PHYSICAL REVIEW B VOLUME 39, NUMBER 10 1 APRIL 1989

Phonon echoes in powders of high-T_c superconducting $YBa_2Cu_3O_{7-\delta}$

H. Nishihara
Institute for Solid State Physics, University of Tokyo, Roppongi 7, Tokyo 106, Japan

K. Hayashi
Laboratory for Solid State Chemistry, Okayama University of Science, Ridaicho 1, Okayama 700, Japan

Y. Okuda
Department of Applied Physics, Tokyo Institute of Technology, Ohokayama, Tokyo 152, Japan

K. Kajimura
Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan
(Received 11 August 1988; revised manuscript received 9 January 1989)

Strong rf phonon echoes have been observed in the superconducting state of powders of high-T_c $YBa_2Cu_3O_{7-\delta}$. We suggest that the coupling mechanism between rf fields and acoustic modes is different from that in the usual phonon echoes, judging from the sudden disappearance of the echoes at $T_c = 90$ K and from the angular dependence of the echo intensity. The temperature dependence of T_2^{-1} is tentatively ascribed to the ultrasonic attenuation due to electrons, and the energy gap parameter $2\Delta/k_BT_c$ is estimated to be 3–7.

The observation of induced transient radiation from a type-II superconductor in the form of two-pulse echoes, which are not the usual nuclear magnetic resonance (NMR) spin echoes, was first reported in powdered samples of V-Ti and Nb-Zr alloys.[1–3] The phonon echoes, which are due to acoustic oscillations of loosely packed powders and are also called radio-frequency (rf) powder echoes or dynamic polarization echoes, were observed in various kinds of powders, including insulating ferrite powders, piezoelectric powders, and normal metallic powders, and have been extensively studied.[4–7] In particular, phonon echoes in normal and superconducting metal powders were found to be created by the anharmonicity of mechanical oscillators excited by rf fields in static magnetic fields.[5] The echo-decay time T_2 of the phonon echoes was assumed to be determined by the energy loss of an individual oscillator through mechanisms of internal energy losses such as scattering with thermal phonons and conduction electrons, interaction with crystalline imperfections, and mode conversion at the particle surfaces, and of external energy loss such as energy transfer to the surrounding gaseous medium from the surface.[5] We report here the first observation of similar echoes in powders of the high-T_c superconducting oxide $YBa_2Cu_3O_{7-\delta}$. The echo is observed only in the superconducting state and has a striking temperature dependence of T_2^{-1} below T_c.

Strong phonon echoes have been observed for powders of high-T_c superconducting $YBa_2Cu_3O_{7-\delta}$ sealed in quartz ampoules with helium gas for heat exchange with use of a conventional phase-coherent NMR apparatus. Tests were also made on powders of $H_xYBa_2Cu_3O_{7-\delta}$ treated with hydrogen gas at 40 atm at 50 °C or 100 °C for 60 min, since hydrogen gas is expected to change the superconducting state of the surface of each small particle; in these tests, however, essentially similar echoes were observed. In contrast, no echoes were observed in powders of nonsuperconducting tetragonal $H_xYBa_2Cu_3O_{7-\delta}$ $(x \geqq 0)$. Properties of the observed echoes are as follows: (i) The amplitude is not strongly frequency dependent. (ii) No echoes were observed in weak applied fields of less than 3 kOe, but the amplitude of the echoes increased with increasing applied field strength with hysteresis in earlier sweeps. (iii) The rf phase of the secondary echo is the same as that of the main echo. (iv) The echoes are of maximum strength when the rf pulses are approximately equal, and their amplitude is much stronger than that expected from an NMR signal. (v) A weak stimulated echo is observed following a third rf pulse. (vi) All the echoes disappear when powders are fixed by solidification with liquid nitrogen. (vii) As the pulse interval (τ) is increased, the echo amplitude decays monotonously (exponentially with a time constant T_2). (viii) T_2 becomes longer as the frequency is decreased although τ must be increased because of the longer blocking time of the receiving system.

The properties listed above are quite similar to those of the phonon echoes reported.[1–7] However, the remarkable features in the present case are the temperature dependence of the echo intensity (Fig. 1) and that of the echo-decay rate T_2^{-1} (Fig. 2). A further interesting feature is the angular dependence of the echo intensity shown in Fig. 3, where the echo intensity as a function of the angle between rf and static magnetic fields is shown, together with the theoretical predictions for the excitations of longitudinal (L) and transverse (T) acoustic waves.[5] Echo intensity decreases rapidly as the temperature approaches the superconducting critical temperature T_c of 90 K. The temperature dependence of the echo intensity at a constant pulse interval τ is mostly due to the shortening of T_2 or the increase of the echo-decay rate T_2^{-1} as the temperature approaches T_c, as is seen in Fig. 2. However, the echo disappears abruptly at T_c even in cases where T_2 is

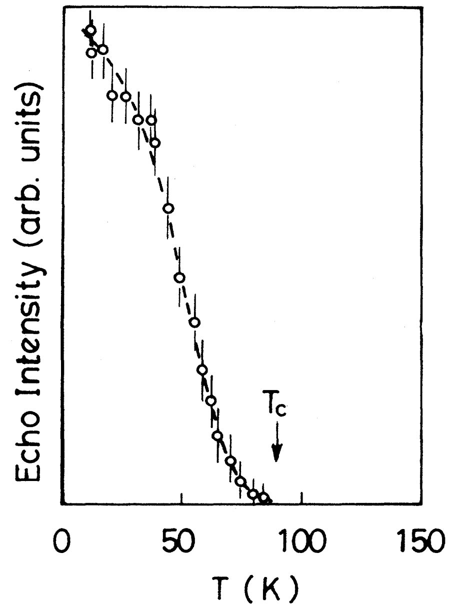

FIG. 1. An example of the temperature dependence of the intensity of a phonon echo with τ of 10 μsec at a frequency of 28 MHz and an applied field of 14 kOe for powders of high-T_c superconducting $YBa_2Cu_3O_{7-\delta}$. The broken line is a guide for the eye.

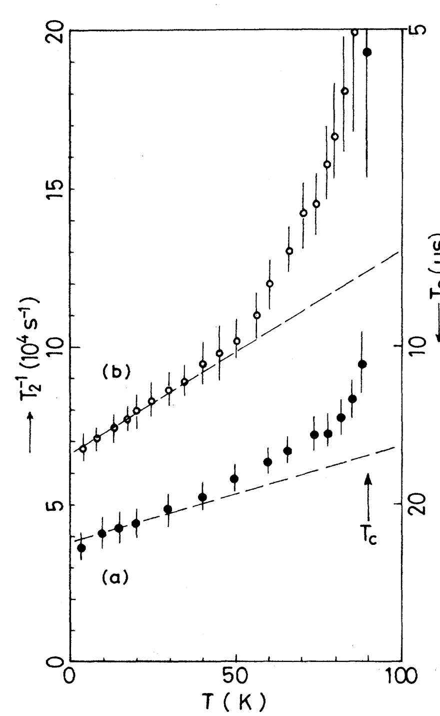

FIG. 2. Typical examples of the temperature dependence of the echo-decay rate T_2^{-1} of phonon echoes for powders of (a) $YBa_2Cu_3O_{7-\delta}$ at a frequency of 15 MHz and an applied field of 18 kOe, and (b) $YBa_2Cu_3O_{7-\delta}$ treated with hydrogen gas of 50 atm at 50 °C for 60 min at 28 MHz and 18 kOe. Assumed background contributions are shown by broken lines (see text).

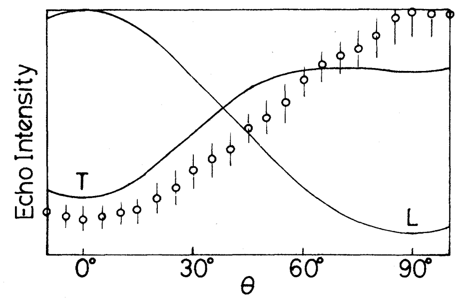

FIG. 3. A typical example of the angular dependence of the echo intensity of rf phonon echoes at 4.2 K and 28 MHz as a function of the angle θ between rf and static fields for powders of $YBa_2Cu_3O_{7-\delta}$ treated with hydrogen of 50 atm at 50 °C for 60 min. Theoretical curves for excitations of longitudinal (L) and transverse (T) acoustic modes (Ref. 5) are shown.

sufficiently long at the temperature 1° below T_c for low frequencies, and the present echoes seem to be inherent to the superconducting state of type-II superconductors. This is also found to be true for the case of the recently discovered high-T_c Tl-Ba-Ca-Cu-O system.[8] In order to explain the present experimental results qualitatively, we propose a new tentative model of signal enhancement in phonon echoes as follows: Echoes are formed by the anharmonic acoustic oscillations of powders as in usual phonon echoes since properties (i)-(viii) are quite similar to those of usual phonon echoes. However, the coupling mechanism between the rf field and the acoustic oscillations can be different, as we see from the abrupt disappearance of the echoes at T_c and the angular dependence of the echo intensity, which is not explained by the excitation of either longitudinal or transverse acoustic waves. The lower and upper critical fields in $YBa_2Cu_3O_{7-\delta}$ have large anisotropies which result in a large anisotropy of the diamagnetic magnetization in the mixed superconducting state.[9] By making good use of this property, the c axes of small particles in powder are easily oriented perpendicularly to the direction of the applied field.[10] rf fields induce acoustic oscillations of each particle by this property. Also, the acoustic echo oscillations created can be detected by the oscillations of diamagnetic magnetizations which induce echo voltages across the rf coil directly. This mechanism of the signal enhancement in the observation of phonon echoes is effective only in the superconducting state of strongly anisotropic superconductors. A similar mechanism of the enhancement will arise if the pinning of the fluxoids to each particle is sufficiently strong. The simple angular dependence in Fig. 3, which is similar to the usual case of NMR, seems to be due to the fact that the excitation of the acoustic oscillations and the receiving of the echo voltages are more effective when the coil axis is perpendicular to the direction of the external field.

A rather gradual temperature dependence of T_2^{-1} was observed in usual phonon echoes for metallic powders; for example, T_2^{-1} is roughly expressed as $1+0.004$ T (10^4 sec^{-1}) for Nb powders in the temperature range 4–230 K at 19 MHz,[5] but the origin of the decay rate among mechanisms listed above is not clearly identified. Only one example is reported for Ni powders in which the field dependence of T_2^{-1} agrees with the losses measured directly by ultrasonic absorption.[11] Since the observed temperature dependence of T_2^{-1} in Fig. 2 looks like the curve of the ultrasonic attenuation coefficient α as a function of temperature in the superconducting state,[12] we consider the possibility that the decay rate of the present case is governed by the intrinsic losses. The echoes decay with decay rate T_2^{-1} associated with the attenuation of the amplitude of acoustic oscillations. The acoustic oscillations are phonons with small k's and small energies and are attenuated by the scattering of electrons via electron-phonon interactions. Therefore, we can assume that the echo-decay rate T_2^{-1} is directly proportional to the acoustic attenuation coefficient α. In the superconducting state,

$$T_2^{-1} = A\alpha_s + (T_2^{-1})_{\text{bgr}}, \quad (1)$$

where A is a constant and $(T_2^{-1})_{\text{bgr}}$ is a background contribution which is due to extrinsic mechanisms. We check whether or not the temperature dependence of T_2^{-1} could be understood by the Bardeen-Cooper-Schrieffer (BCS) theory. As the attenuation coefficient becomes negligible at temperature lower than $T_c/4$ in the BCS theory, we assume the existence of temperature-dependent background contributions in Fig. 2. We roughly estimate the background contribution $(T_2^{-1})_{\text{bgr}}$ by assuming a form of $aT+b$ and by fitting the experimental data $(T_2^{-1})_{\text{expt}}$ at $T<T_c/4$ to the form, with the results $(T_2^{-1})_{bgr}=3.8+0.0031T$ and $6.6+0.0064T$ (10^4 sec^{-1}) for the examples in Figs. 2(a) and 2(b), respectively. It should be noted that the background contributions are comparable with the decay rate in Nb powder in the normal state. The reduced rates $(T_2^{-1})_r = (T_2^{-1})_{\text{expt}} - (T_2^{-1})_{\text{bgr}}$ are plotted in Fig. 4 as a function of $1000/T$, and the energy-gap parameter $2\Delta/k_BT_c$ is estimated to be 3–7 which is consistent with the BCS value of 3.5. Thus the observed temperature dependence of T_2^{-1} of phonon echoes can be understood qualitatively by the BCS theory, although it is compared only in the superconducting state. The data of T_2^{-1} of $(3\text{–}20)\times10^4$ sec^{-1} amount to α of 0.5–3.5 dB/cm if a value of the sound velocity v of 5×10^5 cm/sec (Ref. 13) and a relation

$$\alpha = (vT_2)^{-1} 20 \log_{10} e \quad (2)$$

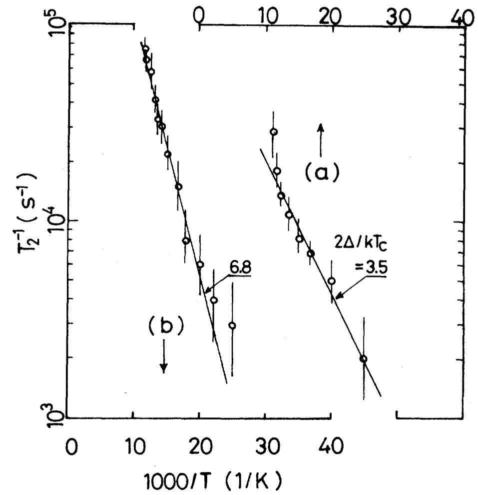

FIG. 4. Estimated extrinsic background contribution to the echo-decay rates are subtracted from the experimental data in Fig. 2 and the resultant rates $(T_2^{-1})_r = (T_2^{-1})_{\text{expt}} - (T_2^{-1})_{\text{bgr}}$ are plotted as a function of $1000/T$. The estimated values of energy gap parameters $2\Delta/k_BT_c$ are also given (see text).

are used. The values are comparable with reported values of α of 0.1–1 dB/cm at similar frequencies.[14]

The successful observation of the effect of ultrasonic attenuation in the phonon echoes in powders seems to be due to rather strong electron-phonon interaction which gives a dominant contribution to the echo-decay rate exceeding extrinsic background contributions. Since it is very difficult to prepare large single crystals of high-T_c oxides with high quality, the present method will become a good method to investigate the ultrasonic attenuation in high-T_c superconducting oxides.

We thank H. Yasuoka, N. Nishida, T. Ohtani, T. Shimizu, T. Imai, and Y. Iye for stimulating conversations.

[1] I. B. Goldberg, E. Ehrenfreund, and M. Weger, Phys. Rev. Lett. **20**, 539 (1968).
[2] H. Alloul and C. Froidevaux, Phys. Rev. Lett. **20**, 1235 (1988), and references therein.
[3] R. J. Snodgrass, Phys. Rev. Lett. **24**, 864 (1970).
[4] M. Rubinstein and G. H. Strauss, Phys. Lett. **14**, 277 (1965).
[5] F. Tsuruoka and K. Kajimura, Phys. Rev. B **22**, 5092 (1980).
[6] K. Fossheim, K. Kajimura, T. G. Kazyaka, R. L. Melcher, and N. S. Shiren, Phys. Rev. B **17**, 964 (1978).
[7] See, for review, *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1982), Vol. 16, Chaps. 4–6; see also Refs. 5 and 6.
[8] H. Nishihara *et al.* (unpublished).
[9] See, e.g., Y. Iye, T. Tamegai, H. Takeya, and H. Takei, Jpn. J. Appl. Phys. **26**, L1057 (1987).
[10] See, e.g., T. Shimizu, H. Yasuoka, T. Imai, T. Tsuda, T. Takabatake, Y. Nakazawa, and M. Ishikawa, J. Phys. Soc. Jpn. **57**, 2494 (1988), and references therein.
[11] S. Cupca and C. W. Searle, J. Appl. Phys. **45**, 5460 (1974), and references therein.
[12] See, e.g., J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964), Sec. 3-2.
[13] See, e.g., M. Suzuki, Y. Okuda, I. Iwasa, A. J. Ikushima, T. Takabatake, Y. Nakazawa, and M. Ishikawa, Jpn. J. Appl. Phys. **27**, Suppl. 27-1, 50 (1988).
[14] H. Yusheng, L. Sihan, Z. Baiwen, X. Jiong, C. Wanqui, L. Yue, Z. Jian, L. Caidong, L. Jianzhong, L. Chuanyi, and Y. Daole, J. Phys. C **21**, L783 (1988).