Divergent Thermal Diffusivity at a Mean-Field Tricritical Point

E. K. Hobbie,[a] H. Y. Liu,[b] and C. C. Huang
School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455
Ch. Bahr and G. Heppke
Institute for Physical and Theoretical Chemistry, Technical University of Berlin, D-1000 Berlin 12, Germany
(Received 16 May 1991)

A sharp divergence is observed in the thermal diffusivity very close to the transition temperature of a smectic-A–smectic-C transition that is known to be at a mean-field tricritical point. Similar but less pronounced behavior near other smectic-A–smectic-C transitions reveals a relationship between the size of this anomaly and the proximity of the system to a tricritical point. An application of the Ginzburg criterion suggests that this novel behavior might indicate a crossover to an asymptotic critical regime.

PACS numbers: 64.70.Md, 61.30.–v, 64.60.Kw

A number of recent papers have reported striking behavior that gives insight into the nature of the smectic-A (Sm-A) to smectic-C (Sm-C) or chiral smectic-C (Sm-C^*) transition. Measurements of static properties such as tilt angle, polarization, susceptibility, and heat capacity are well characterized by a simple Landau model, the tricritical (TC) nature of which has been demonstrated explicitly [1–3]. In contrast to this, however, measurements of sound velocity and damping show marked pretransitional fluctuation effects [4] above T_c for a compound whose heat capacity is well described by the extended mean-field model [5]. A recent Letter has addressed this discrepancy using the Ginzburg criterion to calculate the width of the critical region for the different quantities in question [6]. The authors propose that the crossover to critical behavior in the elastic constants occurs much further away from T_c than for the specific heat. This is the first time that such behavior has been recognized. In this paper we present thermal diffusivity (D_T) data near the Sm-A–Sm-C transition of racemic 4-(3-methyl-2-chlorobutanyloxy)-4′-heptyloxybiphenyl (A7) that show a distinct crossover. This compound is appealing because it is chemically stable and is known [1], within our experimental resolution, to be at a mean-field tricritical point (TCP). Over most of the temperature range, D_T exhibits mean-field behavior via the Landau-Khalatnikov effect. Close to T_c, however, there is a very dramatic divergence. This unusual feature is a characteristic of all the Sm-A–Sm-C(Sm-C^*) transitions we have studied; however, in the case of A7 it is considerably more pronounced, suggesting a relationship between the width and height of the observed anomaly and the degree of tricriticality. An application of the Ginzburg criterion reveals that this peak occurs within a temperature window where fluctuations should be significant, and that the width of this window increases as the parameter t_0 characterizing the TC Sm-A–Sm-C transition decreases. The possibility of a similar link between the critical behavior observed in sound-velocity measurements and the TC nature of the Sm-A–Sm-C transition is mentioned in Ref. [6]; however, an explanation of why the critical singularity in thermal transport would be divergent is not clear.

Our data are analyzed using model C (Ref. [7]), which follows as a reasonable approximation from a rigorous hydrodynamic theory of smectic liquid crystals [8]. The appropriate free energy and equations of motion are

$$f=f_0+\int d^3x[r\psi^2+u\psi^4+d\psi^6+\tfrac{1}{2}c_i(\nabla_i\psi)^2 + \gamma_m m\psi^2+\tfrac{1}{2}(TC_0)^{-1}m^2], \quad (1)$$

$$\partial\psi/\partial t=-\Gamma_0\delta f/\delta\psi+\theta, \quad (2)$$

$$\partial m/\partial t=T\kappa_{ij}\nabla_i\nabla_j(\delta f/\delta m)+\zeta, \quad (3)$$

where C_0 is the heat capacity per unit volume, κ_{ij} is the thermal conductivity, and the thermal diffusivity is $D_T^{ij}=C_0^{-1}\kappa_{ij}$. There is a dissipative coupling between ψ and m via $\gamma_m=-\partial r/\partial m=-C_0^{-1}\partial r/\partial T$, where $r=a(T-T_c)/T_c$. θ and ζ are Gaussian noise sources with correlations such that the proper equilibrium distribution is maintained and the fluctuation-dissipation theorem is satisfied [7]. From Eq. (3), the component of the effective thermal current density along $\hat{\mathbf{n}}$ is

$$\mathbf{j}\cdot\hat{\mathbf{n}}=-D_T(\hat{\mathbf{n}})\hat{\mathbf{n}}\cdot\nabla\{TC_0\gamma_m\psi^2+m\},$$

and $D_T(\hat{\mathbf{n}})=\hat{n}_iD_T^{ij}\hat{n}_j$ is given to leading order in γ_m by [9]

$$D_T(\hat{\mathbf{n}})\approx 6k_BT^2C_0[F_s^{-1}(\hat{\mathbf{n}})+B(\hat{\mathbf{n}})]^{-1},$$

where $B(\hat{\mathbf{n}})$ is a smooth background and $F_s^{-1}(\hat{\mathbf{n}})$ is the $k\to 0$, $\omega\to 0$ limit of

$$\gamma_m^2C_0^2T^2\int\int dt\,d^3x\,e^{i\mathbf{k}\cdot\mathbf{x}-i\omega t}\langle\psi(\mathbf{x},t)\hat{\mathbf{n}}\cdot\nabla\psi(\mathbf{x},t)\psi(0,0)\hat{\mathbf{n}}\cdot\nabla\psi(0,0)\rangle_0.$$

Here $\langle\rangle_0$ denotes an average with respect to the uncoupled free energy. Writing $\psi=\langle\psi\rangle+\delta\psi$, this is evaluated in the Gaussian approximation [9] to give

$$D_T^{ij}=\delta_{ij}T^{-1}C_0[\gamma_m^2C_0^2\langle\psi\rangle^2\tau\chi\xi_i^{-2}I_1+\gamma_m^2C_0^2\tau\chi^2(\xi_1\xi_2\xi_3)^{-1}\xi_i^{-2}k_BTI_2+B_i]^{-1}. \quad (4)$$

Since $\langle\psi\rangle=0$ above T_c, the first term is only present for $T<T_c$ and is the classical "Landau-Khalatnikov" term that dominates for a mean-field transition. The second term is the contribution from "critical" fluctuations both above and below T_c, which for a mean-field transition will be a small Gaussian correction. C_0, $\langle\psi\rangle$, and χ are given in terms of the parameter $t_0=u^2/3ad$ from the extended mean-field model [5]. I_1 and I_2 are dimensionless integrals, $\tau=\chi/\Gamma_0$ is the relaxation time of ψ, and $\xi_i=(c_i\chi)^{1/2}$. In contrast to the case of strain fluctuations, where the coupling to ψ is highly anisotropic [6,10], the coupling in model C is isotropic, and in Eq. (4) the thermal transport anisotropy follows the shape anisotropy of the tilt fluctuations (that of ξ_i), in qualitative agreement with measurements done on smectic liquid crystals by Rondelez, Urbach, and Hervet [11]. With the exception of this amplitude anisotropy, Eq. (4) predicts that the singularity in D_T is isotropic, since ξ_i is believed to diverge isotropically for the Sm-A-Sm-C transition. In terms of model C, then, the singular T dependence of D_T, as well as any deviation from mean-field behavior, should be apparent in unaligned samples, where the effective correlation length is $\xi=(\xi_1\xi_2\xi_3)^{1/3}$. In Eq. (1) there is a term in f below T_c from phase fluctuations like $\frac{1}{2}\rho_i(\nabla_i\phi)^2$. For $T<T_c$ this leads to a term $\sim\Gamma_\phi^{-1}(\partial\rho/\partial T)^2$ in the background. Our data suggest [12] that the ϕ fluctuations are long range (ρ small) and make no measurable contribution to D_T for $d=3$.

The ac calorimetry technique used is described in detail elsewhere [13]. C_0 and D_T are measured simultaneously as a function of T. Although it is κ that appears as the Onsager coefficient in Eq. (3), it is D_T that is relevant from a dynamic scaling perspective. D_T is also more sensitive to the fitting, and a fit of κ follows trivially from a fit of C_0 and D_T. C_0 data for the sample described here, fitted by the extended mean-field model [1,5], are displayed in Fig. 1. T_c is 72.206 °C and t_0 was found to be less than 10^{-5} ($t_0=0$ within the limit of our resolution), in agreement with previous measurements of C_0 on a different sample of the same compound [1]. For $t_0=0$ both the leading term and the Gaussian contribution in Eq. (4) have the same singular T dependence, and the data have been fitted by

$$D_T=(4\pi)^{-1}\int d\Omega\, D_T(\hat{\mathbf{n}})$$
$$=\tfrac{1}{3}\sum_i D_T^i\approx C_0[A^{\pm}|t|^{-1/2}+B]^{-1},$$

which follows from Eq. (4) when Γ_0 is a smooth function of T and the director distribution is uniform [9]. The fitting parameters are a weakly linear background and an amplitude above and below T_c ($A^{\pm}$) for a total of four. The fit of D_T (Fig. 2) is reasonable, except in the immediate vicinity of T_c. The softening of D_T above T_c from the "slowing down" of the Gaussian tilt fluctuations is barely distinguishable from the background and is al-

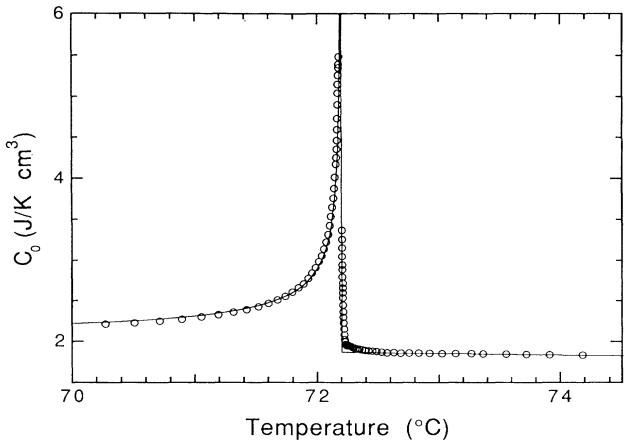

FIG. 1. Heat capacity per unit volume as a function of temperature near the Sm-A-Sm-C transition of A7. The open circles are measured values and the line is the fit.

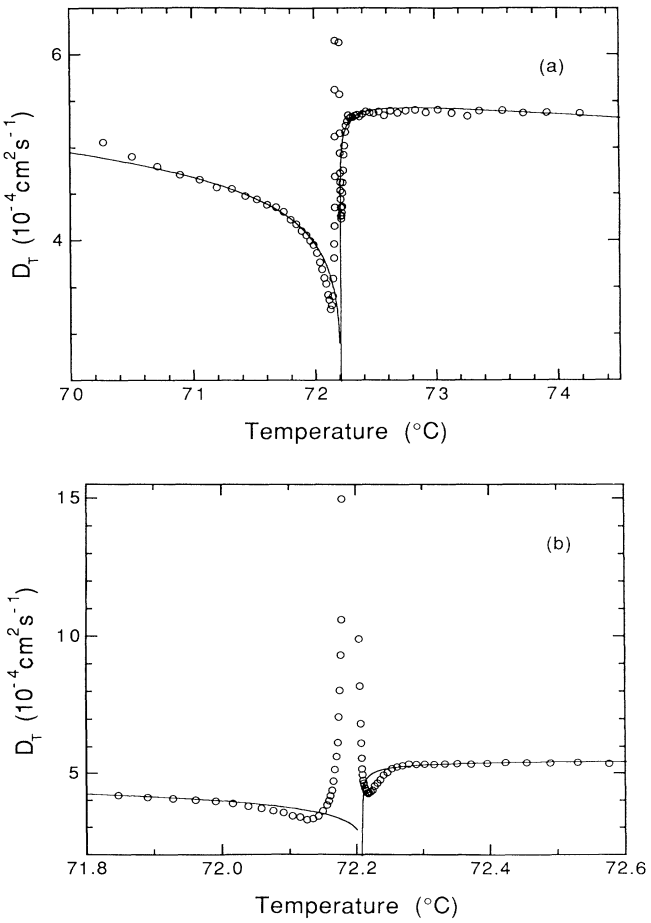

FIG. 2. Measured thermal diffusivity as a function of temperature (open circles) and calculated (line): (a) over the whole temperature range, and (b) close to T_c where the crossover to divergent behavior is very clear.

most lost in the rounding of the mean-field jump, indicating that the second term in Eq. (4) is much smaller than the expected mean-field behavior ($A^+ \approx 0.03A^-$). D_T is more rounded than C_0, however, and $\kappa = C_0 D_T$ shows a weak softening just on the high-T side of the sharp jump at T_c. This suggests that the rounding in D_T for $T > T_c$ is at least in part due to pretransitional fluctuations, and that such a contribution to D_T is significantly larger than any similar contribution to C_0 (which is negligible). As $T \rightarrow T_c$, the D_T data begin to deviate from the fit and show an early minimum at around 12 mK above and 80 mK below T_c. Within this window the data exhibit a very dramatic divergence, extending considerably beyond the (10-90)% width of the jump in C_0, which for A7 is about 15 mK ($\sim 4.5 \times 10^{-5}$ in reduced temperature). This behavior is reproducible, and the width and height are relatively insensitive to sample thickness or the amplitude of the input temperature oscillations. Our data show three distinct regimes. Over most of the T range the mean-field behavior dominates, as expected from the mean-field nature of C_0. Just above T_c, the Gaussian corrections to this may be evident. The final regime in the immediate vicinity of T_c shows a spectacular peak, which we interpret, using the Ginzburg criterion, as a possible crossover to asymptotic critical behavior.

The correlation functions in the above analysis are evaluated with the uncoupled f to obtain the leading behavior in γ_m. For T close to T_c, the "interaction" due to the coupling could be significant. To identify the crossover temperature, the size of the fluctuations induced by the coupling must be compared with the leading-order terms, and the point at which the Gaussian approximation breaks down identified. For the compound A7, $u \approx 0$ in Eq. (1), and above T_c,

$$f(\mathbf{x}) \sim at\psi^2 + \gamma_m m\psi^2 + \tfrac{1}{2}(TC_0)^{-1} m^2 + O(\psi^6) .$$

Since f is quadratic in m, the standard procedure is to carry out the integration over m in the partition function, $Z \sim \int \delta\psi\, \delta m \exp(-\beta f)$, to obtain f_{eff} in terms of ψ alone [7] with the coupling replaced by $-\frac{1}{2} TC_0 \gamma_m^2 \psi^4$. As $T \rightarrow T_c$, the coefficient of the ψ^2 term vanishes like $|T - T_c|$, and at $|\Delta T|^{\pm}$ the ψ^4 term will be the same size as the leading term, indicating a crossover to non-Gaussian behavior [14]. This will occur when $\langle \delta\psi^2 \rangle \sim 2C_0 \Delta T/3a$, or when $|\Delta T|^+/T_c \sim (l/\xi_0^+)^6$ and $|\Delta T|^-/T_c \sim [(l/\xi_0^-)^3 - (l/l')^3]^2$, where $\xi_0 = (\xi_1^0 \xi_2^0 \xi_3^0)^{1/3}$, $l^3 \sim k_B/C_b(T_c)$, and $(l')^3 \sim k_B/A_0$. C_b and A_0 are determined from the fit of C_0: $C_0 = A_0 |t|^{-1/2} + C_b(T)$ ($T < T_c$), and $C_0 = C_b(T)$ ($T > T_c$). The crossover temperatures $|\Delta T|^+ \approx 12$ mK and $|\Delta T|^- \approx 80$ mK obtained from the data imply that $\xi_0^+ \sim 11$ Å and $\xi_0^- \sim 6$ Å, and from the molecular dimensions of A7, $\xi_0 \sim 8$ Å. Regardless of the exact value of ξ_0, the width of the critical regime [15] for C_0 ($\sim k_B^2/\Delta C_0^2 \xi_0^6$) would be at least a factor of $(C_b/\Delta C_0)^2$ smaller than for D_T. Thus any crossover in C_0 would occur well within a 20-mK window around T_c, within the region of rounding. D_T would be more sensitive to fluctuations because the leading term comes from $\langle \psi \rangle^2 \langle \nabla_i \psi(\mathbf{x},t) \nabla_i \psi(0,0) \rangle$, while the leading term in C_0 comes from $\partial \langle \psi \rangle^2 / \partial T$.

We observe a similar divergence in D_T near the Sm-A-Sm-C(Sm-C^*) transitions of other compounds whose C_0 data yield t_0 values much larger than that for A7 (Ref. [16]). These peaks are correspondingly narrower and smaller, and again are reproducible. If the above criterion is applied to a system with a finite positive ψ^4 term in the uncoupled free energy, it follows that since the effective coupling term is negative, the effect would be suppressed when $\Delta C_0 \leq C_b$, where C_b is the background heat capacity and $\Delta C_0 = a^2/2uT_c$ is the heat-capacity jump at T_c (Ref. [5]). As t_0 increases, ΔC_0 will decrease and the width of the peak in D_T should shrink to within the region of rounding in C_0. D_T data for the other compounds we have studied agree with this interpretation.

An interesting feature of the anomaly is that it appears to violate extended dynamic scaling. Equation (4) is compatible with the dynamic scaling hypothesis, since in the critical regime the leading term is $D_T \sim \xi^{2-z}$. The only new feature is that it treats the large background self-consistently [17]. Instead of the expected "critical slowing down," D_T diverges strongly in the critical regime, which is inconsistent with dissipative equations of motion [7]. One possible explanation is that a description in terms of model C is incorrect and there are other non-dissipative anisotropic couplings that become important near T_c; however, the exact nature of the asymptotic critical behavior that follows from model C is not at all clear. From the symmetry of the order parameter, the Sm-A-Sm-C transition should be in the $d = 3$, $n = 2$ universality class [18]. Renormalization-group calculations of model C for $n = 2$ are complicated by the fact that m relaxes slower than ψ, yet the two modes remain coupled, which suggests a violation of dynamic scaling [19]. The same problem arises in the dynamics of ^{3}He-^{4}He mixtures, where it is evident that any breakdown of dynamic scaling for model C when $n = 2$ should be most pronounced at a TCP (Ref. [20]). More work is needed to understand this effect, as well as the fundamental nature of the Sm-A-Sm-C transition.

In Ref. [6] Benguigui and Martinoty suggest a possible link between the strong tilt-angle-strain coupling, which appears to be responsible for the large critical region observed with ultrasound, and the TC nature of the Sm-A-Sm-C transition. A recent theory has proposed that coupling between ψ and the smectic layer fluctuations can lead to a first-order transition [21]. It is known that chiral materials with a large spontaneous polarization tend to be first order, and in general the continuous Sm-A-Sm-C (or Sm-C^*) transition moves toward a TCP as the temperature width of the Sm-A phase decreases [22]. Hence it is possible that the strong coupling to the strains (particularly the component normal to the planes) may be somehow related to the tricriticality of the Sm-A-Sm-C transition. The strains σ_i couple to ψ like

[6,10] $\frac{1}{2}\gamma_u\sigma_3\psi^2$, $\frac{1}{2}\gamma_\rho(\sigma_1+\sigma_2+\sigma_3)\psi^2$, and $\frac{1}{2}c_{ij}\sigma_i\sigma_j$, with the coupling constants $\gamma_u=-\partial r/\partial\sigma_3$ and $\gamma_\rho=-\partial r/\partial\rho$. By integrating out the σ_i (this is equivalent to the transformation to G in Ref. [6]), an argument similar to the one above suggests that fluctuation effects should be apparent above T_c for the compound terephthal-bis-butylaniline (TBBA) (Ref. [6]). At what temperature the crossover occurs depends strongly on the size of γ_u, γ_ρ, and t_0. This might explain why one compound shows critical behavior as far away as 10 K while another appears to show no fluctuation effects [6,23], and hence it would be interesting to do ultrasound measurements on a strongly TC compound such as A7.

We would like to thank C. Dasgupta and J. W. Halley for useful discussions, J. Douglas and J. V. Sengers for critical reading of the manuscript, and D. R. Nelson for pointing out the possible relevance of Ref. [20]. This work was supported in part by the Graduate School of the University of Minnesota, NSF Grant No. DMR-85-03419, and the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich No. 335).

---

[a]Present address: Materials Science and Engineering Laboratory, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

[b]Present address: Picker International Inc., Highland Heights, OH 44132.

[1] H. Y. Liu, C. C. Huang, Ch. Bahr, and G. Heppke, Phys. Rev. Lett. **61**, 345 (1988).

[2] J. Boerio-Goates, C. W. Garland, and R. Shashidhar, Phys. Rev. A **41**, 3192 (1990).

[3] Ch. Bahr and G. Heppke, Phys. Rev. Lett. **65**, 3297 (1990); Phys. Rev. A **41**, 4335 (1990).

[4] D. Collin, J. L. Gallani, and P. Martinoty, Phys. Rev. Lett. **61**, 102 (1988); **58**, 245 (1987).

[5] C. C. Huang and J. M. Viner, Phys. Rev. A **25**, 3385 (1982); *Liquid Crystals and Ordered Fluids*, edited by A. Giffen and J. F. Johnson (Plenum, New York, 1984), Vol. 4, p. 643.

[6] L. Benguigui and P. Martinoty, Phys. Rev. Lett. **63**, 774 (1989).

[7] P. C. Hohenberg and B.I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[8] P. C. Martin, O. Parodi, and P. S. Pershan, Phys. Rev. A **6**, 2401 (1972).

[9] E. K. Hobbie and C. C. Huang, Phys. Rev. A **39**, 4154 (1989). The fit of D_T for 7O.4 in this reference, using a simple scaling argument, is incomplete because it neglects the "Landau-Khalatnikov" term that will dominate for this transition. The data can be fitted nicely by Eq. (4) when the first term is included. For the Sm-A-Hex-B transition the second term in Eq. (4) will dominate.

[10] B. S. Andereck and J. Swift, Phys. Rev. A **25**, 1084 (1982).

[11] F. Rondelez, W. Urbach, and H. Hervet, Phys. Rev. Lett. **41**, 1058 (1978); W. Urbach, H. Hervet, and F. Rondelez, Mol. Cryst. Liq. Cryst. **46**, 209 (1978).

[12] For $d=3$, $\langle\phi(\mathbf{x})\phi(0)\rangle\sim(\rho r)^{-1}$ gives $\xi_\phi\sim\rho^{-1}$. The Van Hove result for the phase contribution to F_x^{-1} is proportional to $(T_c-T)^{-1}$, which we do not see.

[13] C. C. Huang, J. M. Viner, and J. C. Novak, Rev. Sci. Instrum. **56**, 1390 (1985).

[14] The temperature above T_c at which the ψ^4 term is the same size as the ψ^2 term in $f/V\sim at\psi^2+u\psi^4+c|\nabla\psi|^2$, and thus the Gaussian approximation fails, is $t_g\sim(k_BT_c)^2u^2/a^4\xi_0^6$. The same formula applies below T_c (V.L. Ginzburg, Fiz. Tverd. Tela **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1960)]).

[15] Exact verification of the Ginzburg criterion requires knowledge of ξ_0 and a constant prefactor. $\xi_0\sim8$ Å is estimated from the effective molecular volume of A7. There is also $\sim10\%$ uncertainty in the measured sample thickness, which rescales both ΔC_0 and C_b by the same constant factor. For example, ΔC_0 and C_b are $\sim20\%$ larger for the sample described in Ref. [1]. The above unknowns cancel, however, when the ratio of the crossover temperatures is taken, since what remains is $(C_b/\Delta C_0)^2$. This slight uncertainty has no influence on the fitting.

[16] E. K. Hobbie and C. C. Huang, Phys. Rev. A **36**, 5459 (1987).

[17] The inverse additivity of the singular and background parts of D_T follows from model C when $\kappa=C_0D_T$ and $B(\hat{\mathbf{n}})$ is from $\langle\hat{\mathbf{n}}\cdot\nabla m(\mathbf{x},t)\hat{\mathbf{n}}\cdot\nabla m(0,0)\rangle_0$.

[18] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **21**, 49 (1973).

[19] B. I. Halperin, P. C. Hohenberg, and S. Ma, Phys. Rev. B **10**, 139 (1974); **13**, 4119 (1976).

[20] E. D. Siggia and D. R. Nelson, Phys. Rev. B **15**, 1427 (1977).

[21] J. V. Sellinger, J. Phys. (Paris) **49**, 1387 (1988).

[22] C. C. Huang and S. C. Lien, Phys. Rev. A **31**, 2621 (1985).

[23] S. Bhattacharya, B. Y. Cheng, B. K. Sarma, and J. B. Ketterson, Phys. Rev. Lett. **49**, 1015 (1982).