Another satisfying feature of δ is that the peculiar BAs which has $f_i \simeq 0$ and a large negative value for ρ (making δ positive) is right on the curve of Fig. 2 along with say ZnSe which has about the same positive δ (but which arises from the opposite situation $\rho = 0$ and large f_i). This is powerful evidence that δ is truly a fundamental measure of the total fractional acentricity. In this light we can say that CuCl and InN which have δ's of $\simeq \pm 75\%$, respectively, are about as close to the maximum possible distortion ($\delta = \pm 100\%$) and consequently the largest Δ (4×10^{-6} esu) one can get in these crystals before there is a phase change[5] to a six-fold-coordinated structure.

In conclusion, we have shown the importance of the acentricity produced by the displacement of the bond charge off center. Without adjustable parameters, this effect completely explains the "anomalous" sign of ZnO and SiO_2 as well as the very small value for Δ in BeO. It is very important to be aware of such possible cancellations (i.e., $\delta \simeq 0$) if one wants to find materials with large nonlinear coefficients.

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ISING MODEL WITH A TRANSVERSE FIELD

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The phase transition in the Ising model has been studied as a function of an applied transverse field, by Green's function and series-expansion methods. The critical indices are probably independent of the applied field except at $T = 0$ where they appear to be related to those of the Ising model in one higher dimension.

The Ising model in a transverse field can be represented by the Hamiltonian

$$\mathcal{H} = -\Gamma \sum_i S_{ix} - \tfrac{1}{2} \sum_{ij} J_{ij} S_{iz} S_{jz}, \qquad (1)$$

where S_{ix}, S_{iz} are spin-$\frac{1}{2}$ operators and where the sums extend over the points of a lattice. This model corresponds to the pseudospin formulation of phase-transition problems and may be used to study order-disorder ferroelectrics with a tunneling effect[1] or the magnetic ordering in materials with singlet crystal-field ground states.[2] It is one of the simplest models where a phase transition takes place at a finite external field.[3] There exists a phase boundary in the Γ-T plane as shown in Fig. 1, where results calculated by various methods for a simple cubic lattice with nearest-neighbor interactions are plotted. The curve is limited by the points $\Gamma = 0$, $T = T_c$ (Ising model) and $T = 0$, and $\Gamma = \Gamma_c$, where Γ_c is the critical transverse field. In the region above the curve the S_z components are disordered although $\langle S_{ix} \rangle \neq 0$. The transverse field plays a role which is in many ways similar to the temperature and the critical temperature decreases as the field increases.

The system has first been studied using a Green's function method,[4] where the equations of motion for the Green's functions were decoupled by a scheme introduced by Callen[5] for the Heisenberg model. The high-temperature susceptibility is calculated in a self-consistent way and diverges at the critical temperature. The phase boundary curve thus obtained is plotted in Fig. 1 (curve 3). In the limit $\Gamma \to 0$ this approximation corresponds to the spherical model of the Ising case.

A better result is obtained from a series expansion of the susceptibility[6] in $(\beta J)^n$, where $\beta = 1/kT$:

$$\chi = \sum_{n=0}^{\infty} \alpha_n (\beta\Gamma)(J\beta)^n. \qquad (2)$$

This series has been calculated up to $n = 5$ from

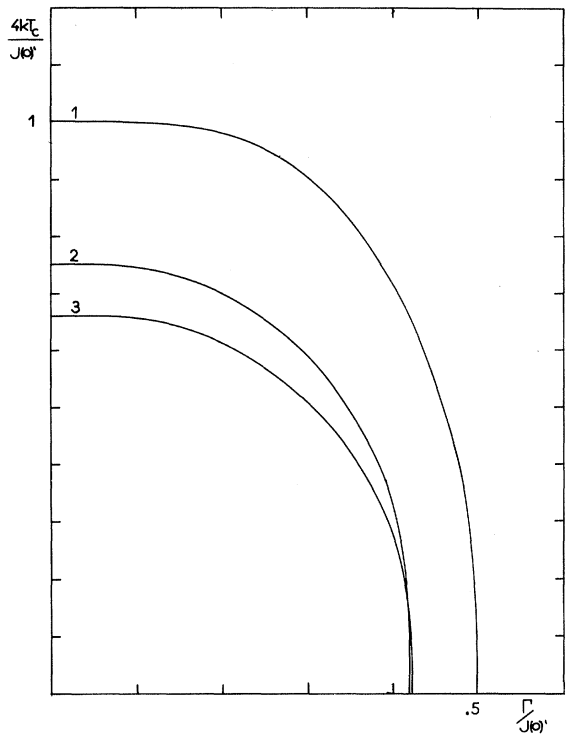

FIG. 1. Phase boundary curve in Γ-T plane for a cubic lattice with nearest-neighbor interactions from (1) molecular field, (2) series expansion, (3) Green's function method.

a thermodynamic perturbation theory[7] and diagrammatic techniques. The presence of the transverse part in (1) makes the evaluation of the diagrams more complicated than in the Ising case and a computer has been used. The first singularity of the series (2) was obtained for eight different values of $\Gamma\beta$ using the Padé approximant method for both a simple cubic and a quadratic lattice with nearest-neighbor interactions. The calculation with fixed $\Gamma\beta$ gives the variation of χ along a line through the origin in the Γ-T plane. However, for this type of series the nature of the singularity is independent of the direction in which the critical curve is approached, provided it is not tangentially. If (2) is expressed in polar coordinates θ, r with

$$\Gamma\beta = \cot\theta, \quad (\Gamma/J)^2 + (1/\beta J)^2 = r^2, \tag{3}$$

then

$$\chi = \sum_n \alpha_n(\theta) r^{-n} \sim [r - r_c(\theta)]^{-\gamma(\theta)} \tag{4}$$

in the critical region. From the Padé approximant we obtain the critical curve, either as $r_c(\theta)$ or as $T_c(\Gamma)$ which is plotted in Fig. 1. $\gamma(\theta)$ or $\gamma(\Gamma)$ may also be obtained and is plotted in Fig. 2 for the simple cubic and quadratic lattices.

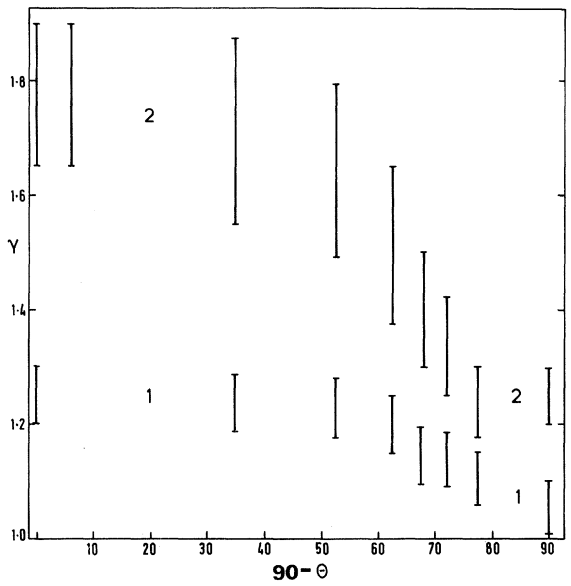

FIG. 2. The critical exponent γ as a function of $90° - \theta$ for (1) simple cubic and (2) quadratic lattices.

γ is fairly constant at the value in the Ising model until θ approaches zero where T_c is becoming small. There it decreases and appears to approach the value of γ obtained for the Ising model in one higher dimension.

The values of γ obtained from a few terms in the series are subject to a wide error and are naturally suspect. In particular it has been conjectured[8] that γ will depend only on the dimensionality of the system and not vary continuously with a parameter such as Γ. We have therefore examined the situation near $\theta = 0$ where the series may be written

$$\chi = \sum b_n(\theta)(J/\Gamma)^n. \tag{5}$$

Near $\theta = 0$,

$$b_n(\theta) = b_n(0) + c_n e^{-2\cot\theta} \cot^n\theta. \tag{6}$$

The form of the second term indicates a discontinuous change of behavior as $\theta \to 0$. For small values of n this term is not important until finite θ is reached, and this accounts for the change in γ at these values. We therefore believe that γ is constant over the whole range of Γ but changes discontinuously at $\theta = 0$ ($T_c = 0$). This case $T = 0$ has been studied from the ground state of (1). The one-dimensional Ising model with a transverse field and with nearest-neighbor interactions has been studied by one of us[9] using the method developed by Lieb, Schultz, and Mattis[10] in similar spin systems. At $T > 0$ there is no phase transition but at $T = 0$ the system remains ordered up to $\Gamma = \Gamma_0$. The correlation function

$\rho_{nz} = \langle S_{iz} S_{i+n,z} \rangle$ has been calculated and is shown to be equal to the correlation function obtained in a row of spins in Onsager's solution of the two-dimensional Ising model. The main result is that the critical behavior of the Ising model with transverse field in one dimension at $T = 0$ as a function of Γ is identical to the critical behavior of the Ising model without transverse field ($\Gamma = 0$) at finite temperature in two dimensions as a function of T. In the first case the ground-state energy corresponds to an eigenstate whose degeneracy changes at $\Gamma = \Gamma_c$. In the second the free energy depends on the eigenvector of the transfer matrix whose degeneracy changes at $T = T_c$. A similar correspondence is seen in the numerical values of γ shown in Fig. 2 where for dimension d at $T = 0$, $\Gamma = \Gamma_c$, γ takes a value $\gamma^*(d)$ close to that of the Ising model in $d+1$ dimensions, $\gamma(d+1)$. We therefore studied the ground state of (1) for a d-dimensional hypercubic lattice by perturbation theory[11] both in the ordered region $\Gamma < \Gamma_c$ where $\langle S_{iz} \rangle$ is as expanded in Γ/J up to the fourth term and in the disordered region $\Gamma > \Gamma_c$ where the correlation function $G = \sum_n \langle S_{iz} S_{i+n,z} \rangle$ and the energy of the lowest excited state ω_0 have been calculated up to the fifth term as series expansions in J/Γ. In the vicinity of the critical field we suppose that these quantities behave as

$$\langle S_z \rangle \sim (\Gamma_c - \Gamma)^{\beta *},$$
$$G \sim (\Gamma - \Gamma_c)^{-t},$$
$$\omega_0 \sim (\Gamma - \Gamma_c)^{f}. \tag{7}$$

The series were analyzed using a Padé approximant method to get Γ_c, β^*, t, and f and the results are shown in Table I for several values of d. These values are compared with appropriate indices for the Ising model in a lattice of dimension $d+1$. If we suppose that the correlation function $\rho_{nz}(\Gamma)_{T=0} = \langle S_{iz} S_{i+n,z} \rangle$ for a lattice of dimension d behaves in the critical region as the correlation function $\rho_{nz}(T)_{\Gamma=0}$ for a lattice of dimension $d+1$, then $\rho_{nz}(\Gamma) \sim D(Kn)/(n^{d-1+\eta})$, where $K \sim (\Gamma - \Gamma_c)^{\nu}$, and

$$G = \sum_n \rho_{nz}(\Gamma) \sim \int D(Kn) n^{-\eta} dn \sim K^{-1+\eta} \sim (\Gamma - \Gamma_c)^{\nu(-1+\eta)}. \tag{8}$$

But the exponents satisfy the scaling law[12] $\gamma = \nu(2-\eta)$ and we therefore expect

$$t(d) = \gamma(d+1) - \nu(d+1). \tag{9}$$

Although there is some uncertainty due to the limited number of terms in the series it appears that (9) together with the relations

$$\gamma^*(d) = \gamma(d+1), \quad \beta^*(d) = \beta(d+1) \tag{10}$$

are satisfied for $d = 1, 2, 3$, and d very large.

We have also found a relation between t and γ^* through f because of the relation between G and χ. Following Falk and Bruch,[13] t is equal to γ for any value of Γ, except possibly at $T = 0$. Writing $G = \int_{-\infty}^{\infty} S(\omega) d\omega$, we have

$$\chi = \int_{-\infty}^{\infty} d\omega\, S(\omega)(1 - \epsilon^{-\beta\omega})/\omega. \tag{11}$$

In the critical region and for $T \neq 0$, $S(\omega)$ is a narrow curve centered at $\omega = 0$ and thus $\chi = \beta G$. But at $T = 0$, (11) gives $\chi = \int_{-\infty}^{\infty} d\omega\, S(\omega)/\omega$, and if we suppose that $S(\omega) = a(\omega)\delta(\omega - \omega_0)$ (which is exact only for the one-dimensional model), then $\chi = a(\omega_0)/\omega_0 = G/\omega_0$ and thus

$$\gamma^* = t + f. \tag{12}$$

From Table 1 we see that relation (12) is indeed satisfied.

The correspondence between the behavior of the system at $T = 0$ as a function of Γ for a lattice of dimension d and the behavior of the system at $\Gamma = 0$ as a function of T for a lattice of dimension $d+1$ seems valid for any dimension. This analogy appears more reasonable in the formulation of the d-dimensional Ising problem by Schultz, Mattis, and Lieb[14] where the transfer matrix used to express the free energy can be written as the product of two matrices, $\exp V_1$ and $\exp V_2$, where V_1 and V_2 are the transverse part and the Ising part of the Hamiltonian (1) of dimension $d-1$. A similar correspondence

Table I. Critical exponents in various dimensions. Values of γ, β, and ν are taken from Refs. 8 and 16.

d	$\gamma^*(d)$	$\gamma(d+1)$	$\beta^*(d)$	$\beta(d+1)$	$t(d)$	$\gamma(d+1)-\nu(d+1)$	f	$t+f$	$\Gamma_c/J(0)$
1		7/4	1/8	1/8	3/4	3/4	1	7/4	0.25
2	5/4	5/4	0.33	0.315	0.358	0.62	0.63	1.21	0.38
3	1.05	1.03	0.46	0.49	0.53	0.51	0.58	1.11	0.42
∞[a]	1	1	0.5	0.5	0.5	0.5	0.5	1	0.5

[a] Molecular-field approximation.

exists between maximum eigenvalue and eigenvector of the transfer matrix for the ferroelectric two-dimensional model[15] and the ground-state eigenvector for the one-dimensional anisotropic Heisenberg chain.

It appears from our work that the transverse field changes the critical temperature without changing the critical behavior until the critical field is reached, when there is a sudden change in the critical behavior at $T=0$ which becomes like the critical behavior of the Ising system in one higher dimension.

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TRANSIENT OPTICAL ABSORPTION BY SELF-TRAPPED EXCITONS IN ALKALI HALIDE CRYSTALS

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Transient absorption spectra produced by pulsed electron excitation at low temperature have been identified as due to transitions originating in the lowest triplet states of the self-trapped exciton. The current model, comprising an electron plus a self-trapped hole, is shown to provide electronic configurations for the higher excited states which give a good account of the principal features of the spectra.

Exciton self-trapping in simple halide lattices is an established phenomenon. It gives rise to broad-band, strongly Stokes-shifted luminescence which has been studied in alkali,[1] ammonium,[2] and alkaline-earth[3] halides. The self-trapping can be attributed to the formation of a covalent bond between two adjacent excited halide ions, and the resulting X_2^{-2} molecular ion provides metastable singlet and triplet states with which the characteristic short- and long-lived luminescent transitions can be reasonably well explained.[4] In pure materials at low temperatures, a significant fraction of any energy imparted to the electronic system is at some stage stored in these states. The present work concerns absorption spectra arising from the longer-lived states of self-trapped excitons in several alkali halides. The model with which the luminescent transitions have been interpreted will be shown to furnish also a straightforward account of the higher excited states involved in the absorption.

The basic experiment consisted of time-resolved measurements of absorption and emission spectra produced by single-pulse excitation from an electron source of 500 keV mean energy. The apparatus has been described previously.[5] A novel aspect of this system is the use of a light beam which reflects internally at a low angle from the crystal face being irradiated. This geometry maximizes the light path through the irradiated volume, which is thin (≈ 0.5 mm) because of the low penetration of the electron beam. For more accurate spectral resolution, the system was augmented by a simple rotating-mirror scanning device capable of sweeping at rates up to 6 nm/μsec. Repetitive excitation and a digital signal averager were used when it was desired to minimize the intensity of a given pulse in order to hold transient heating effects to tolerable level.[6] The decay times under investigation fell in the 10^{-6}- to 10^{-2}-sec range. No attempt was made to observe the singlet self-trapped exciton states since their lifetimes (1-10 nsec) are only