Since BCS wave functions can be built by pairing electrons $(\vec{k}+\vec{q}, \uparrow)$ and $(-\vec{k}+\vec{q}, \downarrow)$, we must use one-electron states satisfying the quantization condition around the fluxoid

$$(2j+1)\pi = \oint \vec{k}\cdot d\vec{r} \approx 2\pi\xi k \quad (j \text{ an integer})$$

or

$$k \approx (j+\tfrac{1}{2})\xi^{-1}. \quad (11)$$

When the condensed state moves with the velocity $\vec{v}_s(\vec{r})$, the local excitations may have a shifted BCS spectrum

$$\epsilon(\vec{k}, \vec{r}) = |\Delta(\vec{r})| + \hbar\vec{v}_s\cdot\vec{k}. \quad (12)$$

From Eqs. (11) and (12) we see that the excitation spectrum becomes gapless when

$$v_s \geq |\Delta|/\hbar k \approx v_F/(2j+1).$$

In the crossed fields the order-parameter variation moves with the fluxoid velocity cE/H. Therefore, the critical state of the quasiparticle excitation is

$$cE/H = v_F/(2j+1).$$

This relation teaches us that Eq. (5) may be appropriate in this case if the magnetic field H in the equation is replaced by $H/(2j+1)$. Then the excitation condition (10) is rewritten as

$$\alpha^2[E^2/E_{c2}^2 - H^2/(2j+1)^2 H_{c2}^2] = (2l+1\pm 1)^{-2},$$

which coincides with the observed result Eq. (1).

The voltage steps in the current-voltage characteristics have also been observed for superconductive thin wires and whiskers with diameter comparable to the coherence length ξ.[8-10] On the basis of our discussion, these phenomena may be interpreted as phenomena due to coherent quasiparticle excitations in the absence of a magnetic field.

Certain characteristics of these phenomena may have applications in high-speed–computer elements and high-frequency oscillators.

[1]M. Sugahara, Phys. Rev. Lett. 29, 99 (1972).
[2]M. Sugahara, Phys. Rev. B 6, 130 (1972).
[3]See, for example, P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).
[4]See, for example, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford Univ. Press, Oxford, England, 1958), 4th ed.
[5]See, for example, Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. 139, A1163 (1965).
[6]M. Sugahara, Phys. Rev. Lett. 26, 632 (1971).
[7]A. A. Abrikosov, Zh. Eksp. Teor. Fiz. 32, 1442 (1957) [Sov. Phys. JETP 5, 1174 (1957)].
[8]W. W. Webb and R. J. Warburton, Phys. Rev. Lett. 20, 461 (1968); R. J. Warburton and W. W. Webb, Bull. Amer. Phys. Soc. 13, 379 (1968); W. W. Webb, in *Proceedings of the International Conference on Fluctuations in Superconductors, Asilomar, California, 1968,* edited by W. S. Gore and F. Chilton (Stanford Research Institute, Menlo Park, Calif., 1968), p. 259.
[9]G. I. Rochlin, in *Proceedings of the International Conference on Fluctuations in Superconductors, Asilomar, California, 1968,* edited by W. S. Gore and F. Chilton (Stanford Research Institute, Menlo Park, Calif., 1968), p. 261.
[10]J. Meyer and G. V. Minnigerode, Phys. Lett. 38, 529 (1972).

Thermoelectric Anomaly Near a Critical Point

G. A. Thomas, K. Levin, and R. D. Parks
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

(Received 1 May 1972)

New measurements on β-brass reveal an anomaly in the thermopower in the vicinity of the order-disorder phase transition. A simple analysis, which is applicable to a wide class of phase transitions, suggests that the anomaly arises from the scattering of conduction electrons from short-range critical fluctuations and that the thermopower can, in principle, provide a direct measure of correlation functions.

A number of advances have been made recently in our understanding of transport properties in metallic systems near critical points.[1] One of the more important of these was the clarification by Fisher and Langer[2] of the vital role that short-range spin fluctuations play in the scattering of conduction electrons. We suggest that the Fisher-Langer approach can be extended in a simple way to describe the anomaly in the temperature dependence of the thermopower for a wide class of phase transitions. We support this suggestion with measurements of the critical thermopower in β-brass.

Using the Boltzmann equation, Mott and Jones[3] have obtained an expression for the thermopower Q which is applicable to systems of noninteracting electrons which scatter elastically from random scattering centers at a temperature T much less than the Fermi temperature ϵ_F/k_B:

$$Q=\frac{\pi^2 k_B{}^2 T}{3|e|}\frac{\partial\rho(\epsilon_F)}{\partial\epsilon_F}[\rho(\epsilon_F)]^{-1}, \quad (1)$$

where $\rho(\epsilon_F)$ is the electrical resistance, k_B is Boltzmann's constant, and $|e|$ is the magnitude of the electric charge. For a solid with an isotropic Fermi surface, $\rho(\epsilon_F)$ can be expressed in terms of an effective carrier density $n(\epsilon_F)$ and scattering relaxation time $\tau(\epsilon_F)$,

$$\rho(\epsilon_F)=m/n(\epsilon_F)e^2\tau(\epsilon_F). \quad (2)$$

Hereafter we shall write $n(\epsilon_F)=n$ and $\tau(\epsilon_F)=\tau$. The electron lifetime can be decomposed into two terms: τ_n, which varies slowly near the critical temperature T_c; and τ_c, which represents the critical contributions to $1/\tau\equiv 1/\tau_c+1/\tau_n$. Assuming that τ_n behaves like the usual high-temperature relaxation time arising from electron-phonon scattering, it follows[4] that $\tau_n\propto\epsilon_F{}^{3/2}$.

In ferromagnets and antiferromagnets the lifetime τ_c arising from the scattering of free conduction electrons from localized spin fluctuations can be evaluated in the Born approximation and is given by[2]

$$1/\tau_c=K_0 k_F{}^{-3}\int_0^{2k_F} I(k,T)k^3\,dk. \quad (3)$$

$J^{-2}I(k,T)=\Gamma_{ss}(k,T)$ is the Fourier transform of the spin-spin correlation function[2]; J is the exchange constant, k_F is the Fermi momentum, and K_0 is a constant which depends on the magnitude of the localized spins.

Equation (3) can be generalized to apply to binary alloys A-B which undergo order-disorder phase transitions. In this case $I(k,T)$ is given by[5]

$$I(k,T)=\bar{W}^2\Gamma_{\rho\rho}(k,T)+(\Delta\bar{W})^2\Gamma_{cc}(k,T)+\bar{W}\Delta W[\Gamma_{\rho c}(k,T)+\Gamma_{c\rho}(k,T)], \quad (4)$$

and the constant K_0 differs slightly from that appropriate to magnetic phase transitions. In Eq. (4) $\Gamma_{cc}(k,T)$ is the concentration-concentration correlation function; $\Gamma_{\rho\rho}(k,T)$ is the critical part of the density-density correlation function. This term contains the effects on τ_c of scattering from lattice deformations (e.g., soft phonons) which result from concentration fluctuations.[1,6] Similarly, $\Gamma_{\rho c}(k,T)$ and $\Gamma_{c\rho}(k,T)$ are the density-concentration correlation functions. The quantities W and ΔW are given by $\frac{1}{2}(W_A+W_B)$ and $\frac{1}{2}(W_A-W_B)$, respectively, where W_A and W_B are the pseudopotentials for A and B atoms.

An expression for the thermopower above the Debye temperature can be obtained by combining Eqs. (1)–(4):

$$Q=Q_n+A_Q T[4K_0 k_F I(2k_F,T)]\tau, \quad (5)$$

where

$$A_Q=2\pi^2 k_B{}^2/3|e|\epsilon_F=(4.9\times10^{-2}\,\mu\text{V eV K}^{-2})/\epsilon_F$$

and $Q_n=Q_{PD}-\frac{3}{2}A_Q T$. Here Q_{PD} is the temperature independent phonon-drag contribution[4] to Q. In calculating Q_n the free-electron approximation for n has been used.[3] In addition, the critical contribution to n from the lattice expansion[7] has been neglected under the assumption that the relative change in the lattice parameter is small compared to that of Q. Using the results of Ref. 2 it can be shown that for ferromagnets near T_c, $4K_0 k_F I(2k_F,T)$ is of the same order of magnitude and has roughly the same temperature dependence as $1/\tau_c$. Therefore, defining $\rho_n=m/ne^2\tau_n$ and $\rho_c=m/ne^2\tau_c$, it follows that

$$Q\approx Q_n+A_Q T\rho_c/\rho=Q_n+A_\varphi T(1-\rho_n/\rho). \quad (6)$$

Careful thermopower measurements on Ni exist[8] and are consistent with the behavior for Q predicted by Eq. (6). It is of interest, then, to obtain similar data on the critical behavior of Q near an order-disorder phase transition. β-brass is a particularly ideal system to which to apply the above model since the ions which undergo the order-disorder phase transition are truly localized, in contrast to the situation in Ni where the d spins may be partially itinerant.

The data for β-brass were obtained using standard techniques.[9] Fine-gauge reference and thermocouple wires were spot-welded to two points at the ends of the samples, and the samples were hermetically sealed with a vapor-deposited film of SiO (about 10^4 Å thick) to prevent the emanation of Zn. Our tests indicate that coating the sample is a crucial procedure since the Zn vapor causes serious contamination of voltage and thermocouple wires, as well as changes in the sample composition. (The lack of correlation among measurements of Q from sample to sample in previous measurements on β-brass[10] may be attributable to this problem.) Large polycrystalline samples were produced from a mechanically

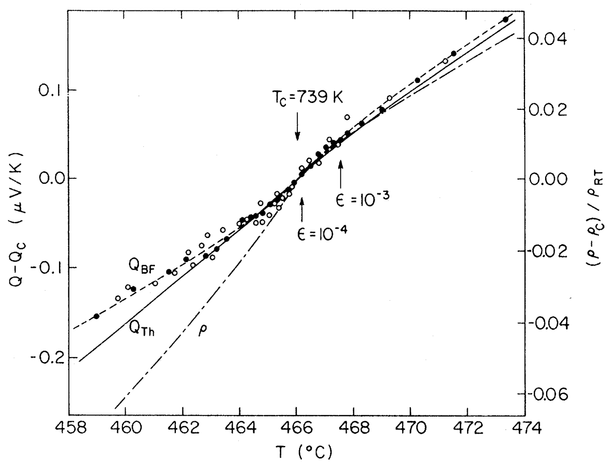

FIG. 1. Anomaly in the temperature dependence of the thermoelectric power of β-brass with Chromel reference. Open and closed circles are for two samples cut from the same boule with $\Delta T = 1$ and 5 K, respectively. Q_c is the value of Q at T_c; the curves labeled Q_{BF}, $Q_{\rm Th}$ [Eq. (6)], and ρ (measured resistivity, see Ref. 11) are explained in the text.

mixed molten solution of 99.999+%-purity Cu and 99.99+%-purity Zn. Measurements were taken with a drift rate of about 2 K/h with periodic reversals of ΔT and detailed checks for linearity of V versus ΔT both above and below T_c.

The thermopower data for two samples with values of $\Delta T = 5$ and 1 K (closed and open circles, respectively) are shown in Fig. 1 along with the resistivity[11,12] (dot-dashed line); the critical anomaly in Q appears to be qualitatively similar to that of ρ. The maximum slope of Q occurs at 739 K. Differential cooling measurements on another piece of the same boule (with 47.01 at.% Zn) indicate a sharp specific-heat peak at the same $T_c = 739$ K. This value of T_c is in agreement with the phase diagram for β-brass as measured by various experimenters.[13] The results were checked in separate experiments with Chromel C and Constantan x reference wires and were found to be the same for both, as would be expected from the known constancy of $Q_c - Q_x$ near 740 K.[14] The qualitative shape of Q for β-brass was also checked using Pt and stainless-steel reference wires. The accuracy of the absolute value of Q near T_c is limited by the uncertainty in the values of Q for the reference wires[15] used, but our values fall around $+1.3 \pm 0.5$ μV/K, a result consistent with the value $+1.7$ μV/K found by Webb.[10]

The fact that the resistivity of β-brass has an anomaly characteristic of a ferromagnet rather than that expected of an antiferromagnet could suggest that the contribution to $I(k,T)$ from the density-density fluctuation $\Gamma_{\rho\rho}(K,T)$ (which is believed to have a ferromagneticlike anomaly[1,6]) dominates the contribution from $\Gamma_{cc}(k,T)$ (which should behave like the spin-spin correlation function for an antiferromagnet[1]). Since the relative change in the lattice constant[16] near T_c is less than 10^{-2} times that of Q, it is reasonable to assume that the anomaly in Q is not dominated by that of the lattice expansion. The approximation in Eq. (6) can, therefore, be directly compared with the data.

The solid line, $Q_{\rm Th}$, in Fig. 1 is a plot of the theoretical expression for Q [Eq. (6)] plus the thermopower of the reference wires[15] with $A_Q = 0.015$ μV/K^2 and $Q_n = -3.44$ μV/K and is in fairly good agreement with the data. On the basis of resistivity measurements[10] ρ_n should be roughly between 4 and 10 $\mu\Omega$ cm near T_c. For simplicity, ρ_n was taken here to be 4.51 $\mu\Omega$ cm (which is the value of ρ at 25°C); the nature of the theoretical fit to the data is insensitive to the choice of ρ_n. Because of lattice and band-structure effects, it is difficult to make a reliable theoretical estimate of Q_n. However, the theoretical and experimental values of A_Q are in reasonable agreement when $\epsilon_{\rm F}$ is taken to be ~7.0 eV which corresponds to the Fermi energy in pure Cu. Finally, the dashed line in Fig. 1, labeled $Q_{\rm BF}$, represents a computer least-squares fit to the data, above and below T_c separately, using the critical exponents which were found to describe the critical temperature dependence of ρ.[11]

An alternative theory to explain the critical behavior of Q has been proposed[8] which suggests that, if the conduction electrons themselves order at the phase transition, Q measures the static entropy associated with the transition. This model, which is without firm theoretical foundation, predicts that $dQ/dT = C_p/T_c n^{\rm eff} q$, where $n^{\rm eff}$ is the effective density of itinerant carriers with charge q which participate in the phase transition, and C_p is the specific heat. The difficulties with this model have been previously summarized.[17]

In order to compare the different theoretical models for Q with experiment, the temperature derivatives of the three curves in Fig. 1 are plotted in Fig. 2. Because of the small signal-to-noise ratio in the data (the noise level is ~10 nV), the quantity $dQ_{\rm BF}/dT \pm \sigma$, where σ is 1 standard deviation, is plotted (shaded area) to represent the data. The dot-dashed line is a plot of the

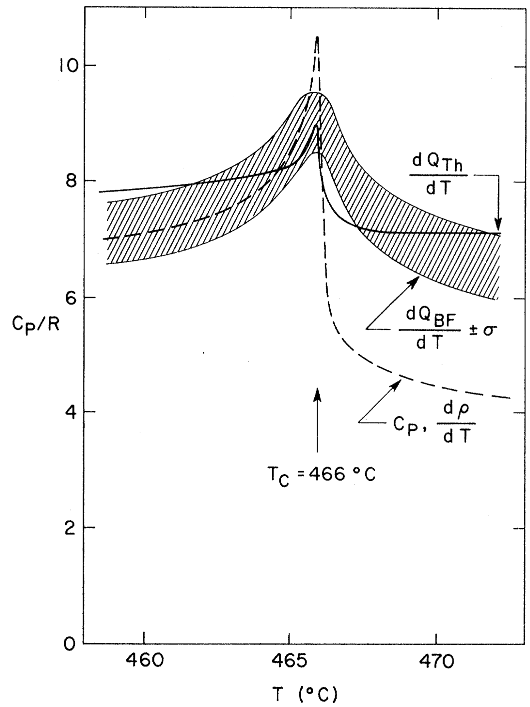

FIG. 2. Temperature derivative of the measured thermopower shown in Fig. 1 with data scatter represented by the shaded area. The scattering theory presented in the text, dQ_{Th}/dT, is seen to give a reasonable description of the observed anomaly. The measured specific heat (see Ref. 11) is significantly different in functional shape.

specific heat, which is proportional to $d\rho/dT$.[11] The quantities dQ_{Th}/dT and dQ_{BF}/dT are multiplied by a constant to make the three curves coincide below T_c. Although the curves representing dQ_{Th}/dT and the data coincide over the entire temperature range, both curves significantly deviate from the specific-heat curve above T_c.[18] The present theory is, therefore, in better agreement with experiment than is the specific-heat model.[8]

We conclude that the physics underlying the thermoelectric power near order-disorder and other second-order phase transitions in metals is fundamentally related to the scattering of conduction electrons by critical fluctuations. The noise in the present data[19] (while allowing a definitive, albeit qualitative, test of the present model versus the specific-heat model promoted in Ref. 8) precludes the demonstration of the difference between the correlation function $I(2k_{\mathrm{F}}, T)$ and the critical resistivity $\rho_c(T)$, i.e., Eq. (5) versus Eq. (6). While $I(2k_{\mathrm{F}}, T)$ and $\rho_c(T)$ are approximately similar, they differ in detail (see, e.g., Ref. 2). It would be interesting to demonstrate this difference as well as the explicit form of $I(2k_{\mathrm{F}}, T)$ by making precise and simultaneous measurements of the thermopower and resistivity anomalies in a system where the anomalies are larger and hence the data scatter is smaller than in the case of β-brass. That the explicit form of the correlation function for $K = 2k_{\mathrm{F}}$ can, in principle, be obtained from measurements of the thermopower is a quite remarkable result, since it is usually assumed that conventional transport measurements depend upon the correlation function only through complicated convolutions, e.g., as in the case of electrical resistivity, given by Eqs. (2) and (3).[20]

We thank M. E. Fisher, B. I. Halperin, C. Herring, and H. K. Schürmann for helpful discussions.

*Work supported by the U. S. Office of Naval Research under Contracts No. N00014-67-A-0398-0010 and No. N00014-67-A-0398-0009.

[1]R. D. Parks, in *Magnetism and Magnetic Materials*, AIP Conference Proceedings No. 5, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1972), p. 630.

[2]M. E. Fisher and J. S. Langer, Phys. Rev. Lett. 20, 665 (1968); P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).

[3]N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, (Oxford Univ. Press, Oxford, England, 1936).

[4]J. M. Ziman, *Electrons and Phonons* (Oxford Univ. Press, Oxford, England, 1967), Chap. IX; J. Jones [in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1956), Vol. 19, Part I, p. 227] has predicted a slightly different Fermi energy dependence for τ_n. If Jones's result is used here, the present calculations are qualitatively unchanged.

[5]A. B. Bhatia and D. E. Thornton, Phys. Rev. B 2, 3004 (1970).

[6]V. M. Nabutovskii and A. Z. Patashinskii, Fiz. Tverd. Tela 10, 3121 (1968) [Sov. Phys. Solid State 10, 2462 (1969)]. The authors suggest that Eq. (3) for a ferromagnet (or antiferromagnet) should be generalized to include density fluctuations (driven by the spin-spin fluctuations).

[7]One case where the contribution to the critical resistivity from the expansion coefficient anomaly is significant is c-axis Gd. See F. C. Zumsteg, F. J. Cadieu, S. Marčelja, and R. D. Parks, Phys. Rev. Lett. 15, 1204 (1970).

[8]J. Dorfman, R. Jaanus, and I. Kikoin, Z. Phys. 54, 277 (1929); K. E. Grew, Phys. Rev. 41, 356 (1932). This experiment was recently repeated and the same interpretation made of the results [S. H. Tang, P. P. Craig, and T. A. Kitchens, Phys. Rev. Lett. 27, 593 (1971)].

[9]See, for example, A. W. Foster, Proc. Leeds Phil. Soc. 2, 401 (1933).

[10]W. Webb, Phys. Rev. 55, 297 (1939).

[11]D. F. Simons and M. B. Salamon, Phys. Rev. Lett. 26, 750 (1971).

[12]The resistivity was computed by numerical integration using the values of $(d\rho/dT)/\rho_{25°C}$ (measured on a sample with the same T_c) of Ref. 11 and using the data of Ref. 10 to obtain $\rho(T_c) = 14.31\ \mu\Omega$ cm and $\rho_{25°C} = 4.51\ \mu\Omega$ cm.

[13]Summaries of results are given in M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), and in J. E. Ashman, Ph.D. thesis, Univ. of Illinois, 1970 (unpublished).

[14]*Smithsonian Physical Tables,* edited by W. E. Forsythe (Smithsonian Institute, Washington, D. C., 1959); and *Reference Tables for Thermocouples,* edited by H. Shenker *et al.*, U. S. National Bureau of Standards, Circular No. 561(U. S. GPO, Washington, D. C., 1955).

[15]*Landolt-Börnstein: Zahlenwerte und Functionen,* edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1959), Vol. II, Part 6.

[16]P. D. Mercia and L. W. Schad, Nat. Bur. Stand. (U. S.), Bull. 14, 571 (1917).

[17]C. Herring, in *Magnetism,* edited by G. Rado and H. Suhl (Academic, New York, 1966), Vol. IV, p. 129; E. C. Stoner, Proc. Leeds Phil. Soc. 2, 149 (1930).

[18]It is possible that the similar disparity observed between dQ/dT and C_p in Ni is not an "experimental artifact" as was suggested by Tang, Craig, and Kitchens (Ref. 8).

[19]This noise reflects the smallness of the thermopower anomaly in β-brass, which, within the framework of the present model, is traceable to the smallness of the resistivity anomaly.

[20]It would seem fair to point out that neutron-scattering experiments have been unable to resolve correlation functions in the immediate vicinity of T_c to better precision than that obtained in the present experiment or from the measurement of only the resistivity anomaly [see, e.g., J. Als-Nielsen, Phys. Rev. 185, 664 (1969)].

Boson Echoes: A New Tool to Study Phonon Interactions

J. Joffrin and A. Levelut
Laboratoire d'Ultrasons, Université Paris VI, 75230 Paris Cedex 05, France*
(Received 5 September 1972)

The phenomenon of boson echoes, which presents some similarities with the spin-echo phenomenon, is explained in terms of phonons. In particular, the nature of the two relaxation times T_1 and T_2 is explored, and they are ascribed to anharmonic and impurity scattering processes, respectively.

In a recent paper[1] we have reported on preliminary experiments on boson echoes, a phenomenon presenting some analogy with spin echoes: A crystal, placed in a cavity, receives two short pulses of hyperfrequency electric field at times 0 and τ; at time 2τ, it reradiates a signal (an echo) at the same frequency. Actually, the effect is strongly different from spin echoes in the following respects: (a) The echo intensity is not a periodic function of the power or length of the pulses; (b) it occurs at any frequency without adjusting a biasing field; (c) its width Δt is determined by the widths of the exciting pulses; and (d) only crystals without a center of symmetry are able to produce this effect. These echoes have been explained as boson echoes.[1]

In this Letter we report on further experiments with two cavities and with two or three pulses (Fig. 1) which enable us to attribute the echoes to the crystal phonon modes and to obtain some insight on their relaxation times. In particular, we may distinguish between the coherence relaxation time T_2 and the relaxation time T_1 of phonon

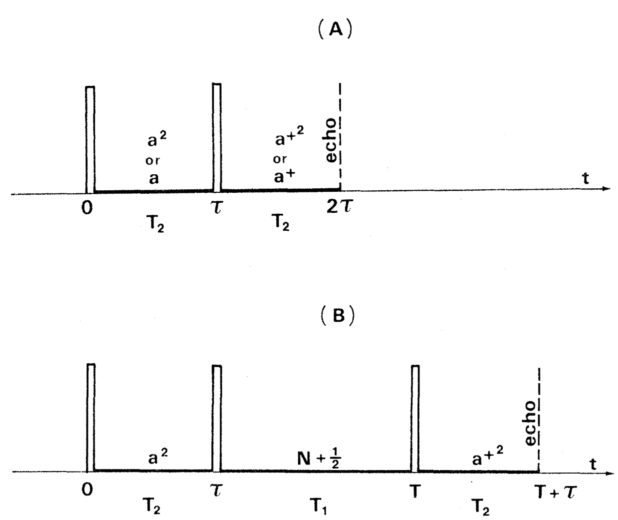

FIG. 1. Schematic of an echo experiment. (a) Two-pulse sequence; (b) three-pulse sequence. Only echoes at times 2τ and $T+\tau$ are represented, with the relaxation times corresponding to each period. The operators a and $a^\dagger$ correspond to dipolar echoes; a^2 and $a^{\dagger 2}$ to quadrupolar echoes.