when corrected for geometrical attenuation, gives an anisotropy A_2 of 0.019, thereby indicating that most if not all ^{57}Fe nuclei in the alloy experience the quadrupole interaction. The loss of coherence in the PAC spectrum can best be explained by a distribution of EFG magnitudes with $\sigma_E = 0.11 \pm 0.02$ mm/sec, thereby accounting for the additional Mössbauer broadening. It is also possible to explain the loss of coherence as due to small magnetic fields, less than 3 kG, mixed with the basic EFG. The agreement between field-spread values σ_E deduced from each set of data shows that there is little room for additional broadening in the Mössbauer spectrum due to isomer shifts. Although a rather large variation of near-neighbor environments appears necessary to explain the field distribution, the isomer shift is apparently little affected by such changes in the near-neighbor environment.

We have shown that TDPAC measurements on ^{57}Fe can be quite useful in interpreting unresolved Mössbauer spectra. The limitations imposed by the small anisotropy of the cascade can be overcome, in many cases, by the use of properly designed multicounter NaI(Tl) spectrometers. Several other applications of the technique come to mind, e.g., the determination of the origin of broadened Mössbauer singlets in disordered alloys such as stainless steel. The techniques may also prove useful in extending the range of possible experiments to materials where low recoilless fractions have made ME measurements difficult or impossible.

The authors wish to thank Dr. L. H. Bennett for useful discussion, Dr. D. Hoppes for providing source preparation facilities and for his comments on the manuscript, and R. D. Robbins for technical assistance.

*Work supported in part by the Office of Saline Water, U. S. Department of the Interior.

†National Research Council–National Bureau of Standards Postdoctoral Research Associate.

[1]F. J. Lynch, IEEE Trans. Nucl. Sci. 13, 140 (1966).

[2]C. Hohenemser, R. Reno, and A. P. Mills, IEEE Trans. Nucl. Sci. 17, No. 3, 390 (1970).

[3]C. Hohenemser, R. Reno, H. C. Benski, and J. Lehr, Phys. Rev. 184, 298 (1970).

[4]G. K. Wertheim and J. H. Wernick, Phys. Rev. 123, 755 (1966).

[5]L. J. Swartzendruber and L. H. Bennett, Phys. Lett. 27A, 141 (1968).

[6]L. H. Bennett and L. J. Swartzendruber. Acta Met. 18, 485 (1970).

[7]L. J. Swartzendruber, L. H. Bennett, and R. E. Watson, J. Appl. Phys. 40, 1489 (1969).

[8]B. Window and C. E. Johnson, Phys. Lett. 29A, 703 (1969).

[9]B. Window, C. E. Johnson, and G. Longworth, J. Phys. C: Proc. Phys. Soc., London 3, S218 (1970).

[10]M. Frauenfelder and R. M. Steffen, in *Alpha-, Beta-, and Gamma-Ray Spectroscopy,* edited by K. Siegbahn (North-Holland, Amsterdam, 1966), Vol. 2, p. 997.

[11]The least-squares-fitting routine was a modified version of that described by B. L. Chrisman and T. A. Tumolillo, Computer Phys. Commun. 2, 322 (1971).

Critical Asymmetry in Local Fluctuations in $SrTiO_3$ for $T \to T_c^-$

K. A. Müller and W. Berlinger
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
(Received 17 July 1972)

A critical asymmetry in local fluctuations of the rotational parameter φ in $SrTiO_3$ for $T < T_c$ and $\langle\varphi\rangle \neq 0$ is observed directly by the asymmetry a_s of the paramagnetic resonance lines of Fe^{3+}-V_O pair centers. The parameter a_s increases in a critical manner for $T \to T_c^-$. It is postulated that such an asymmetry is a general property of second-order phase transitions.

In this Letter we describe a novel phenomenon in the critical behavior of a crystalline solid undergoing a distortive phase transition[1] of second order. It occurs below the phase transition where the (generalized) order parameter $\langle\varphi\rangle$ is nonzero, and consists of an asymmetry in the local fluctuations $\delta\varphi_l$ around the value $\varphi_l{}^m$ at which the probability $P(\varphi_l)$ to observe φ_l is a maximum, i.e., if $\langle\varphi\rangle \neq 0$, then odd moments in $\varphi_l - \varphi_l{}^m$ also differ from zero. This asymmetry increases in a critical manner for $T \to T_c^-$. Its presence is directly observed by the asymmetry of Fe^{3+}-V_O pair paramagnetic resonance lines. It is postulated that this broken symmetry of local fluctuations for nonzero order parameter occurs quite generally.

The electron paramagnetic resonance (EPR) experiments were carried out on $SrTiO_3$ samples used previously.[2] They were 0.2-mm-thick rectangular (110) plates, containing iron as an impurity and transforming below T_c into a tetragonal monodomain as described elsewhere.[2] The c axis of the domain was parallel to the [001] crystal direction. The spectrometer worked at 19.5 GHz. We investigated the *shape* of the EPR lines of the iron–oxygen-vacancy (Fe^{3+}-V_O) pair center[3] for a magnetic field orientation $\vec{H}$ parallel to the pseudocubic [110] direction. The large angular anisotropy of the Fe^{3+}-V_O EPR spectrum makes it very sensitive to *local* rotations $\vec{\varphi}_l$ of the oxygen octahedra.[4] The spectrum was recently analyzed in detail in the tetragonal phase of $SrTiO_3$.[4] For the geometry described above it could be shown that the high-field resonance magnetic field H_r near 3000 G depends linearly on the local rotation $\bar{\varphi}_l^{[001]}$, $\bar{\varphi}_l = 0.626\varphi_l$, around the pseudocubic [001] direction:

$$H_r = H_0 + a\bar{\varphi}_l^{[001]}. \quad (1)$$

$a = 42.5$ G/deg,[4] $\bar{\varphi}_l$ depends on site l and time t. Because of the nonvanishing order parameter, $\langle\varphi^{[001]}\rangle \equiv \langle\varphi_c\rangle \neq 0$, and the alternate rotation of octahedra in the antiferrodistortive phase,[1] two lines corresponding to $\langle\bar{\varphi}_+\rangle$ and $\langle\bar{\varphi}_-\rangle$ are observed below T_c. These are shown in Fig. 1. Recorded are the derivatives with respect to the magnetic field H of the absorption lines, $dL(H)/dH$, as usual in EPR using Zeeman modulation. We designate the maximum and minimum slopes by $A = |dL/dH|_{max}$, $B = |dL/dH|_{min}$. Well below T_c [Fig. 1(c)] each of these lines is symmetric and $A = B$. On approaching T_c, $A/B \neq 1$, which is *not* due to overlap [Figs. 1(b) and 1(a)], and one sees that the lines become asymmetric, but show mirror symmetry with respect to H_0, corresponding to $\langle\varphi^{[001]}\rangle = 0$, Eq. (1). The ratio A/B was used previously by Feher and Kip to characterize asymmetric ESR lines in thick metal plates, where the asymmetry results from the diffusion of mobile electrons in and out of the skin depth.[5] In order to have an asymmetry parameter a_s which vanishes for a symmetric line, we define

$$a_s = A/B - 1. \quad (2)$$

The lines shown in Fig. 1 are pure absorption derivatives. This was verified in two ways. First, we monitored the shape of EPR lines, which are insensitive to φ rotations like the low-field line at $g^e \sim 6$ of the Fe^{3+}-V_O center for $H \| [110]$,[4] or the $\pm\frac{1}{2}$ transitions of the non-charge-compensated Fe^{3+} or Cr^{3+} ions. All these lines remained symmetric near T_c. Second, the phase of the local oscillator signal of our single sideband superheterodyne spectrometer (i.f. = 30 MHz) was shifted. It is well known that, depending on the phase Φ between the local oscillator and the microwave signal, the absorption χ'' ($\Phi = 0$) or dispersion χ' ($\Phi = 90°$) signal of the lines is recorded. By adjusting intermediate phases Φ, one obtains linear combinations of χ' and χ'' signals, yielding lines of variable asymmetry. In shifting Φ we could nearly symmetrize one of the two lines $\bar{\varphi}_+$ or $\bar{\varphi}_-$, but then the other line became proportionally more asymmetric as a result of their mirror symmetry with respect to H_0. This fact enabled us to obtain a_s with increased accuracy by measuring $A\langle\bar{\varphi}_-\rangle = A^-$, $B\langle\bar{\varphi}_-\rangle = B^-$, A^+, and B^+ and computing $a_s = (A^- + A^+)/(B^- + B^+) - 1$, thus eliminating spurious dispersive components in a record. Figure 2 shows the variation of a_s, where for $T \to T_c^-$ the critical increase is clearly seen. Assuming a divergence in a_s with tempera-

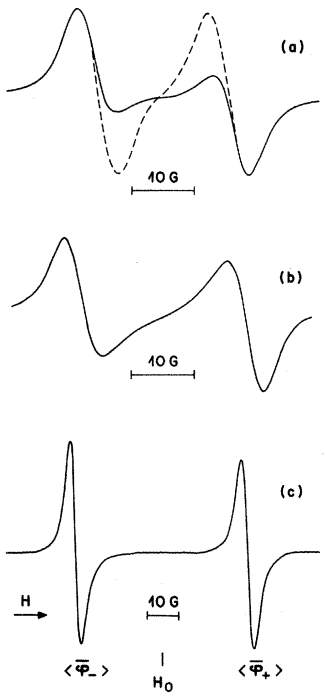

FIG. 1. EPR lines of the Fe^{3+}-V_O center at the K band for $\vec{H} \| [110]$ in a monodomain $SrTiO_3$ sample below T_c, c axis $\| [001]$, at (a) $T = 105$ K, (b) $T = 104.75$ K, (c) $T = 95.5$ K; note the scale change in magnet field sweep. $H_0 = 3090$ G. The dashed curve in (a) represents computer-simulated symmetrical lines with 50% Lorentzian and 50% Gaussian shape with the same width ΔH at $\bar{\varphi}_+$ and $\bar{\varphi}_-$.

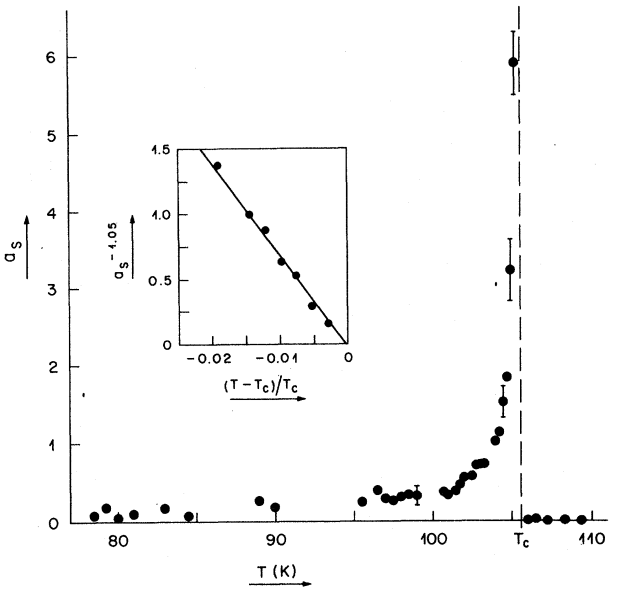

FIG. 2. Measured asymmetry parameter a_s in $SrTiO_3$ for $T \to T_c^-$, and calculated curve with $a_s = a_0(T - T_c)^{-1.05}$.

ture, we find $a_s \propto (T_c - T)^{-n}$, $n = 1.05 \pm 0.15$ for $|\epsilon| < 2 \times 10^{-2}$. In the inset of Fig. 2, $a_s^{-1.05}$ is plotted against $|\epsilon|$ in the critical region.

The asymmetry in the EPR linewidth for $T < T_c$ (Fig. 2) becomes appreciable in the region of $|\epsilon| = |T - T_c|/T_c$ near 10^{-2}, where we know from the $T > T_c$ linewidth data analysis that the regime changes from fast to slow. This change occurs when the majority of the frequency spectrum of the rotational fluctuations becomes slower than the characteristic measuring frequency ω_m of the EPR system of about 100 MHz.[6] In the slow-motion regime the amplitude $L(H)$ of the EPR line is directly proportional to the probability distribution $P(\varphi_l)$ of φ_l if the background line is subtracted. With $P(\varphi_l)$ known, the first moment $\langle \varphi_{+l} \rangle = \langle \varphi \rangle$ can be computed. Further $\varphi_l{}^m$, at which $P(\varphi_l)$ is a maximum, is sited at $dL(H)/dH = 0$ and differs from $\langle \varphi \rangle$. From Fig. 1 we also note that $P(\varphi_l)$ is larger in the region between $\varphi_l{}^m$ and $\varphi_l = 0$. It has been pointed out to us[7] that the latter property of $P(\varphi)$ can easily be obtained by writing down the classical probability distribution of φ,

$$P(\varphi, T) = C(T) \exp[-\Delta F(\varphi, T)], \tag{3}$$

where $\Delta F(\varphi, T) = F(\varphi, T) - F_0(T) = a(T)\varphi^2 + b\varphi^4$ is the Landau *Ansatz* for the free energy.[8] With it one calculates in a straightforward way, close to T_c,

$$\left| \frac{(dP/d\varphi)_{\max}}{(\partial P/\partial \varphi)_{\min}} \right| = \sim \langle \varphi \rangle^{-3} \sim (-\epsilon)^{-3\beta}, \tag{4}$$

where $\beta = \frac{1}{2}$, i.e., $n = 1.5$. In the critical region this analysis is not valid; there $\beta = 0.33 \pm 0.01$ as was previously obtained.[9] Our experimental result, $n = 1.05 \pm 0.15$, suggests that in the critical region $n = 3\beta$ may still hold. In the slow-motion regime the linewidth is dominated by the central mode[10] for $T > T_c$,[11] and this should also be the case for $T < T_c$. Therefore, we conclude that the asymmetry a_s for $T < T_c$ results mainly from the central mode.[7]

From our results we foresee that a breaking in symmetry of local fluctuations is present in all distortive-type[1] phase transitions whenever the overall symmetry is broken, i.e., $T < T_c$ and the order parameter $\langle \eta \rangle$ differs from zero. This means that the symmetry breaking of local fluctuations, in principle, also occurs in weak first-order phase transitions[1] as the only requirement is $\langle \eta \rangle \neq 0$. Now the latter requirement is, of course, the one which is common to the majority of phase transitions like the gas-fluid, the ferromagnetic, etc. Therefore, one may postulate that in the ordered phase the local fluctuations are broken in these cases. The question is whether this is a purely academic statement or whether the quantity in question is accessible by experiment. For other distortive transitions this is possible by EPR. If in a very high magnetic field of over 10^5 kG in nuclear magnetic resonance one can reach the slow-motion regime, then in ferroelectric, magnetic, and liquid-crystal transitions, where NMR has been used successfully,[12] one may observe the effect. Computation of local fluctuations in large-scale computer simulation of phase transitions of exact calculations on models may verify our postulation.

From Fig. 1 it is clear that the asymmetry in the fluctuation of each sublattice in the antiferrodistortive unit cell cancels in the time or ensemble average, which is expected for thermodynamic reasons. In a ferrodistortive transition, where the unit cell does not double below T_c and 180° domains are distinguishable, as in many ferroelectrics, cancelation is achieved in the absence of an external force because 180° domains occur with equal probability. If by application of an external force (electric field, stress, etc.) a monodomain is formed, then the average of the asymmetry in the fluctuations is nonzero.

In conclusion, experimental evidence for the

existence of an asymmetry in local fluctuations around the maximum of the order-parameter probability in the broken symmetry has been presented in a distortive phase transition. This asymmetry increases in a critical manner for $T \to T_c^-$. In theoretical papers Eq. (3) has been used,[13] and an asymmetry in $P(\eta)$ in a small-system Monte Carlo calculation was found.[14] However, neither the critical property of the asymmetry nor the fact that it is accessible by experiment has been recognized so far, as both have been demonstrated in the present work. Until now the dynamics of phase transitions have been investigated in the frequency–wave-vector domain, mainly because of the experimental observation techniques (scattering). It is our opinion that investigations of critical effects in the time-real space domain is useful to gain additional information on the phenomena.

We thank Th. von Waldkirch and T. Schneider for a critical reading of the manuscript and acknowledge discussions with them, K. Binder, E. Courtens, and P. Hohenberg.

[1]For a description of the nomenclature used, see H. Grånicher and K. A. Müller, Mater. Res. Bull. 6, 977 (1971).

[2]K. A. Müller, W. Berlinger, M. Capizzi, and H. Gränicher, Solid State Commun. 8, 549 (1970).

[3]E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins, Phys. Rev. 135, A86 (1964).

[4]Th. von Waldkirch, K. A. Müller, and W. Berlinger, Phys. Rev. B 5, 4324 (1972).

[5]G. Feher and A. F. Kip, Phys. Rev. 98, 337 (1955).

[6]Th. von Waldkirch, K. A. Müller, W. Berlinger, and H. Thomas, Phys. Rev. Lett. 28, 503 (1972).

[7]K. Binder, P. Hohenberg, and T. Schneider, private communication.

[8]L. Landau and E. Lifshitz, *Physique Statistique* (Editions MIR, Moscow, 1967).

[9]K. A. Müller and W. Berlinger, Phys. Rev. Lett. 26, 13 (1971).

[10]T. Riste, E. J. Samuelsen, K. Otnes, and J. Feder, Solid State Commun. 9, 1455 (1971); S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, Bull. Amer. Phys. Soc. 17, 277 (1972).

[11]Th. von Waldkirch, K. A. Müller, and W. Berlinger, Phys. Rev. B 5, 4324 (1972).

[12]R. Blinc, in *Structural Phase Transitions and Soft Modes*, edited by E. J. Samuelsen, E. Andersen, and J. Feder (Universitetsforlaget, Oslo, 1971), p. 97.

[13]G. V. Ryazanov, Zh. Eksp. Teor. Fiz. 52, 1688 (1967) [Sov. Phys. JETP 25, 1122 (1967)].

[14]K. Binder, unpublished.

Low-Temperature Specific Heat of One-Dimensional $K_2Pt(CN)_4Cl_{0.3} \cdot n(H_2O)$

R. L. Greene
IBM Research Laboratory, San Jose, California 95114

and

W. A. Little*
Department of Physics, Stanford University, Stanford, California 94305

(Received 17 July 1972)

We report the low-temperature specific heat of one-dimensional $K_2Pt(CN)_4Cl_{0.3} \cdot n(H_2O)$. Within experimental accuracy the linear temperature contribution to the specific heat is zero. This result is consistent with both the variable-range and interrupted-strand hopping models.

Recently, there has been considerable experimental and theoretical interest in crystalline solids which exhibit one-dimensional (1D) properties.[1-5] In particular, the "mixed-valence" square planar compounds of platinum and iridium have attracted attention because of their large 1D conductivity (1–100 Ω^{-1} cm^{-1} at room temperature) and their possible use as a base structure for a higher-temperature superconductor.[6] In these compounds the planar complexes stack to form linear chains of metal atoms, the chains being insulated from each other by the organic side groups. The metal atom is partially oxidized, and in the band picture the overlapping d_{z^2} orbitals of the metal atoms from a partially filled 1D band.

Two very similar models have been proposed to explain the properties of these 1D compounds.[7] One model, first discussed by Bloch, Weisman, and Varma,[2] is based on x-ray crystallographic data which show that structural disorder exists along the 1D chain, and in such a system it is