

TABLE I. Fitting parameters for simple model.

Curve in Fig. 1.	Temperature (K)	Surface	$x_{\text{max}}^a$	$a$	$b$
B	455	Pb on Nb	0.0028	0.10	0.46
D	460	Nb	0.0028	0.04	2.5
E	310	Nb	0.0026	0.0005	2000

<sup>a</sup>Atomic fraction of H in Nb.

<sup>b</sup>Extrapolated from run B by Sievert's law using  $E_{\text{sol}} = 16.48$  kcal/mole  $\text{H}_2$  (Ref. 12).

diffusion through this layer is not a rate-limiting step, then in principle the surface parameters that determine adsorption and dissociation can be varied independently of bulk parameters, such as the heat of solution, to achieve a desired result, such as the high bulk uptake rate. Hence, by using composite systems, both surface and bulk parameters can be optimized by using the proper combination of metals.

We thank M. El-Batanouny, K. G. Lynn, and D. O. Welch for discussions of this work and R. J. Smith for his LEED measurements. This work was performed under the auspices of the U. S.

Department of Energy.

- <sup>1</sup>J. A. Pryde and C. G. Titcomb, *Trans. Faraday Soc.* **65**, 2758 (1969).
- <sup>2</sup>S. M. Ko and L. D. Schmidt, *Surf. Sci.* **42**, 508 (1974).
- <sup>3</sup>L. Johnson, M. F. Dresser, and E. E. Donaldson, *J. Vac. Sci. Technol.* **9**, 857 (1972).
- <sup>4</sup>S. M. Ko and L. D. Schmidt, *Surf. Sci.* **47**, 558 (1975).
- <sup>5</sup>K. F. Poulter and J. A. Pryde, in *Proceedings of the Fourth International Vacuum Congress, Manchester, April 1968* (Institute of Physics and the Physical Society, London, 1969), p. 111.
- <sup>6</sup>E. Fromm and H. Uchida, *Vak. Tech.* **26**, 174 (1977).
- <sup>7</sup>N. Boes and H. Züchner, *Z. Naturforsch.* **31a**, 754 (1976).
- <sup>8</sup>H. Schultz, *Mater. Sci. Eng.* **3**, 189 (1968/69).
- <sup>9</sup>G. Perriot, *J. Phys. (Paris)* **28**, 472 (1967).
- <sup>10</sup>G. Pfeiffer and H. Wipf, *J. Phys. F* **6**, 167 (1976).
- <sup>11</sup>P. A. Redhead, J. P. Halson, and E. V. Koreulsen, *The Physical Bases of Ultra High Vacuum* (Chapman and Hall, London, 1968).
- <sup>12</sup>J. A. Pryde and C. G. Titcomb, *J. Phys. C* **5**, 1293 (1972).
- <sup>13</sup>H. Conrad, G. Ertl, and E. E. Latta, *Surf. Sci.* **41**, 435 (1974).
- <sup>14</sup>D. I. Hagen and E. E. Donaldson, *Surf. Sci.* **45**, 61 (1974).

## Strain Defects in Alkali Halides: A Heuristic Model for Glasses

Baruch Fischer and Michael W. Klein<sup>(a)</sup>

*Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

(Received 6 March 1979)

We present an idealized solvable model for the low-temperature properties of strain defects dissolved in alkali halides. The predicted specific heat and thermal conductivity are very much like those for glasses. Our calculation suggests a strong analogy between the low-temperature properties of strain defects and those of glasses.

The low-temperature properties of glasses<sup>1</sup> have been of considerable interest during the past few years. A number of anomalous properties of glassy materials have been explained using the idea of two-level tunneling states proposed by Anderson, Halperin, and Varma<sup>2</sup> and by Phillips<sup>3</sup> (AHVP).

Whereas the AHVP model explains the general features of the glass at low temperatures, it considers the tunneling units as essentially isolated and presents no microscopic picture for the origin for the constant density of states at low energies. However, in order to explain the pho-

non-echo<sup>4</sup> and the hole-burning experiments<sup>5</sup> one must consider strain interactions between the two-level tunneling states as was discussed by Black and Halperin.<sup>6</sup> It was recently also pointed out<sup>7</sup> that strain interactions may play an important role in giving the appropriate broad distribution of tunneling states.

The purpose of this paper is to present an idealized model which shows that small concentrations of strain dipoles, like  $\text{CN}^-$ , dissolved in alkali-halide crystals produce very similar low-temperature properties to that observed in glasses when strain interactions between the tun-

neling CN<sup>-</sup> units are considered. The system under consideration presents, to our knowledge, the first model in which *glasslike* thermal properties are shown to arise *purely* from strain interactions between tunneling units with a well-defined tunneling matrix element. By no means do we assert that these ideas are necessarily applicable to real glasses which are believed to have two-level tunneling states proposed by AHVP.

An isolated noninteracting CN<sup>-</sup> ion in the alkali-halide host forms a strain dipole of ellipsoidal form<sup>8-10</sup> with a traceless strain tensor  $\vec{\lambda}$ .  $\vec{\lambda}$  has a number of fixed discrete orientations at low temperatures. The orientations are believed to be in the  $\langle 111 \rangle$  directions for CN<sup>-</sup> in KCl and in the  $\langle 100 \rangle$  directions<sup>8,11</sup> for CN<sup>-</sup> in NaCl.

Figure 1 shows the energy levels for an isolated CN<sup>-</sup> in an externally applied strain<sup>12</sup> field in the  $x$  direction. In Fig. 1(a) and CN<sup>-</sup> has six orientations in the  $\langle 100 \rangle$  directions (CN<sup>-</sup> in NaCl) with a 90-deg tunneling matrix element  $-\Delta/2$ , whereas in Fig. 1(b) the CN<sup>-</sup> is allowed to have four orientations in the  $\pm x$  and  $\pm y$  directions only with tunneling matrix element  $-\Delta$ . A calculation shows that the qualitative physical features of the specific heat  $C$  and the thermal conductivity  $\kappa$  are similar for the four- and six-orientational strain tensors. However, since the eigenvalues of the former can be obtained exactly, we adopt the four-orientational tensor as our model.

The expression for the strain interaction between a pair of CN<sup>-</sup> units is calculated in Eqs. (3) and (4) of Ref. 7. The effect of the random

positions of the strain units results in a probability distribution  $p(\xi)$  of the strain fields  $\xi$ . Calculations<sup>13</sup> give that  $p(\xi)$  has a Gaussian form  $p(\xi) \propto \exp[-\xi^2/(2\delta_1^2)]$  for  $\xi \gg \delta_1$  and  $p(\xi) \approx \pi^{-1} \delta/(\delta^2 + \xi^2)$  for  $\xi < \delta$ , where  $\delta$  and  $\delta_1$  are effective widths of the distributions for the Lorentzian and Gaussian, respectively, and  $\delta$  is given in Eqs. (6) and (7) of Ref. 7.

In the realistic CN<sup>-</sup> system the strain fields arise from the CN<sup>-</sup> interacting with each other. In order to make the problem tractable, we adopt a mean-field approach in which a given strain tensor experiences a total strain field, internal plus external, which is a random variable.<sup>13</sup> We next idealize the model further by making two assumptions: (1) The strain dipoles are allowed to have four orientations only (in the  $\pm x$  and  $\pm y$  directions): (2) We replace the strain on a dipole by a random *external* strain field which may have either a Gaussian or Lorentzian probability distribution. Thus we abstract our problem into a solvable model satisfying these two assumptions, and a meaningful comparison with any physical system will be limited by the validity of these two assumptions. Assumption (2) explicitly neglects any contribution to the thermal properties arising from the decrease in strain fields as the dipole disorder and neglects cooperative effects between the dipoles (which, by a more correct treatment we find to undergo a spin-glass-like phase transition). Approximation (2) is likely to give a representation of the physical CN<sup>-</sup> system only when  $T \ll \delta$ .

The Hamiltonian  $H$  for a four-orientational dipole with a strain field  $\xi$  in the  $x$  direction is

$$H = H_0 + H_1, \tag{1}$$

where

$$H_0 = \begin{pmatrix} F & -G \\ -G & -F \end{pmatrix}; \quad H_1 = \begin{pmatrix} F' & -G' \\ -G' & -F' \end{pmatrix} \delta e_p \tag{2}$$

with

$$F = \begin{pmatrix} \xi & 0 \\ 0 & -\xi \end{pmatrix}, \quad G = \begin{pmatrix} \Delta & \Delta \\ \Delta & \Delta \end{pmatrix},$$

$$F' = \frac{\partial F}{\partial e_p}, \quad G' = \begin{pmatrix} \partial G \\ \partial e_p \end{pmatrix},$$

where  $\delta e_p$  is the strain distortion due to the phonons. We also denote the phonon tunneling-dipole couplings  $\gamma$  and  $\gamma'$  by the relation  $\gamma = \frac{1}{2}(\partial \xi / \partial \mathcal{E})$ ,  $\gamma' = \frac{1}{2}(\partial \Delta / \partial \mathcal{E})$ . The four eigenvalues of the Hamil-

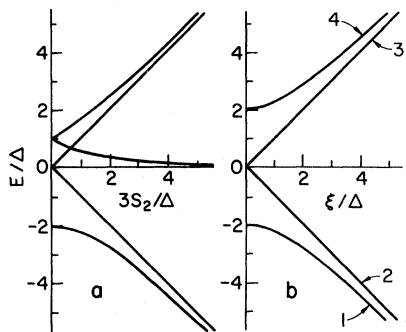


FIG. 1. (a) Energy splitting of the six-orientational defect with 90-deg tunneling of  $-\Delta/2$  as a function of an applied stress of  $(2S/\Delta)(1, 0, 0)$ . (b) Energy splitting of the four-orientational defect with 90-deg tunneling of  $-\Delta$  as a function of  $\xi = \frac{1}{2}(S_1 - S_2)$ , where  $S_1$  and  $S_2$  are the stresses in the  $x$  and  $y$  directions, respectively. The four levels are labelled 1 to 4 to refer to the energies in the text.

tonian  $H_0$  are

$$\epsilon_{1,4} = \pm (\xi^2 + 4\Delta^2)^{1/2}, \quad \epsilon_{2,3} = \pm \xi, \quad (3)$$

where the subscripts 1 and 3 refer to the + sign.  $\gamma$  and  $\gamma'$  are assumed to be constants independent of the phonon modes. In the usual glass problem  $\gamma'$  is considered to be small compared to  $\gamma$ , however, for the  $\text{CN}^-$  system in alkali halides there

$$C = \frac{k_B^2 T N_d}{8} \int_{-\infty}^{\infty} \left\{ \left[ \frac{x+y}{\cosh \frac{1}{2}(x+y)} \right]^2 + \left[ \frac{x-y}{\cosh \frac{1}{2}(x-y)} \right]^2 \right\} P\left(\frac{x}{\beta}\right) dx, \quad (4)$$

where  $x = \beta\xi$ ,  $y = [x^2 + 4(\beta\Delta)^2]^{1/2}$ , and  $p(x/\beta)$  is the probability density of  $\xi$ . Changing variables of integration in Eq. (4) gives

$$C = k_B^2 T N_d \int_0^{\infty} \frac{u^2 + (\beta\Delta)^2}{\cosh^2 u} p\left(\frac{u^2 - (\beta\Delta)^2}{\beta u}\right) du. \quad (5)$$

We consider several cases of interest and show the corresponding specific heat in Fig. 2.

**Case I.**—Gaussian field distribution,  $p(\xi) = (2\pi\delta^2)^{-1/2} \exp[-\frac{1}{2}(\xi/\delta)^2]$ . For this case we distinguish three different regions of temperature: (i) With  $\beta\Delta^2/\delta \gg 1$  and  $\delta \gg \Delta$ , Eq. (5) gives, for very low  $T$ ,  $C \approx k_B^2 N_d w^{2/3} \exp[-3w^{2/3}]$ , where  $w = \Delta^2/T\delta$ ; (ii) with  $\beta\Delta \approx 1$  and  $\beta\delta \gg 1$  it gives  $C \approx N_d (2/\pi)^{1/2} \Delta^2/(T\delta)$ ; and (iii) with  $\beta\Delta \ll 1$  and  $\beta\delta \gg 1$ , now  $C \approx k_B^2 T N_d (2/\pi)^{1/2} [\pi^2 + (\beta\Delta)^2]/\delta$ . For this case,  $C$  increases exponentially with increasing  $T$  for very low  $T$ , then decreases proportionally to  $T^{-1}$  for  $T \approx \Delta$ , and for higher  $T$  (still  $T \ll \delta$ )  $C \propto N_d T/\delta$ , i.e.,  $C$  is linear in  $T$ .

**Case II.**—Lorentzian distribution of  $\xi$ ,  $p(\xi) = \pi^{-1} \delta/(\delta^2 + \xi^2)$ . Here again we distinguish three regions of temperature: (iv) If  $\beta\Delta \gg 1$ ,  $\delta \gg \Delta$ , and  $\delta/\beta \ll \Delta^2$ , then  $C \approx k_B^2 T N_d^2 (\delta/N_d) \Delta^{-2}$ ; (v) with  $\beta\Delta \approx 1$  and  $\delta/\Delta \gg 1$ , here  $C \propto N_d \Delta^2/\delta T$ ; and (vi) with  $\beta\Delta \ll 1$  and  $\beta\delta \gg 1$ , we obtain  $C = \frac{1}{12} k_B^2 T \pi N_d/\delta$ . Thus for a Lorentzian distribution of fields the predicted  $C$  for very low  $T$  ( $T \ll \Delta$ ) is proportional to  $T N_d^2$ ; for  $T \approx \Delta$ ,  $C \propto N_d/T$ ; and for  $T \gg \Delta$  (still  $T \ll \delta$ ),  $C \propto T N_d/\delta$ . Since for the Lorentzian distribution  $\delta \propto N_d$ , the specific heat for  $T \gg \Delta$  ( $T \ll \delta$ ) is linear in  $T$  and independent of  $N_d$ .

The low-temperature specific heat of  $\text{CN}^-$  in NaCl was measured by Reddy and co-workers.<sup>14,15</sup> In the 200- and 1000-ppm samples,  $C$  increases as  $T$  increases from 0.3 K, comes to a maximum, then decreases and comes to a minimum around 1 K. Above 1 K,  $C$  is approximately linear in  $T$ . Qualitatively this behavior is according to our model discussed above. For the 5000-ppm sam-

ple,  $C$  is linear in  $T$  from about 0.3 to 3 K with no dip in  $C$  observed. This result can be qualitatively understood if one assumes the soft-tunneling model in which  $\Delta$  is a function of the strain field. For low-concentration samples,  $\xi$  is relatively weak and the decrease in  $\Delta$  is not appreciable. However, for the 5000-ppm sample,  $\delta$  is large which results in an appreciable probability for small values (as well as large values) of  $\Delta$ . If this interpretation is valid, then a dip in  $C$  for the 5000-ppm  $\text{CN}^-$  should occur below 0.3 K. Using  $C_{11} = 4.87$ ,  $C_{12} = 1.24$ , and  $C_{44} = 1.26$ , each in units of  $10^{11}$  ergs/cm<sup>3</sup> for NaCl, we calculate  $C$ . For a (100) stress<sup>9</sup>  $\mu v_0 = 5.5 \times 10^{-24}$  cm<sup>3</sup> for KCl and  $\mu_{\text{NaCl}} = 0.58$ . From the ratio of

is experimental evidence that  $\gamma'$  is appreciable.<sup>8,14</sup> Therefore for large strain fields we use a soft-tunneling model<sup>8</sup> in which  $\Delta$  and therefore  $\gamma'$  changes with  $\xi$ . Certain values of  $\Delta$  decrease with strain, others increase.<sup>8</sup> The random strain interaction results in a set of random  $\Delta$ 's.

The partition function for a single strain dipole in the presence of a strain field in the [100] direction is  $Z_1 = 2[\cosh\beta\xi + \cosh\beta(\xi^2 + 4\Delta^2)^{1/2}]$ . Thus, the specific heat  $C$  is given by

ple,  $C$  is linear in  $T$  from about 0.3 to 3 K with no dip in  $C$  observed. This result can be qualitatively understood if one assumes the soft-tunneling model in which  $\Delta$  is a function of the strain field. For low-concentration samples,  $\xi$  is relatively weak and the decrease in  $\Delta$  is not appreciable. However, for the 5000-ppm sample,  $\delta$  is large which results in an appreciable probability for small values (as well as large values) of  $\Delta$ . If this interpretation is valid, then a dip in  $C$  for the 5000-ppm  $\text{CN}^-$  should occur below 0.3 K. Using  $C_{11} = 4.87$ ,  $C_{12} = 1.24$ , and  $C_{44} = 1.26$ , each in units of  $10^{11}$  ergs/cm<sup>3</sup> for NaCl, we calculate  $C$ . For a (100) stress<sup>9</sup>  $\mu v_0 = 5.5 \times 10^{-24}$  cm<sup>3</sup> for KCl and  $\mu_{\text{NaCl}} = 0.58$ . From the ratio of

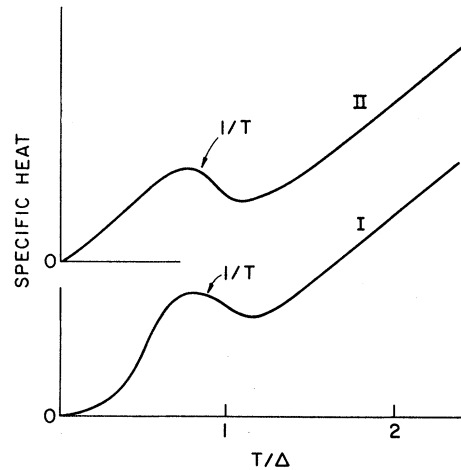


FIG. 2. Qualitative sketch of the low-temperature specific heat as a function of the temperature  $T$ . Curve I is the sketch for the Gaussian distributed strain fields and shows an exponentially low specific heat as  $T \rightarrow 0$ . Curve II is for the Lorentzian distribution of fields. Both curves are linear in  $T$  in the high- $T$  region shown in the graph. For purposes of clarity the origins of the curves are displaced from each other.

the unit cells for KCl and NaCl we obtain  $(\mu v_0)_{\text{NaCl}} \approx 4.4 \times 10^{-24} \text{ cm}^2$ . Assuming  $\gamma \approx \frac{1}{2} \text{ eV}$  we obtain  $\delta = 1.2 \times 10^{-35} N_d \text{ ergs/cm}^3$ . This gives  $C \approx k_B^2 \pi T N_d / 12\delta = 420T \text{ ergs/cm}^3$  for  $T > \Delta$  and  $T \ll \delta$ . This is about one-fourth of the measured  $C$  for the 1000- and 5000-ppm samples. This result is reasonable considering the approximations made. For the 200-ppm sample we expect a good deal of disordering of the dipoles around 2 K and approximation (2) breaks down.

The thermal conductivity  $\kappa$  is next calculated with use of the expression<sup>16,17</sup>

$$\kappa = \frac{1}{3} \int C(\omega) l(\omega) v d\omega, \quad (6)$$

where  $C(\omega)$  and  $l(\omega)$  are the phonon specific heat

and mean free path,  $l(\omega) = [l_{\text{res}}^{-1} + l_{\text{rel}}^{-1}]^{-1}$ , where  $l_{\text{res}}$  and  $l_{\text{rel}}$  are the mean free paths due to resonant and relaxation processes from the  $\text{CN}^-$  tunneling units, respectively. At very low  $T$  the contribution from  $l_{\text{rel}}^{-1}$  decreases at least proportional to  $T^3$  and is negligible whenever  $l_{\text{res}}^{-1}$  is appreciable. However, for  $T < 2\Delta$ , where  $l_{\text{res}}^{-1}$  is exponentially small  $l_{\text{rel}}^{-1}$  will play an important role in determining  $\kappa$ . The matrix element of transition  $M_{ij}$  between levels  $i$  and  $j$  is  $M_{ij} = \langle \psi_i | H_1 | \psi_j \rangle$ , where  $\psi_i$  and  $\psi_j$  are the eigenstates of  $H_0$ . We have  $M_{23}^2 = \gamma^2$  and  $M_{14}^2 = (\gamma\Delta - \gamma'\xi)^2 / (\xi^2 + 4\Delta^2)$  and  $M_{ij} = 0$  for all other  $i$  and  $j$ . Thus for large  $\xi$  ( $\xi > 2\Delta$ ),  $M_{14} = \gamma'$ ; and for small  $\xi$ ,  $M_{14}^2 \approx \gamma^2/4$  and<sup>16,17</sup>

$$l_{\text{res}}^{-1} = \frac{2\pi}{\hbar\rho v_i^3} \int_0^\infty p(\xi) d\xi \frac{M_{14}^2 \sinh \beta y \delta(\hbar\omega - 2y) + M_{23}^2 \sinh \beta \xi \delta(\hbar\omega - 2\xi)}{\cosh \beta y + \cosh \beta \xi} \omega, \quad (7)$$

where  $y = (\xi^2 + 4\Delta^2)^{1/2}$ . Integrating Eq. (7) and approximating  $M_{14}^2$  by its large field value of  $\gamma'^2$  give

$$l_{\text{res}}^{-1} \approx \frac{\pi}{\rho v^3} \frac{\gamma^2 p(\hbar\omega/2) \omega \sinh(\beta\hbar\omega/2)}{\cosh(\beta\hbar\omega/2) + \cosh[(\beta/2)(\omega^2 + 16\omega^2)^{1/2}]} + \frac{\gamma'^2 U(z) p(z/2) (z/\hbar) \sinh(\beta z/2)}{\cosh(\beta\hbar\omega/2) + \cosh(\beta z/2)}, \quad (8)$$

where  $z^2 = (\hbar\omega)^2 - 16\Delta^2$ , and  $U(x)$  is the unit step function, i.e.,  $U(x) = 1$  for  $x > 0$  and  $U(x) = 0$  for  $x < 0$ .

Substituting Eq. (8) into Eq. (6) and letting  $\gamma \approx 0.5 \text{ eV}$  and  $\gamma' \approx 0.2 \text{ eV}$ <sup>8,18</sup> give

$$\begin{aligned} \kappa &\approx AT^2, \quad T > 2\Delta; \\ \kappa &\approx BT^0, \quad \Delta < T < 2\Delta, \end{aligned} \quad (9)$$

where  $A \approx 12\rho v k_B^3 \eta(3) v / [h^2 \gamma^2 \pi^3 N_d p(0)]^{-1}$ , and

$$\eta(3) = \sum_{n=1}^{\infty} (2n+1)^{-3} = 1.202.$$

Thus  $A \approx 7 \times 10^{-6} \text{ W/cm deg}^3$ .  $B$  is obtained by substituting  $l_{\text{rel}}^{-1}$  in Eq. (6), where  $l_{\text{rel}}^{-1}$  is proportional to  $T^3$  for  $T > 2\Delta$  and  $l_{\text{rel}}^{-1}$  becomes proportional to  $T^3 \exp(-\Delta/T)$  for  $T \ll \Delta$ .

In this paper we discuss only  $\kappa$  and  $C$ ; however, our model predicts anomalous properties in the sound velocity and absorption as well as in the phonon echo measurements.

In conclusion we have presented an idealized model which for the first time shows that strain dipoles dissolved in ordered crystals will have glasslike properties. We believe that further experimental as well as theoretical study of the  $\text{CN}^-$  system may contribute towards understanding the low-temperature properties of strain dipoles as well as glasses in general.

We are grateful to A. C. Anderson for numerous discussions on this subject. We also thank

M. V. Klein and H. J. Stapleton for some very helpful comments. This work was supported in part by the National Science Foundation under Contract No. DMR-77-23999.

<sup>(a)</sup> On leave from Department of Physics, Bar-Ilan University, Ramat-Gan, Israel.

<sup>1</sup> R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

<sup>2</sup> P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

<sup>3</sup> W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

<sup>4</sup> B. Golding and J. E. Graebner, Phys. Rev. Lett. **37**, 852, 1105(E) (1976).

<sup>5</sup> W. Arnold, C. Martinon, and S. Hunklinger, J. Phys. (Paris), Colloq. **39**, C6-691 (1978).

<sup>6</sup> J. L. Black and B. I. Halperin, Phys. Rev. B **16**, 2879 (1977).

<sup>7</sup> M. W. Klein, B. Fischer, A. C. Anderson, and P. J. Anthony, Phys. Rev. B **17**, 4997 (1978).

<sup>8</sup> H. U. Beyeler, Phys. Rev. B **11**, 3078 (1975).

<sup>9</sup> N. E. Byer and H. S. Sack, Phys. Status Solidi **30**, 579 (1968).

<sup>10</sup> F. Bridges, Crit. Rev. Solid State Sci. **5**, 1 (1975).

<sup>11</sup> F. Lüty, Phys. Rev. B **10**, 3677 (1974); A. Diaz-Gongora and F. Lüty, Solid State Commun. **14**, 923 (1974).

<sup>12</sup> Consider a strain tensor  $\bar{\lambda}_a = \mu(2, -1, -1)$  and  $\bar{\lambda}_b = \mu(-1, 2, -1)$  in the directions  $a$  and  $b$  and let the

stress due to interactions  $\bar{S}$  have diagonal components  $S_1$ ,  $S_2$ , and  $S_3$ . Then the difference in strain energy between the two orientations is  $2\xi = (2S_1 - S_2 - S_3) - (-S_1 + 2S_2 - S_3) = 3(S_1 - S_2)$ .  $\xi$  is the parameter which enters Eq. (3).

<sup>13</sup>M. W. Klein, L. J. Schowalter, and P. Shukla, *Phys. Rev. B* **19**, 1492 (1979). This work also discusses the question of a possible hole of  $p(\xi)$  near  $\xi = 0$ .

<sup>14</sup>B. Reddy, Ph.D. thesis, University of Utah, 1974

(unpublished).

<sup>15</sup>W. D. Seward, V. Reddy, and J. W. Shaner, *Solid State Commun.* **11**, 1569 (1972).

<sup>16</sup>S. Hunklinger and W. Arnold, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1976), Vol. 12, p. 155.

<sup>17</sup>J. Jackle, *Z. Phys.* **257**, 212 (1972).

<sup>18</sup>This value of  $\gamma'$  is for  $\text{KCl-CN}^-$ ;  $\gamma'$  for  $\text{NaCl-CN}^-$  is not known.

## Crossover from First-Order to Continuous Phase Transition Induced by Symmetry-Breaking Fields

Michel Kerszberg and David Mukamel

*Department of Nuclear Physics, Weizmann Institute of Science, Rehovot, Israel*

(Received 27 April 1979)

The crossover from first order to continuous transition induced by a symmetry-breaking field  $g$  in an  $n=2$  cubic model, for which a stable fixed point is not accessible, is studied. It is shown that unlike previously studied cases, the  $(g, T)$  phase diagram is rather complicated, exhibiting critical end points, tricritical, and fourth-order critical points. It is suggested that this phase diagram be studied experimentally in ferroelectric  $\text{Tb}_2(\text{MoO}_4)_3$  by applying uniaxial and shear stresses.

It has recently been shown that a variety of systems, which are predicted to exhibit continuous phase transitions within mean-field theory, yield first-order transitions due to critical fluctuations.<sup>1-7</sup> Within the renormalization-group approach, this may occur either when the appropriate model does not possess a stable fixed point<sup>1-4</sup> or when the stable fixed point is not physically accessible.<sup>5,6</sup> However, by applying a symmetry-breaking field  $g$ , the dimensionality of the order parameter is reduced. The system may then flow to a stable fixed point, and a continuous transition is restored.<sup>8-11</sup> This situation has been observed experimentally<sup>12</sup> in  $\text{MnO}$  and more recently<sup>13</sup> in  $\text{RbCaF}_3$ . These systems exhibit a first-order phase transition which becomes second order when a sufficiently strong uniaxial stress is applied.

The  $(g, T)$  phase diagram associated with various models has been studied by renormalization-group techniques,<sup>9</sup> perturbation theory,<sup>9</sup> high-temperature expansions,<sup>11</sup> and Monte Carlo calculations.<sup>11</sup> The models which were studied were found to exhibit a relatively simple phase diagram displaying a phase transition line with a tricritical point at a finite, nonzero  $g$  [see Fig. 1(a)]. In the present Letter, we show that in certain cases, depending upon the symmetry of the system and the field  $g$ , the phase diagram is more

complicated, as shown in Figs. 1(b) and 2. These phase diagrams exhibit critical end points, tricritical, and fourth-order critical points. The calculation is performed for an  $n=2$  component vector model with cubic anisotropy, which is the appropriate model for the ferroelectric transition in tetragonal<sup>14</sup>  $\text{Tb}_2(\text{MoO}_4)_3$ . It is predicted that the phase diagram of Fig. 2 should be observed experimentally by applying uniaxial and shear stresses in various directions in the  $x$ - $y$  plane. We believe that similar phase diagrams should be observed in some of the physical systems which do not possess a stable fixed point, such as<sup>1-4</sup>  $\text{UO}_2$ ,  $\text{MnO}$ ,  $\text{Cr}$ , and  $\text{Eu}$ , by applying a magnetic field or a uniaxial stress in certain directions. We shall discuss this problem in a future publication.<sup>15</sup>

Consider an  $n=2$  component cubic model described by the following Landau-Ginzburg-Wilson (LGW) Hamiltonian:

$$H = \int \mathcal{H} d^d x, \quad (1a)$$

$$\mathcal{H} = -\frac{1}{2} r (\varphi_1^2 + \varphi_2^2) - \frac{1}{2} [(\nabla \varphi_1)^2 + (\nabla \varphi_2)^2] - u(\varphi_1^4 + \varphi_2^4) - v \varphi_1^2 \varphi_2^2. \quad (1b)$$

For stability of the free energy, we require  $u > 0$  and  $2u + v > 0$ . The critical behavior associated with this model has been studied by several authors.<sup>16</sup> It has been shown that in  $d = 4 - \epsilon$  dimen-