hexagonal.[6] Directions of the crystal axes were arbitrary and slowly drifting with time, which excludes a relevant influence of the rectangular chamber walls on crystal formation. Frequently imperfections like step dislocations were observed. When the electric field was decreased again below E_c', the dimple crystal "melted" without noticeable hysteresis.

We finally note that the dimples making up the lattice are found to exist also as individual isolated entities if the charge density is low. Since each dimple holds about 10^6 negative ions, these dimples strongly repel each other as a result of Coulomb interaction. The dimple lattice can therefore be regarded as a kind of macroscopic two-dimensional Wigner crystal.[14-16] Interestingly enough, the ion density in each dimple is so high that the individual ions there might also form a two-dimensional crystal, however with a lattice constant three orders of magnitude smaller. It is a pleasure to thank H. Kinder for valuable discussions, and W. Bosch and T. Rapp for experimental assistance. This work was supported by the Deutsche Forschungsgemeinschaft.

---

[1] For a review see, e.g., C. C. Grimes, Surface Sci. 73, 379 (1978).

[2] P. Leiderer, M. Wanner, and W. Schoepe, in Proceedings of the Fifteenth International Conference on Low Temperature Physics, Grenoble, France 23–29 August 1978 (to be published).

[3] V. B. Shikin, Zh. Eksp. Teor. Fiz. 58, 1748 (1970) [Sov. Phys. JETP 31, 936 (1970)].

[4] L. P. Gorkov and D. M. Chernikova, Pis'ma Zh. Eksp. Teor. Fiz. 18, 119 (1973) [JETP Lett. 18, 68 (1973)].

[5] K. Mima, H. Ikezi, and A. Hasegawa, Phys. Rev. B 14, 3953 (1976).

[6] L. P. Gorkov and D. M. Chernikova, Dokl. Akad. Nauk SSSR 228, 829 (1976) [Sov. Phys. Dokl. 21, 328 (1976)].

[7] P. Leiderer, H. Poisel, and M. Wanner, J. Low Temp. Phys. 28, 167 (1977).

[8] In a more accurate treatment damping of the ripplons has to be taken into account (see, e.g., Ref. 7).

[9] The fields were not measured directly, but calculated from $E=U/d$, where U is the voltage between the capacitor plastes and $d=2.7$ mm is the distance of the interface from the bottom plate.

[10] R. Williams and R. S. Crandall, Phys. Lett. 36A, 35 (1971).

[11] This was easily achieved by adjusting the wire potential such that the interface was not distorted in the vicinity of the wire.

[12] P. Leiderer and M. Wanner, Phys. Rev. Lett. 41, 480 (1978).

[13] A similar instability has been observed with electrons at the free surface of liquid helium by M. S. Khaikin, in Proceedings of the Fifteenth International Conference on Low Temperature Physics, Grenoble, France 23–29 August 1978 (to be published).

[14] R. S. Crandall and R. Williams, Phys. Lett. 34A, 404 (1971).

[15] P. M. Platzman and H. Fukuyama, Phys. Rev. B 10, 3150 (1974).

[16] R. W. Hockney and T. R. Brown, J. Phys. C 8, 1813 (1975).

NMR Observation of Static Low-Temperature Clusters above the Phase Transition in the H-Bonded Antiferroelectric Squaric Acid ($C_4O_4H_2$)

Michael Mehring and Dirk Suwelack
Institut für Physik, Universität Dortmund, 46 Dortmund 50, Germany

(Received 27 June 1978)

Static low-temperature clusters above the phase transition in the H-bonded antiferroelectric squaric acid are observed by high-resolution ^{13}C NMR spectroscopy. Cluster formation and decay at different temperatures is observed to depend strongly on the type of impurity center inducing the cluster. Connection with the appearance of a "central peak" in light and neutron scattering is drawn.

The appearence of an extremely narrow "central peak" whose intensity diverges as the transition is approached was first observed in neutron- and light-scattering experiments on potassium dihydrogen phosphate[1] (KDP) and strontium titanate.[2,3] This central-peak phenomenon has been observed since then in several other substances, when approaching a structural phase transition. The question whether the central peak is static or dynamic in nature[4] is not yet settled.

It therefore is not surprising that a number of Letters appeared recently which either advocate the static[5,6] or the dynamic picture,[7-10] depending on one's belief in the available theory. The appropriate theories for either case, of course, exist and were first developed from modifications of the soft-mode theory,[11,12] which predicted a central-peak linewidth of 10^9 to 10^{12} Hz, much larger than experimental width. None of these theories reproduced the experimental observation that the width of the central peak is very narrow compared to the phonon width, even at temperatures well above T_c. In order to account for the narrow experimental width, which in the light-scattering and neutron-scattering experiments was essentially the instrumental width, Halperin and Varma[13] and more recently Höck and Thomas[14] developed defect models of the central-peak phenomenon, i.e., impurities in the crystal are held to be responsible for cluster formation of "polarized" low-temperature clusters within the high-temperature phase. These clusters are considered to be dynamic in nature, where the correlation time can reach $\tau \simeq 10^{-8}$ sec, appropriate for accounting for the linewidth of light-scattering and neutron-scattering data; in the latter case the linewidth was pushed down to $\tau^{-1} \simeq 10^7$ sec^{-1} by neutron spin-echo spectroscopy[15] in the case of $SrTiO_3$. Correspondingly, magnetic resonance data could be fitted to these theoretical expectations[4,7-9,16] and this suggested a correlation time of 10^{-8}–10^{-9} sec for the "relaxing defect cell."[13]

In this Letter, we advocate the "static-cluster" picture of the central peak in accord with recent speckle interference measurements by Durvasula and Gammon[5] and with older suggestions by Axe, Shapiro, Shirane, and Riste.[17] We shall demonstrate for the first time by advanced magnetic-resonance techniques[18] that in the H-bonded antiferroelectric squaric acid ($C_4O_4H_2$) (i) the static polarized clusters of the low-temperature phase with a nonvanishing order parameter η_1 can be observed above the phase transition as is evident from Fig. 1, (ii) the static clusters are pinned by impurities (like deuterium) which reduce fluctuations, whereas (iii) dynamic clusters of the high-temperature phase are created by impurities (like chromium) which enhance fluctuations. We believe that the occurrence of the static clusters is a general phenomenon and is indeed responsible for many of the observed elastic "central peaks" in light-scattering and neutron-scattering experiments on structural phase transitions. The lack of resolution in these experimental methods as compared with high-resolution NMR techniques[19] leave the confirmation of static clusters to the latter.

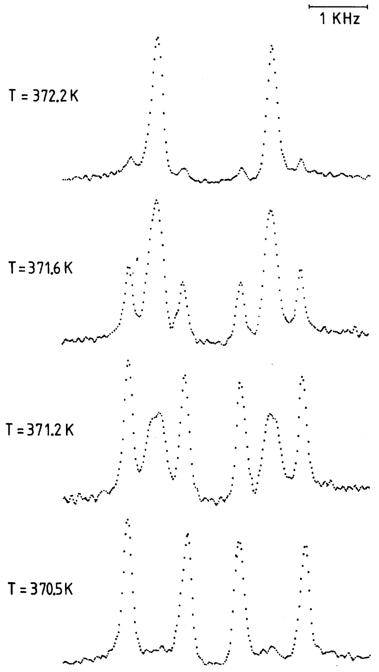

FIG. 1. ^{13}C spectra of a squaric acid single crystal (0.03% Cr) near the phase transition with arbitrary orientation of the magnetic field. Lower curve: Four lines due to the low-temperature phase, where the line separation of the left and right pair of lines corresponds to the order parameter. Upper curve: Each line pair is almost completely collapsed into a single line due to the high-temperature disordered phase. The spectra in between show the coexistence of low- and high-temperature clusters.

Blinc and coworkers[20] have shown that ^{31}P NMR can monitor the order-disorder phase transition in KDP. Proton-enhanced nuclear-induction spectroscopy[18] has been successfully applied for the first time to the investigation of a structural phase transition by us recently.[21] There it was demonstrated that the chemical-shift tensor of the naturally abundant ^{13}C nuclei (1.1% abundance) is a suitable local monitor of the anitferroelectric-to-paraelectric phase transition in squaric acid. The spectral line splitting due to the chemical-shift tensor was shown to be directly proportional to the order parameter.[21] Critical behavior near $T_c = 370$ K was observed, which could be fitted to a power law as

$$\Delta\sigma = \sigma_0[(T_c - T)/T_c]^\beta \qquad (1)$$

with $\beta = 0.14$. Here, $\Delta\sigma$ corresponds to the spectral line separation due to chemical-shift interaction of two different ^{13}C nuclei in the C_4O_4 unit, which become equivalent above the transition temperature; i.e., they result in a single line.

"Bulk" methods like optical birefringence,[22] neutron-scattering experiments,[23] and ultrasonic[24] and dielectric measurements[25] performed on squaric acid revealed a second-order phase transition with a similar critical exponent β, which was attributed to the two-dimensional nature of the planar crystal structure. We would like to point out that bulk methods average over a large volume and observe therefore an "averaged" order parameter whereas the high-resolution NMR technique observes a "local" property, and is therefore capable of distinguishing between areas of different order parameter.

Figure 1 (bottom) shows the four lines of the ^{13}C NMR spectrum in a single crystal of squaric acid due to the four carbon nuclei in the C_4O_4 subunit at a frequency of 67.9 MHz. The ^{13}C NMR spectra were obtained by means of a home-built double-resonance setup and a superconducting magnet (6.3 T) by employing proton-enhanced nuclear-induction spectroscopy.[18,19] The temperature of the sample was controlled to within 0.1 K. Single crystals of squaric acid were grown by slow evaporation of an aqueous solution. The four lines seen in Fig. 1 (bottom trace) correspond to molecules in the low-temperature phase. The line separation $\Delta\sigma$ of two corresponding lines does not completely go to zero when approaching T_c as Eq. (1) would suggest and as was observed by the bulk methods mentioned above.[22,23] On the contrary $\Delta\sigma$ is observed to approach a fixed value $\Delta\sigma_1$ at the critical temperature T_c; i.e., the order parameter η does not vanish continuously, but reaches a minimum value of 54% of its room-temperature value. Upon increasing the temperature, a "central line" between each line pair occurs, which corresponds to molecules in the high-temperature phase. Figure 1 demonstrates this behavior and displays the coexistence of both phases clearly. The line separation of the pairs (about 1 kHz) displays the order parameter in the low-temperature-phase cluster, which must have a lifetime longer than 0.1 sec as obtained from linewidth and spin-echo data. The central line corresponding to high-temperature clusters again has at least the same lifetime. These clusters, however, show some dynamics, corresponding to a hopping process with a rate larger than 10^5 sec^{-1}, as indicated also by the linewidth and spin-echo measurements. This will be discussed in more detail elsewhere. The nonvanishing order parameter at T_c indicates either a crossover to first order, or the onset of antiphase fluctuations as suggested by Cook.[26]

The integral NMR intensities I_h and I_l of the high- and the low-temperature clusters, respectively, correspond to the number of nuclei in these particular clusters. The volume concentrations $C_h = I_h/I_0$ and $C_l = I_l/I_0$, with $I_0 = I_h + I_l$, of the particular clusters as shown in Fig. 2 are therefore obtained from a computer fit to experimental spectra like those shown in Fig. 1. The critical temperature T_c defined by the condition $C_h = C_l = \frac{1}{2}$ can be obtained from the data immediately. In order to derive other parameters for several data sets from differently doped crystals, the following empirical formula was found to be useful:

$$C_h/C_l = \exp(K\epsilon), \tag{2}$$

with

$$\epsilon = (T - T_c)/T_c, \tag{3}$$

where $1/K$ is a measure of the relative temperature interval T/T_c over which the variation of the cluster size occurs (see Fig. 2). With $C_h + C_l = 1$, Eq. (2) may be written as

$$C_l = [\exp(K\epsilon) + 1]^{-1}. \tag{4}$$

Spectra similar to those in Fig. 1 and evaluated as in Fig. 2 were obtained for different kinds of doping with the following: (1) Cr paramagnetic ions of less than 0.1 mole%; (2) deuteration up to 5 mole%.

All impurity concentrations reported here are "nominal" concentrations referring to the crystal-growing solution; i.e., the concentration in the crystal will be smaller. Even in undoped samples

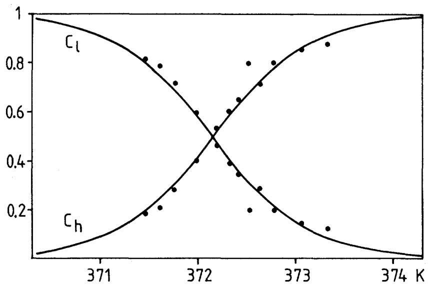

FIG. 2. Relative intensity of the low- and high-temperature clusters vs temperature obtained from data as shown in Fig. 1. The solid lines correspond to Eq. (4) with the parameters K and T_c evaluated as described in the text.

TABLE I. Critical parameters T_c and $1/K$ for different impurity concentrations X_{Cr} and X_{D} for type-1 and type-2 defects.

X_{D} (%)	X_{Cr} (%)	T_c (K)	$10^{+3}/K$
0	0.03	371.31	1.32
0	0.01	372.60	0.90
0	0.00	373.17	0.82
1	0.01	373.66	1.30
2	0.01	375.57	2.22
5	0.01	375.76	3.51

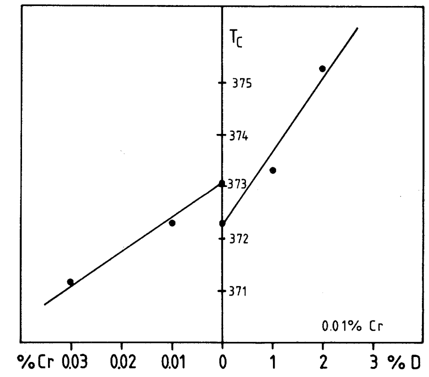

FIG. 3. Variation of the critical temperature T_c vs nominal defect concentration for the two different types of impurities (Cr and D) as discussed in the text. Note that the deuterated samples are all doped with 0.01% Cr.

we observed the same phenomenon, although in a much narrower temperature range. As can be seen from Table I the parameter K depends on the defect concentration as

$$\frac{1}{K}=\frac{1}{K_0}+\frac{C_i}{K_i},\quad i=1,2, \tag{5}$$

where K_0 is the characteristic constant due to the natural abundance of defects (i.e., strain, impurities, deuterium, etc.) or may reflect antiphase fluctuations,[26] and where K_i refers to the specific impurity introduced with a concentration C_i. Here K_1 and K_2 correspond to defects of type 1 (Cr) and defects of type 2 (D), respectively. From Table I, type-1 defects are seen to be far more effective (small K_i) in cluster formation than are the deuterium defects (type 2). This is also borne out by the change in the critical temperature T_c, which is plotted versus defect concentration C_i, $i=1,2$, in Fig. 3.

There the different behavior of type-1 and type-2 defects is evident; i.e., a drastic decrease of T_c with increasing Cr (type 1) concentration and a less drastic increase of T_c with increasing deuterium (type 2) concentration is noted. The existing theories[12,13,26] of cluster formation do not provide an analytical expression for the observed concentration dependence as displayed in Fig. 3 and in the table. We therefore pass this question to the theoreticians in the field.

Summarizing, we would like to note that essentially static clusters in coexistence with dynamic clusters have been observed in squaric acid at the phase transition. A continuous variation of cluster concentration near T_c is observed. Impurities not only increase (type 2) or decrease (type 1) the transition temperature T_c but also widen the temperature interval over which cluster formation is observed. It is therefore believed that the impurities act as pinning forces. The occurrence of a crossover phenomenon might hint at a multicritical point as was already suggested by Petersson.[27] Moreover the applicability of high-resolution NMR techniques[19] to the investigation of cluster formation near structural phase transitions was demonstrated for the first time. The obtained resolution is seen to be several orders of magnitudes higher than with any other method.

Enlightening discussions with Professor R. Blinc, H. Thomas, H. Cummins, J. Petersson, and A. Hüller have elucidated this subject. We are also indebted to J. D. Becker for interesting discussions and assistance. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

---

[1] N. C. Lagakos and H. Z. Cummins, Phys. Rev. B 10, 1063 (1974).

[2] S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, Phys. Rev. B 6, 4332 (1972).

[3] T. Riste, E. J. Samuelsen, K. Otnes, and J. Feder, Solid State Commun. 9, 1455 (1971).

[4] R. Blinc, B. Zeks, and R. A. Tahir-Kheli, to be published.

[5] L. N. Durvasula and Robert W. Gammon, Phys. Rev. Lett. 38, 1081 (1977).

[6] J. B. Hastings, S. M. Shapiro, and B. C. Frazer, Phys. Rev. Lett. 40, 237 (1978).

[7] K. A. Müller, N. S. Dalal, and W. Berlinger, Phys. Rev. Lett. 36, 1504 (1976).

[8] K. A. Müller and W. Berlinger, Phys. Rev. Lett. 37, 916 (1976).

[9] J. Gaillard, P. Gloux, and K. A. Müller, Phys. Rev.

Lett. 38, 1216 (1977).

[10] E. Courtens, Phys. Rev. Lett. 39, 561 (1977).

[11] R. Blinc and B. Zeks, in *Soft Modes in Ferroelectrics and Antiferroelectrics*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1974).

[12] See *Anharmonic Lattices, Structural Transitions and Melting*, edited by T. Riste (Noordhoft, Leiden, 1974).

[13] B. I. Halperin and C. M. Varma, Phys. Rev. B 14, 4030 (1976).

[14] K. H. Höck and H. Thomas, Z. Phys. B27, 267 (1977).

[15] F. Mezei, private communication.

[16] R. Blinc and J. L. Bjorkstam, Phys. Rev. Lett. 23, 788 (1969); G. J. Adriaenssens, J. L. Bjorkstam, and J. Aikins, J. Magn. Reson. 7, 99 (1972).

[17] See Ref. 12, p. 23.

[18] A. Pines, M. Gibby, and J. S. Waugh, J. Chem. Phys. 56, 1776 (1972), and 59, 569 (1973).

[19] M. Mehring, *High Resolution NMR in Solids* (Springer, Berlin, 1976), Vol. 11.

[20] R. Blinc, M. Burgar, V. Rutar, J. Seliger, and I. Zupancic, Phys. Rev. Lett. 38, 92 (1977).

[21] J. Becker, D. Suwelack, and M. Mehring, Solid State Commun. 25, 1145 (1978).

[22] D. Semmingsen and J. Feder, Solid State Commun. 15, 1369 (1974).

[23] E. J. Samuelson and D. Semmingsen, Solid State Commun. 17, 217 (1975), and J. Phys. Chem. Solids 38, 1275 (1977).

[24] N. Rehwald, to be published.

[25] H. D. Maier, D. Müller, and J. Petersson, to be published.

[26] H. E. Cook, Phys. Rev. B 15, 1477 (1977).

[27] J. Petersson, private communication.

Valence Transition in Chemically Collapsed Cerium

M. A. Manheimer[(a)] and R. D. Parks
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

(Received 21 August 1978; revised manuscript received 8 January 1979)

The scaling behavior of the Landau equation of state which describes the valence transition in cerium is studied as a function of the size and valence of various chemical additives. Two major results are the relatively direct determination of the valence N of cerium at the critical point (viz., $N=3.65$) and the finding that the presence of chemical additives leads to a lattice-mediated rather than Coulombic bootstrapping term, which addresses the long-standing question of what is the driving mechanism for the valence transition.

Cerium, being the only chemical element known to undergo (in the fcc phase) a valence transition with temperature, has been studied extensively during the past two decades, and is a primary archetype of so-called Anderson lattice systems. These systems, whose unusual behavior results from the close proximity of a localized (usually $4f$) level to the Fermi level, exhibit a variety of interesting many-body phenomena.[1] These include valence transitions (e.g., Ce or SmS), mixed (nonintegral) valence (e.g., Ce, SmS, or $CePd_3$), and exotic magnetically ordered states (e.g., $CeAl_2$) characterized by spatial modulations in both the magnitude and direction of the moments.

The valence of an Anderson lattice in the mixed-valence state reflects the degree of hybridization of the local state with the conduction-electron state.[2] Of the various experimental approaches used previously to determine (mixed) valence, the measurement of lattice constant is the most straightforward. Implicit in the practical utilization of this method is (1) the assumption of a linear (or some other) relationship between the lattice constant and the (mixed) valence and (2) a knowledge of the lattice constants for the two integral valence values which bracket the mixed valence. The present study, which yields the valence of cerium at the critical point of the chemically induced valence transition, focuses on the scaling properties for different chemical additives of the Landau equation of state which describes the valence transition. This equation, which was shown previously[3,4] to be valid for $Ce_{1-x}Th_x$ in a relatively large region of x-T space encompassing the critical point ($x_0=0.265$, $T_0=148$ K), where x plays effectively the role of the pressure, is of the form

$$\delta T = a(\delta\rho)^3 + b\,\delta x\,\delta\rho + c\,\delta x, \qquad (1)$$

where the dimensionless quantities δT, δx, and $\delta\rho$ (resistivity) are all scaled to their critical values, e.g., $\delta T=(T-T_0)/T_0$. Since it was established previously[3,4] that the electrical resistivity couples linearly to the order parameter, viz., $\langle n_{4f}\rangle$, the average occupancy of the local