energy transfer efficiency obtained from the ratio of emission peak intensities.

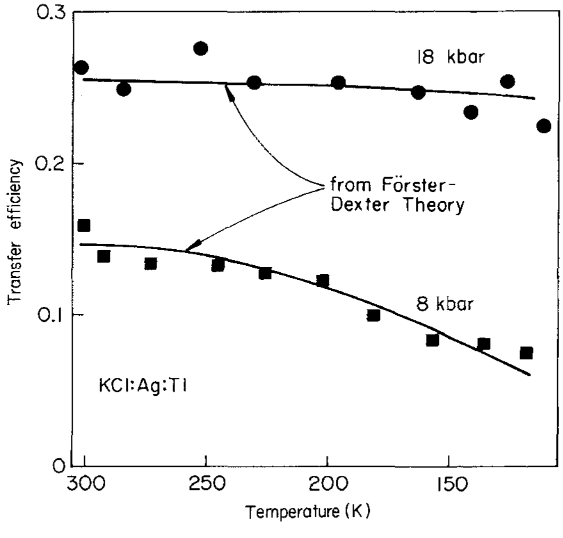

FIG. 18. Comparison of calculated and measured efficiencies as a function of temperature at 8 and 18 kilobars (KCl:Ag:Tl).

We present here a study by House and Drickamer (1977a and b) of ZnS as a prototype, although similar results have been obtained for related systems. *Figure 19* presents a schematic outline of the principal electronic states and excitations. The basic excitation is from the top of the valence band to the bottom of the conduction band. Two types of dopants are added (in concentrations ~0.01 atom %). A Cu^+ or Ag^+ ion acts as a hole trap. It is a deep trap, of energy $E_A \sim 1$–1.5 eV above the valence band, and thus is strongly localized. There is a variety of evidence that its position *vis-à-vis* the top of the valence band is quite independent of pressure. A second compensating ion (e.g. Cl^-, Al^{+3}) acts as an electron trap with a trap depth E_D of 0.1–0.2 eV. This trap depth is sensitive to conditions, and the delocalization of the electron trap wavefunction is strongly dependent on E_D. The luminescence efficiency depends directly on the overlap and thus on the delocalization of E_D. The relevant equation for the intensity (Prener and Williams, 1956; Thomas *et al.*, 1965) can be written

$$I(r) \propto \frac{1}{\tau} \int r^2 W(r) G(r)\, dr \tag{6}$$

where $W(r)$, the radiative recombination rate, is given by

$$W(r) = \text{const}\ X (r/a^*)^{2(N-1)} \exp(-2r/Na^*) \tag{7}$$

Here

$$N = \frac{E^{*1/2}}{E_D},\quad E^* = \frac{e^2}{2a^*\varepsilon},\quad a^* = \frac{h^2\varepsilon}{m^* e^2}$$

m^* is the effective electronic mass and ε is the dielectric constant. The distribution function $G(r)$ used corresponded to a random distribution of impurities.

The major pressure dependence of the intensity arises through N and thus through E_D. We use here two independent ways of measuring E_D as a function of pressure. First, we measure the shift of the absorption edge and the emission peak with pressure and

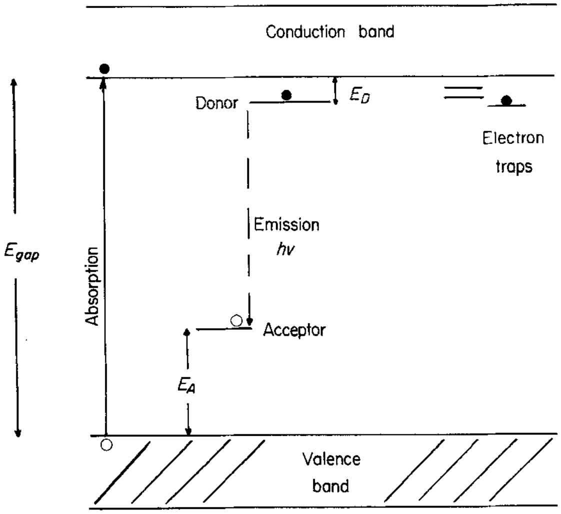

FIG. 19. Schematic diagram of band structure and impurity levels (ZnS doped with donors and acceptors).

take the difference of these as the change in E_D with pressure. It is assumed that the hole trap energy E_A is independent of pressure. There are several pieces of evidence that this is a reasonable assumption, but establishing a small number from the difference between two large numbers always involves an element of risk. (We checked the measurement of E_D by a second method (Hook and Drickamer, 1978).) *Figure 20* shows the shift of the absorption edge and the luminescence emission with pressure. It is clear that E_D increases significantly as pressure increases. In *Figure 21* we compare the relative efficiency as calculated from Eq. (6) with the measured values. The agreement is remarkably good. (In the lower part of the figure are shown two lifetimes which are essentially independent of pressure. The complex decay was approximated as a double exponential. The independence of pressure is consistent with our assumption that E_A is pressure independent.)

In spite of the satisfactory comparison of theory with experiment, it is desirable to check the pressure effect of E_D by a second method (Hook and Drickamer, 1978). If the sample of ZnS is irradiated at say 77 K, no emission is observed. Heating the sample after irradiation generates an emission which maximizes at some temperature T_m. If the heating is performed so that the temperature–time curve is linear, it is straightforward to extract E_D from the heating rate and T_m. In *Figure 22* values of the change E_D with pressure from thermoluminescence data are compared with the value from the steady-state measurements discussed earlier. The discrepancy is nowhere greater than 0.01 eV which is surely within the error of the experiments and of the theory. It is encouraging that rather different heating rates generated the same value for E_D.

These results illustrate again the ability of pressure to test a model of a material of both theoretical and practical interest.

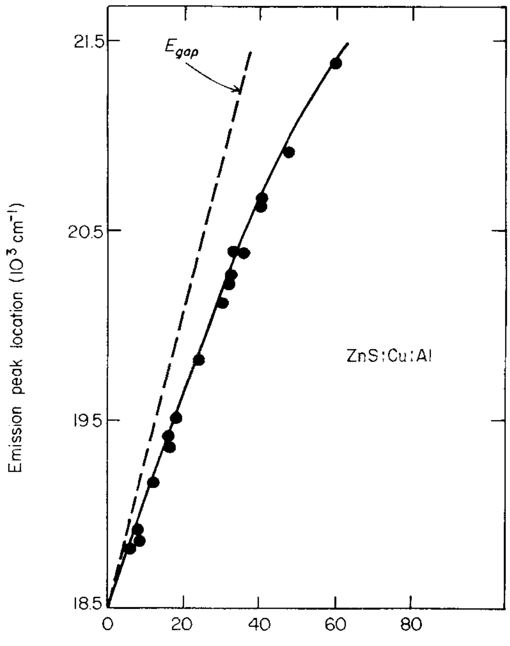

FIG. 20. Shift of absorption edge and of luminescence emission peak with pressure (ZnS:Cu:Al).

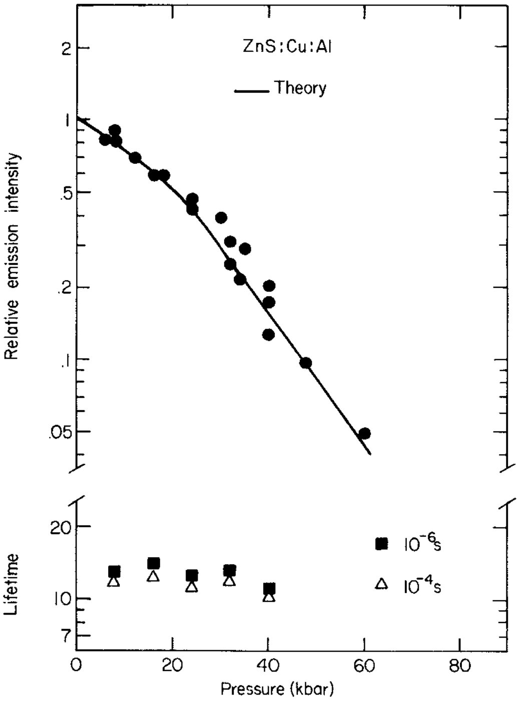

FIG. 21. Comparison of relative values of calculated and measured efficiencies (ZnS:Cu:Al).

EMISSION FROM EDA COMPLEXES

A variety of electron donor-acceptor (EDA) complexes exhibit emission from either of two states depending on the rigidity of the medium. A sampling of studies includes those of Mataga and Murata (1969), Kobayashi *et al.* (1971), Egawa *et al.* (1971) and Prochorow (1974). Based on the effects of temperature and solvent there have been speculations that the effect of increasing viscosity is to increase the energy barrier to transformation along an electronic coordinate associated with the emission. One would then expect that the rate of rearrangement should be strongly dependent on temperature at constant viscosity; in fact the temperature coefficient should increase with increasing viscosity.

A series of EDA complexes of tetracyanobenzene (TCNB) with aromatic hydrocarbons, especially xylenes have been studied by Thomas and Drickamer (1981a and b). These EDA complexes exhibit emission from a geometry like the ground state (the FC state) in rigid media and from quite a different geometric arrangement (the EO state) in fluid media. A series of paraffin hydrocarbon solvents were used: methylcyclohexane (MCH), heptamethylnonane (HMN), tetramethylpentadecane (TMPD) and a mixed solvent. These have about the same polarizability but have very different pressure coefficients of viscosity so that a range of $\sim 10^5$ in viscosity can be covered at constant temperature.

At both 25°C and 0°C the distribution of emission at steady state between the two states and the time dependent emission (decay) have been measured as a function of pressure. From these results one can extract the rate of rearrangement k_{RE} from the FC to EQ state. In *Figure 23* we plot log k_{RE} vs log η. Clearly k_{RE} is independent of solvent,

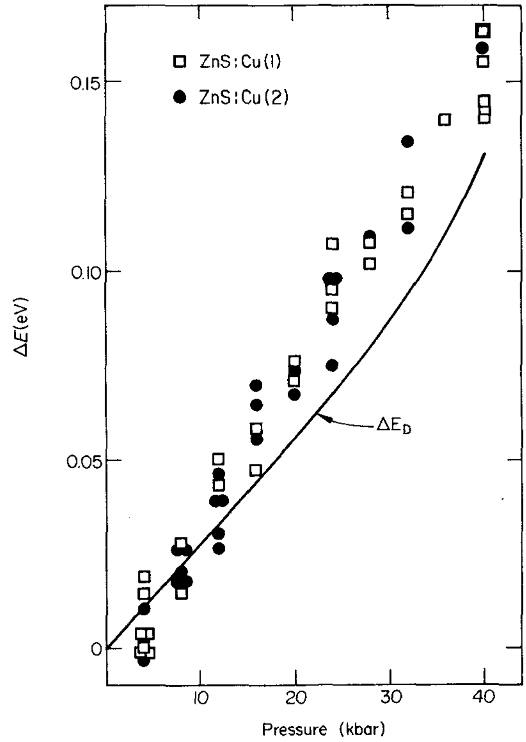

FIG. 22. Comparison of E_D (donor trap depth) vs pressure from thermoluminescence and steady state measurements.

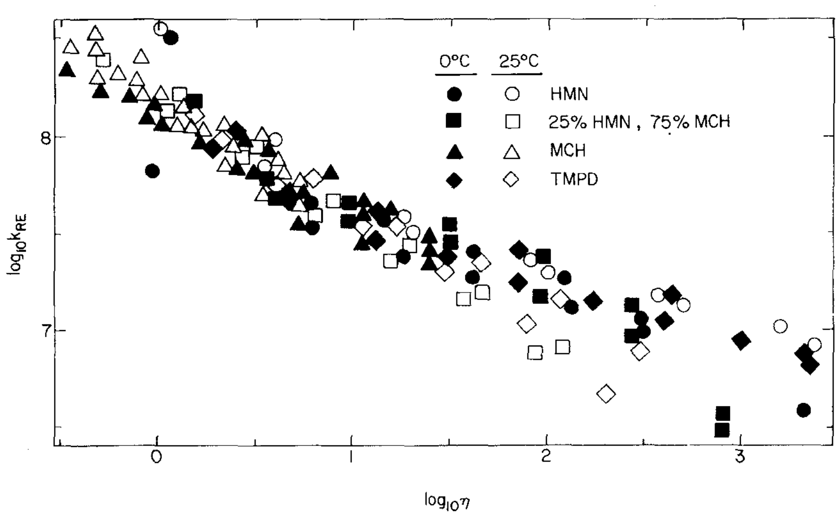

FIG. 23. Log k_{RE} vs log η (viscosity) at 0°C and 25°C.

donor, or temperature except in so far as these effect viscosity. The slope at quite low viscosity is ~ -1 but above three poise it is constant at -0.39 independent of temperature. A more direct check of the slope is obtained from the ratio

$$x = \left[\frac{\log \dfrac{k_{RE}(25)}{k_{RE}(0)}}{\log \dfrac{\eta(25)}{\eta(0)}} \right]_{P,\ \text{solvent}} \tag{8}$$

x was found to vary from -1 at low viscosities to an average value of -0.42 above 2–3 poise. The effect of viscosity is clearly a diffusional one, involving rearrangement of surrounding molecules to provide an appropriate environment for one state or the other. From the Debye equation for molecular relaxation as a function of viscosity one can write

$$k_{RE} = C \frac{T}{\eta} \tag{9}$$

This predicts a relaxation rate inversely proportional to viscosity with a small temperature dependence. Exactly this condition obtains in the low-viscosity region. The Debye equation was derived for rigid spheres. MCH, the solvent used for the lower viscosity data, is a reasonable approximation to this condition. The other solvents are long flexible molecules and segmental motion or rotation around the long axis could permit rearrangement without contributing significantly to viscous flow.

This study illustrates the ability of pressure to vary bulk properties *at constant temperature* and thus to discriminate between alternate descriptions of an electronic process.

THE RADIATIVE RATE AND THE LOW-FREQUENCY DIELECTRIC CONSTANT

One of the basic properties of a luminescing system is the rate of radiative emission k_r defined by the equation

$$k_r = \frac{\phi}{\tau}$$

where ϕ is the quantum yield and τ is the lifetime of the radiation.

Strickler and Berg (1962) derived a formula expressing the fluorescence radiative rate (k_f^{theor}) in terms of experimentally measurable quantities. This formula is of the form

$$k_f^{\text{theor}} = \frac{1}{\tau_0} = 2.88 \times 10^{-9} \frac{n_F^3}{n_A} < \bar{v}_F^{-3} > AV^{-1} \left(\frac{g_\ell}{g_u} \right) \int \frac{e(\bar{v})}{\bar{v}} \, d\bar{v}, \tag{10}$$

where n_F and n_A are the mean refractive indices of the solvent over the fluorescence and $S_0 \rightarrow S_1$ absorption spectra, respectively; $< v_F^{-3} > AV^{-1}$ is the reciprocal of the average value of v^{-3} over the fluorescence spectrum; g_ℓ and g_u are the degeneracies of the lower and upper states, respectively; $e(\bar{v})$ is the molar extinction coefficient; the integral is taken over the $S_0 \rightarrow S_1$ absorption spectrum; and τ_0 is the maximum possible mean lifetime of state S_1 where spontaneous emission to state ℓ is the only mechanism of deactivation.

In a recent study of luminescence of indole and indole derivatives as a function of pressure in various solvents, Politis and Drickamer (1981) showed that k_r correlates quite well with the low-frequency dielectric constant ε. There is no basis in any general theory for such a correlation.

In order to investigate this relationship further, Salman and Drickamer (1982a and b) measured k_r for four molecules in a series of solvents. The molecules included two (indole and 3-hydroxyflavone) where the emission is an allowed transition of $\pi-\pi^*$ character with lifetime in the nanosecond range, and two—tricarbonylchloro-4,7-diphenyl-1,10-phenanthrolinerhenium (I) (complex A) and tricarbonylchloro-1,10-phenanthrolinerhenium (I) (complex B)—where the excited state is triplet in character and arises from a metal-to-phenanthroline charge transfer. These exhibited lifetimes of the order of hundreds of nanoseconds. Six solvents were used, ranging from non-polar molecules like *n*-octane and *m*-xylene with dielectric constants in the range 2–3 to acetonitrile with a dielectric constant of 38.8 at one atmosphere and 295 K. These molecules have in common the fact that they freeze at 295 K at pressures below 10 kilobars.

For non-polar molecules $\varepsilon \approx n^2$, where n is the refractive index, and there is little or no discontinuity in ε at the freezing point. Polar molecules have a large orientational polarizability, and after freezing there is a large drop in ε as the molecules can no longer reorient in an electric field. In the solid state their low-frequency dielectric constant is of the same order as that for nonpolar molecules.

On *Figures 24–26* we exhibit plots of $\varepsilon/\varepsilon_0$ and k_r/k_{r0} for indole, 3-hydroxyflavone,

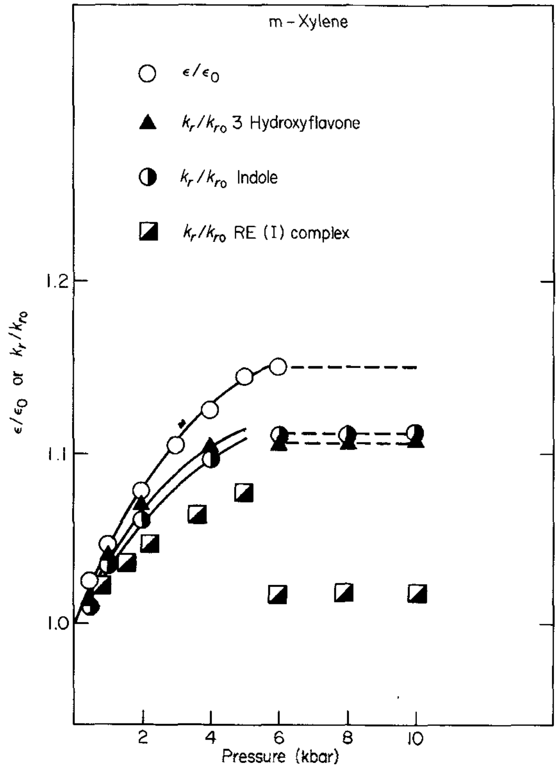

FIG. 24. $\varepsilon/\varepsilon_0$ and k_r/k_{r0} for three solutes in *m*-xylene.

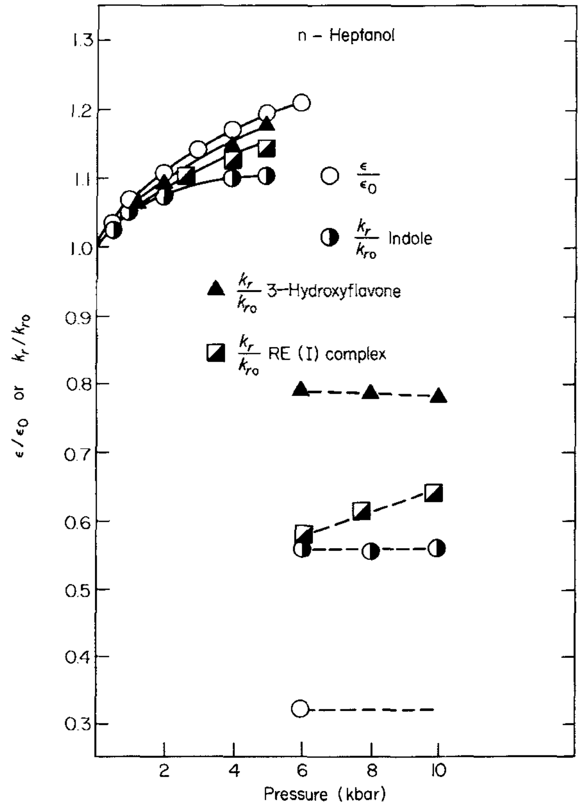

FIG. 25. $\varepsilon/\varepsilon_0$ and k_r/k_{r0} for three solutes in *n*-heptanol.

and complex (B) in *m*-xylene ($\varepsilon_0 = 2.75$), *n*-heptanol ($\varepsilon_0 = 6.7$), and acetonitrile ($\varepsilon_0 = 38.8$). We see that for the first solvent there is virtually no discontinuity in $\varepsilon/\varepsilon_0$ or k_r/k_{r0} at the freezing point, while for CH_3CN the discontinuity for both quantities is very large, and for *n*-heptanol it is intermediate. Also, within each phase the behavior of k_r/k_{r0} mirrors that of $\varepsilon/\varepsilon_0$. The results for complex (A) and for the other solvents are completely analogous.

This experimental observation could only be unequivocally established from high-pressure measurements. A number of speculative explanations are possible but we prefer to leave these results as a challenge for fundamental theoretical analysis.

SUMMARY

We have endeavored to illustrate a variety of high-pressure studies of electronic phenomena. The examples have necessarily been modest in number and presented only in outline. Nevertheless it is hoped that this 'broad brush' treatment gives a picture which is sufficiently clear and sharply focused to be convincing as to the significance of pressure for discovering and explaining electronic processes.

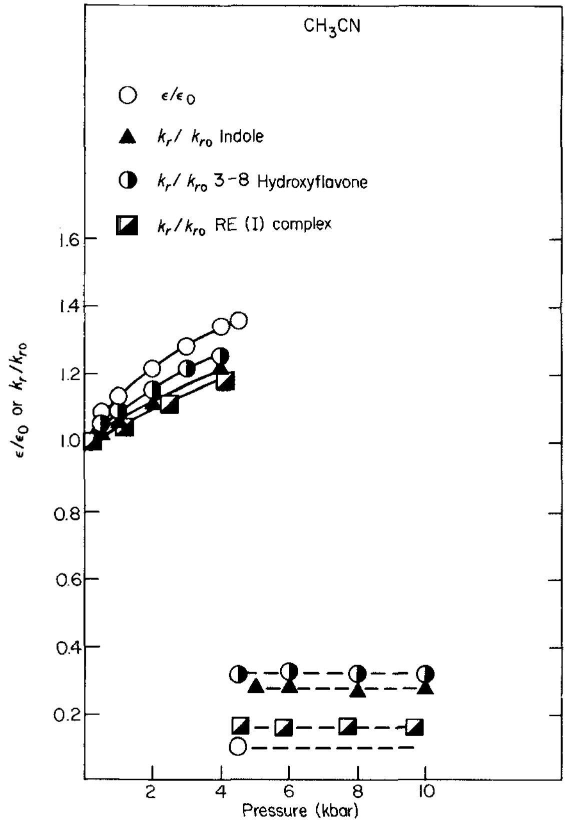

FIG. 26. $\varepsilon/\varepsilon_0$ and k_r/k_{r0} for three solutes in acetonitrile.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge support from the Department of Energy (Materials Science Division) under contract DE-AC02-76ER01198.

REFERENCES

BALCHAN, A. S. and DRICKAMER, H. F. (1961). *J. Chem. Phys. 34*, 1948.

BARGERON, C. B., AVINOR, M. and DRICKAMER, H. G. (1971). *Inorg. Chem.*, *10*, 1338.

BETHE, H. A. (1929). *Ann. Phys.*, *3*, 133.

BIEG, K. W. and DRICKAMER, H. G. (1977). *J. Chem. Phys.*, *66*, 1437.

BROWN, G. H. (ed.). (1971). *Photochromism*, New York: Wiley Interscience.

CHAKRAVARTY, S., ROSE, J. H., WOOD, D. and ASHCROFT, N. W. (1981). *Phys. Rev.*, *B24*, 1624.

DEXTER, D. L. (1953). *J. Chem. Phys.*, *21*, 836.

DRICKAMER, H. G. (1965). In *Solid State Physics: Vol. 17*, pp. 1–133 (eds. F. Seitz and D. Turnbull), New York: Academic Press.

DRICKAMER, H. G. and FRANK, C. W. (1973). *Electronic Transitions and the High Pressure Chemistry and Physics of Solids*, London: Chapman and Hall.

DUNN, K. S. and BUNDY, F. P. (1980). *J. Chem. Phys.*, *72*, 2936.

EGAWA, K., NAKASHIMA, N., MATAGA, N. and KAMANAKA, Ch. (1971). *Chem. Phys. Lett.*, *8*, 108.

FÖRSTER, Th. (1948). *Ann. Phys.*, *2*, 55.

FRIEDLI, C. and ASHCROFT, N. W. (1977). *Phys. Rev.*, *B16*, 662.

HOCKERT, E. N. and DRICKAMER, H. G. (1977a). *J. Chem. Phys.*, *67*, 5178.

HOCKERT, E. N. and DRICKAMER, H. G. (1977b). *J. Chem. Phys.*, *67*, 5189.

HOOK, J. W., III and DRICKAMER, H. G. (1978). *J. Appl. Phys.*, *49*, 2503.

HOUSE, G. L. and DRICKAMER, H. G. (1977a). *J. Chem. Phys.*, *67*, 3221.

HOUSE, G. L. and DRICKAMER, H. G. (1977b). *J. Chem. Phys.*, *67*, 3229.

JAYARAMAN, A., DERNIER, P. and LONGINOTTI, L. D. (1975a). *Phys. Rev.*, *B11*, 2783.

JAYARAMAN, A., DERNIER, P. and LONGINOTTI, L. D. (1975b). *High Temp.—High Pressure*, *7*, 1.

KOBAYASHI, T., YOSHIHARA, K. and NAGAKURA, S. (1971). *Bull. Chem. Soc. Japan*, *44*, 2603.

LYNCH, R. W. and DRICKAMER, H. G. (1966). *J. Chem. Phys.*, *45*, 1020.

MATAGA, N. and MURATA, Y. (1969). *J. Am. Chem. Soc.*, *91*, 3144.

MCMAHAN, A. K., HOARD, B. L. and ROSS, M. (1977). *Phys. Rev.*, *B15*, 726.

MCWHAN, D. B. and REMEIKA, J. P. (1970). *Phys. Rev.*, *B2*, 3734.

MITCHELL, D. J., DRICKAMER, H. G. and SCHUSTER, G. B. (1977). *J. Am. Chem. Soc.*, *99*, 7489.

MOTT, N. F. (1961). *Phil. Mag.*, *6*, 287.

POLITIS, T. G. and DRICKAMER, H. G. (1981). *J. Chem. Phys.*, *75*, 3203.

PRENER, J. S. and WILLIAMS, F. E. (1956). *J. Chem. Phys.*, *25*, 361.

PROCHOROW, J. (1974). *J. Lumin.*, *9*, 131.

RIGGLEMAN, B. M. and DRICKAMER, H. G. (1962). *J. Chem. Phys.*, *37*, 446.

RIGGLEMAN, B. M. and DRICKAMER, H. G. (1963). *J. Chem. Phys.*, *38*, 2721.

SALMAN, O. A. and DRICKAMER, H. G. (1982a). *J. Chem. Phys.*, *77*, 3329.

SALMAN, O. A. and DRICKAMER, H. G. (1982b). *J. Chem. Phys.*, *77*, 3337.

SEITZ, F. (1940). *Modern Theory of Solids*, New York: McGraw-Hill.

SHIMOMURA, O., TAKEMURA, K., FUJII, Y., MINOMURA, S., MORI, M., NODA, Y. and YAMADA, Y. (1978). *Phys. Rev.*, *B18*, 715.

SLATER, J. C. (1965). *Quantum Theory of Molecules and Solids: Vol. 2*, New York: McGraw-Hill.

STRICKLER, S. J. and BERG, R. A. (1962). *J. Chem. Phys.*, *37*, 814.

SUCHAN, H. L., WIEDERHORN, S. and DRICKAMER, H. G. (1959). *J. Chem. Phys.*, *31*, 355.

SYASSEN, K., TAKEMURA, K., TUPS, H. and OTTO, A. (1981). In *Physics of Solids Under Pressure* (eds. J. S. Schilling and R. N. Shelton), Amsterdam: North-Holland.

TAKAMURA, K., FUJII, Y., MINOMURA, S. and SHIMOMURA, O. (1979), *Solid State Commun.*, *30*, 137.

TAKEMURA, K., MINOMURA, S., SHIMOMURA, O. and FUJII, Y. (1980). *Phys. Rev. Lett.*, *45*, 1881.

TAKEMURA, K. MINOMURA, S., SHIMOMURA, O., FUJII, Y. and AXE, J. D. (1982). *Phys. Rev.*, *B26*, 598.

THOMAS, D. J., HOPFIELD, J. J. and AUGUSTINIAK, W. M. (1965). *Phys. Rev.*, *A140*, 202.

THOMAS, M. M. and DRICKAMER, H. G. (1981a). *J. Chem. Phys.*, *74*, 3198.

THOMAS, M. M. and DRICKAMER, H. G. (1981b). *J. Chem. Phys.*, *75*, 5246.

TYNER, C. E. and DRICKAMER, H. G. (1977). *J. Chem. Phys.*, *67*, 4103.

VAN STRAATEN, J., WIJNGAARDEN, R. J. and SILVERA, L. F. (1982). *Phys. Rev. Lett.*, *48*, 97.

VAN VECHTEN, J. A. (1973). *Phys. Rev.*, *B4*, 1479.

VAN VLECK, J. H. (1932). *Phys. Rev.*, *41*, 208.

VAN VLECK, J. H. (1935a). *J. Chem. Phys.*, *3*, 803.

VAN VLECK, J. H. (1935b). *J. Chem. Phys.*, *3*, 807.

YIN, M. T. and COHEN, M. L. (1980). *Phys. Rev. Lett.*, *45*, 1004.