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Magnetodielectric and magnetoelastic coupling in Co$_4$Nb$_2$O$_9$ below Néel temperature

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The dielectric constant of Co$_4$Nb$_2$O$_9$ shows an obvious upturn below Néel temperature ($T_N$), and the magnetic field enhances this anomaly. Thus the magnetodielectric effect exists in the entire temperature region below $T_N$, not only near $T_N$ as reported previously. At the same time, the strain exhibits a drop below $T_N$, and the magnetic field suppresses this anomaly, demonstrating magnetoelastic coupling in Co$_4$Nb$_2$O$_9$.

The origin of dielectric anomaly and magnetodielectric effect below $T_N$ may be related to the phonon mode shifts induced by magnetoelastic coupling.

Co$_4$Nb$_2$O$_9$ is a collinear antiferromagnet with a spin-flop transition at a critical field of about 12 kOe, and a dielectric peak around Néel temperature ($T_N$) under the magnetic field larger than this critical field is found by Kolodiazhnyi et al.\textsuperscript{1} Subsequently, magnetic field induced electric polarization and electric field control of magnetism is observed below $T_N$ by Fang et al.\textsuperscript{2} More recently, Khanh et al. investigated magnetic structure and magnetoelastic response in single crystal sample, and the results suggest the in-plane antiferromagnetic order and the formation of a ferrotoroidic order in Co$_4$Nb$_2$O$_9$.\textsuperscript{3} However, none of them get much attention to the dielectric property below $T_N$. In this paper, we found that the dielectric constant shows an upturn below $T_N$, and the magnetic field of 5 T enhances this anomaly. Thus the magnetodielectric coupling exists in the entire temperature range below $T_N$. Furthermore, we also found that the strain shows a drop below $T_N$, and this anomaly is strongly suppressed by the magnetic field of 5 T. This phenomenon indicates the magnetoelastic coupling below $T_N$. The origin of the dielectric anomaly and the magnetodielectric effect below $T_N$ may be related to the phonon mode shifts induced by magnetoelastic coupling.

Co$_4$Nb$_2$O$_9$ polycrystalline sample was prepared by solid state reaction method. The stoichiometric mixtures of Co$_3$O$_4$ (99.9% metals basis, Aladdin) and Nb$_2$O$_5$ (99.9%, Aladdin) were ground and sintered at 1173 K for 10 hours. The resulting powders were pressed into pellets and then sintered at 1373 K for 6 hours. The structure of as-prepared sample was checked by X-ray diffraction (XRD) at room temperature. The magnetic property was measured by a superconducting quantum interference device (SQUID, Quantum Design). The dielectric property was measured by a LCR meter (TH2829C, Changzhou Tonghui Electronic) connected to physical properties measurement system (PPMS, Quantum Design). The strain, i.e., the normalized change in sample length $L(T)/L(280K)-1$, was measured using a strain gauge (BA120-05AA-150(11), Zhonghang Electronic Measuring Instruments).

Figure 1 displays the XRD pattern of the sample. All the observed peaks can be indexed with $\alpha$-Al$_2$O$_3$-type trigonal structure, no impurity phase was detected. Co$^{2+}$ and Nb$^{5+}$ ions are distributed on the Al sites with a ratio of 2:1, and Co$^{2+}$ ions occupy two non-equivalent sites.

Temperature dependence of magnetization under the external magnetic field of 100 Oe shown in Figure 2 indicates $T_N \approx 27$ K. Linear fit of temperature dependence of inverse magnetization yields a Weiss temperature of about -76.7 K.

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Temperature dependence of dielectric constant ($\varepsilon'$) at 30 kHz under the magnetic field of 0 T and 5 T is displayed in Figure 3(a). For zero magnetic field, $\varepsilon'$ is nearly temperature independent in the high temperature region, and the onset of a strong upturn of $\varepsilon'$ with cooling is clearly observed near $T_N$. Then $\varepsilon'$ gradually tends to be constant with cooling to the lowest temperature. The magnetic field has no effect on $\varepsilon'$ in the high temperature region, but induce a sharp peak around $T_N$ in the $\varepsilon'$-$T$ curve as reported previously.\(^1\) The magnetic field also shifts up the plateaus of $\varepsilon'$ in the low temperature region under zero magnetic field.

The temperature dependence of magnetocapacitance (defined as $MC = \varepsilon'(H)/\varepsilon'(0T) - 1$) is shown in Figure 3(b). It has the similar shape as the $\varepsilon'$-$T$ curve under the magnetic field of 5 T. Although it is not so big as the MC around $T_N$, the MC in the low temperature region is also quite considerable, and should not be neglected. While it was reported that there was no sign of MC saturation at $T_N$ under magnetic fields as high as 9 T,\(^1\) the MC at the temperature obviously lower than $T_N$ (e.g., 20 K) has already become saturated under the magnetic field of about 4 T (see the inset of Figure 3(b)).

FIG. 1. XRD pattern at room temperature. The short red sticks denote the positions of the diffraction peaks.

FIG. 2. Temperature dependence of magnetization (left scale, red solid square) and inverse magnetization (right scale, blue open circle) under 100 Oe. The black straight line is linear fit of inverse magnetization.
is interesting to see that the shape of MC~H curve exhibited in the inset of Figure 3(b) is quite like the shape of M~H curve for ferromagnets, whereas Co$_4$Nb$_2$O$_9$ is an antiferromagnet.

It was reported in Ref. 2 that the magnetic field induces the spontaneous electric polarization in Co$_4$Nb$_2$O$_9$ below $T_N$, and this polarization can be switched by reversing the cooling electric field, indicating the magnetic field induced ferroelectricity. This magnetoelectric nature explains the dielectric peak at $T_N$, but may not explain dielectric anomaly below $T_N$ and its magnetic field dependence. Many magnetoelectric compounds, such as Cr$_2$WO$_6$, MnTiO$_3$, Cr$_2$O$_3$, do not show dielectric anomaly below magnetic ordering temperature. Magnetodielectric effect may be correlated with magnetoelastic coupling, because they can coexist in many novel complex materials, such as CoCr$_2$S$_4$, TbFe$_2$(BO$_3$)$_4$, FeVO$_4$. Magnetoelastic coupling may also exist in the magnetodielectric compound Co$_4$Nb$_2$O$_9$, so the temperature dependence of strain under the magnetic field of 0 T and 5 T was measured. The result is displayed in Figure 4. The temperature dependent strain between $T_N$ and 80 K can be well described using a fit according to the behavior of a normal anharmonic solid: $L(T) = (1 + A/[\exp(\theta/T) - 1])L_0$, where $L_0$ is the sample length extrapolated to 0 K, $\theta$ is an averaged Debye temperature. Under zero magnetic field, the strain shows a significant drop below $T_N$ compared with the extrapolated curve for a normal anharmonic solid. The magnetic field of 5 T strongly suppresses this drop, but it still exists. The magnetostriction, defined as $L(H)/L(0T) - 1$, increases monotonously with decreasing temperature below $T_N$, as shown in the inset of Figure 4. This magnetostrictive effect and the strain anomaly below $T_N$ indicate the magnetoelastic coupling in Co$_4$Nb$_2$O$_9$.
The observed dielectric anomaly and magnetodielectric effect below $T_N$ might be only associated with the abnormal change of the sample length and magnetostriction below $T_N$ because the dielectric constant ($\varepsilon'$) is calculated from the surface area ($S$) and thickness ($d$) of the sample which were only measured at room temperature and the capacitance ($C_p$) of the sample which was measured in the entire temperature region through the formula: $C_p = \varepsilon_0 \varepsilon' S/d$, where $\varepsilon_0$ is the permittivity of the free space. However, the magnetodielectric effect and the relative change of $\varepsilon'$ below $T_N$ have the magnitude order of about $10^{-3}$, while magnetostriction and the relative change of the sample length below $T_N$ only has the magnitude order of about $10^{-5}$. Therefore, the observed dielectric anomaly and magnetodielectric effect are the intrinsic properties of the sample.

While it is suggested that the magnetodielectric effect around $T_N$ is unlikely to be caused by spin-phonon coupling in view of pronounced low frequency dielectric dispersion, the magnetodielectric effect at the temperatures obviously lower than $T_N$ may be related to spin-phonon coupling because $\varepsilon'$ is nearly frequency independent in this temperature region (not shown). Spin-phonon coupling has been described by many authors. These authors have shown that the frequency shift of a given phonon mode is determined by spin-correlation function: $\omega = \omega_0 + \lambda \langle S_i \cdot S_j \rangle$. Here, $\omega$ is the renormalized phonon frequency, $\omega_0$ is eigenfrequency in the absence of spin-phonon coupling, $\lambda$ is spin-phonon coupling constant. The magnetoelastic coupling in Co$_4$Nb$_2$O$_9$ would stretches or elongates the bonds, and modulate the magnetic exchange interaction. As a result, the spin-correlation function $\langle S_i \cdot S_j \rangle$ would be changed, so does the phonon mode frequencies.

Generally speaking, the static dielectric constant ($\varepsilon_s$) is associated with optical-phonon mode frequencies and optical dielectric constant ($\varepsilon_{\infty}$) via the Lyddane-Sachs-Teller relationship:

$$\varepsilon_s = \varepsilon_{\infty} \prod_i \frac{\omega_{LO,i}}{\omega_{TO,i}}$$

where $\omega_{LO,i}$ and $\omega_{TO,i}$ are the long-wavelength longitudinal and transverse optical-phonon mode frequencies, respectively. This equation has been used to explain the dielectric anomaly of many compounds (e. g., MnO, MnF$_2$) below their magnetic ordering temperatures. The frequency shift of the optical-phonon modes in Co$_4$Nb$_2$O$_9$ induced by magnetoelastic coupling will cause dielectric anomaly and magnetodielectric effect below $T_N$, as what the experimental result is.

In summary, we have studied dielectric constant and strain of Co$_4$Nb$_2$O$_9$ and found that the dielectric constant shows an upturn below $T_N$, and the magnetic field enhances this anomaly. Thus considerable magnetodielectric effect also exists far below $T_N$. Furthermore, we also found that the strain shows a drop below $T_N$, and this anomaly is strongly suppressed by the magnetic field,
indicating the magnetoelastic coupling below $T_N$. The origin of dielectric anomaly below $T_N$ and magnetic effect on it may be related to the phonon mode shifts induced by magnetoelastic coupling.

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1. T. Kolodiazhnyi, H. Sakurai, and N. Vittayakorn, Appl. Phys. Lett. 99, 132906 (2011).
2. Y. Fang, Y. Q. Song, W. P. Zhou, R. Zhao, R. J. Tang, H. Yang, L. Y. Lv, S. G. Yang, D. H. Wang, and Y. W. Du, Sci. Rep. 4, 3860 (2014).
3. N. D. Khanh, N. Abe, H. Sagayama, A. Nakao, T. Hanashima, R. Kiyanagi, Y. Tokunaga, and T. Arima, Phys. Rev. B 93, 075117 (2016).
4. Y. Fang, L. Y. Wang, Y. Q. Song, T. Tang, D. H. Wang, and Y. W. Du, Appl. Phys. Lett. 104, 132908 (2014).
5. N. Mufti, G. R. Blake, M. Mostovoy, S. Riyadi, A. A. Nugroho, and T. T. M. Palstra, Phys. Rev. B 83, 104416 (2011).
6. A. Iyama and T. Kimura, Phys. Rev. B 87, 180408 (2013).
7. K. Dey, A. Karmakar, A. Indra, S. Majumdar, U. Rütt, O. Gutowski, M. v. Zimmermann, and S. Giri, Phys. Rev. B 92, 024401 (2015).
8. U. Adem, L. Wang, D. Fausti, W. Schottenhamel, P. H. M. van Loosdrecht, A. Vasiliev, L. N. Bezmaternykh, B. Büchner, C. Hess, and R. Klingeler, Phys. Rev. B 82, 064406 (2010).
9. B. Kundys, C. Martin, and C. Simon, Phys. Rev. B 80, 172103 (2009).
10. W. Baltensperger, J. Appl. Phys. 41, 1052 (1970).
11. P. Brüesch and F. D’Ambrogio, Phys. Status Solidi B 50, 513 (1972).
12. D. J. Lockwood and M. G. Cottam, J. Appl. Phys. 64, 5876 (1988).
13. J. M. Wesselinowa and A. T. Apostolov, J. Phys.: Condens. Matter 8, 473 (1996).
14. R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).
15. M. S. Seehra and R. E. Helmick, Phys. Rev. B 24, 5098 (1981).
16. M. S. Seehra and R. E. Helmick, J. Appl. Phys. 55, 2330 (1984).