Magnetostriction of the spin–Peierls magnet $CuGeO_3$

G. A. Petrakovskiĭ and A. M. Vorotynov

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

H. Szymczak and L. Gladczuk

Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland
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The temperature dependence of the longitudinal magnetostriction of a $CuGeO_3$ single crystal is measured within the temperature range 4.2–20 K in a magnetic field of 10 T. As the temperature is raised above 4.2 K, the magnetostriction at first increases from vanishingly small values, attains a maximum at a temperature of approximately 12 K, and then abruptly drops as the temperature approaches the spin-Peierls transition. The results are interpreted on the basis of a simple model utilizing the real pattern of magnetic excitations in the spin system. © *1998 American Institute of Physics.* [S1063-7834(98)02309-0]

It has now been reliably established that the low-temperature decay of the magnetic susceptibility of an orthorhombic $CuGeO_3$ crystal is attributable, in large part at least, to the spin-Peierls phase transition of this magnet into a singlet dimerized state. This phenomenon essentially entails the capability of an antiferromagnetic chain of spins $S=1/2$ situated in a three-dimensional lattice to go over to the dimerized state at temperatures below a certain critical value. The transition is accompanied by doubling of the lattice period along the axis of the chain and, from the magnetic standpoint, is characterized by a singlet ground state. The spectrum of magnetic singlet-triplet excitations has a characteristic energy gap, which governs such salient features of the magnetic properties of a spin-Peierls magnet as low-temperature exponential decay of the magnetic susceptibility and the intensity of magnetic resonance, as well as the magnetization jumps at a certain critical value of the magnetic field.

These considerations spotlight the importance of investigating spin-phonon interactions in spin-Peierls systems.[1–4] The investigation of the magnetostriction of $CuGeO_3$ single crystals at various temperatures has shown that its temperature dependence is nonmonotonic and that the magnetostriction has a maximum at a temperature of approximately 10 K. We have proposed a simple model of this behavior of the magnetostriction of a spin-Peierls magnet.[4] Here we describe a more detailed measurement of the temperature dependence of the magnetostriction of a $CuGeO_3$ single crystal and submit a more correct analysis of the model for explaining the results.

1. EXPERIMENTAL RESULTS

The $CuGeO_3$ single crystals used for the measurements were grown by the technology described in Ref. 5. The samples were prepared from blue single crystals. Measurements of the magnetic susceptibility of the crystals have shown that the spin-Peierls transition temperature is $T_{sP}=14.2$ K and that a low-temperature rise of the susceptibility is not observed. The latter result attests to the high quality of the crystals.[6]

The magnetostriction was measured by a tensometric method using low-magnetoresistance strain gauges in the temperature range 4.2–25 K. The results are shown in Figs. 1 and 2. Curves *1* are plotted for cooling and subsequent heating of the sample without any external magnetic field; curves *2* are plotted for cooling and heating of the sample in an external magnetic field $H=10$ T. It follows from the data in the figures that when a magnetic field is applied, the sample increases in size, corresponding to positive longitudinal magnetostriction along the *c* and *b* axes of the crystal.

The magnetostriction-temperature curves *3* have been obtained by subtracting curve *1* from curve *2*. It is evident that the magnetostriction is small at temperatures below 5 K, increases as the temperature is raised, attains a maximum at $T=12-13$ K, and then drops to vanishingly small values at the spin-Peierls transition temperature. We note that a similar behavior of the temperature dependence of the magnetostriction of $CuGeO_3$ has been observed Ammerahl *et al.*[3]

2. DISCUSSION OF THE RESULTS

We have previously[4] proposed a simple model that can be used to explain the unusual behavior of the magnetostriction of a spin-Peierls magnet as a function of the temperature in comparison with conventional magnetic materials. This model is based on a very simple representation of the spin-Peierls state of a two-level singlet-triplet system. At $T=0$ K this kind of system is nonmagnetic, and the spin subsystem of the crystal does not influence the lattice. As the temperature is raised, the triplet states becomes populated, and the magnetic subsystem influences the equilibrium lattice strains by way of magnetostrictive coupling. It is obvious that the temperature dependence of this influence is associated with the population variation of the triplet states of

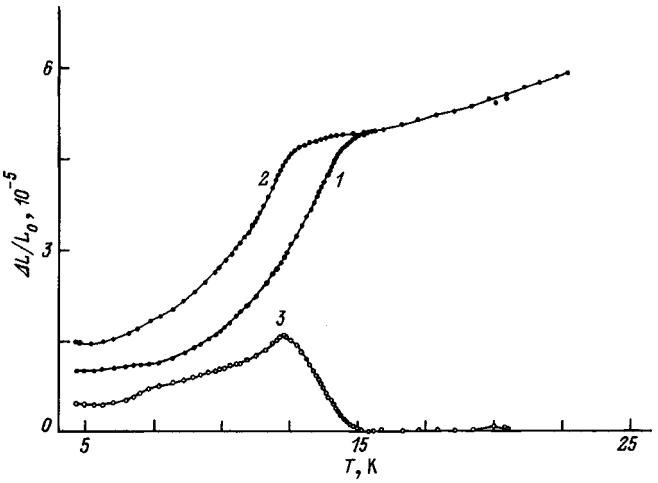

FIG. 1. Temperature dependence of the lattice strain of a $CuGeO_3$ crystal along the *b* axis. *1*) Magnetic field $H=0$; *2*) magnetic field $H=10$ T applied along the *b* axis; *3*) magnetostriction (obtained by subtracting curve *1* from curve *2*).

the system. The application of a magnetic field alters the singlet-triplet energy gap, causing the population of the triplet states and, hence, the ''magnetic'' contribution to the lattice strain to change. At high temperature, where the populations of the triplet and singlet states equalize, the influence of a magnetic field on the equilibrium lattice strains through vanishes by virtue of the decrease in the energy gap.

Neutron-diffraction examinations[7] have shown that magnetic excitations of the spin-Peierls system form a triplet band with maximum dispersion along the *c* axis of the crystal. Consequently, to analyze the spin-Peierls system more correctly, it is necessary to investigate the band of magnetic singlet excitations instead of the triplet excited level. Inasmuch as exchange interaction within the chain of spins of the Cu^{2+} ions of the $CuGeO_3$ crystal is an order of magnitude larger than exchange interactions between chains, we can consider only spin excitations along the *c* axis. The dispersion relation for such excitations can be written in the form[8]

$$w(k)^2=[\Delta^2+(w_M^2-\Delta^2)\sin^2(k)], \tag{1}$$

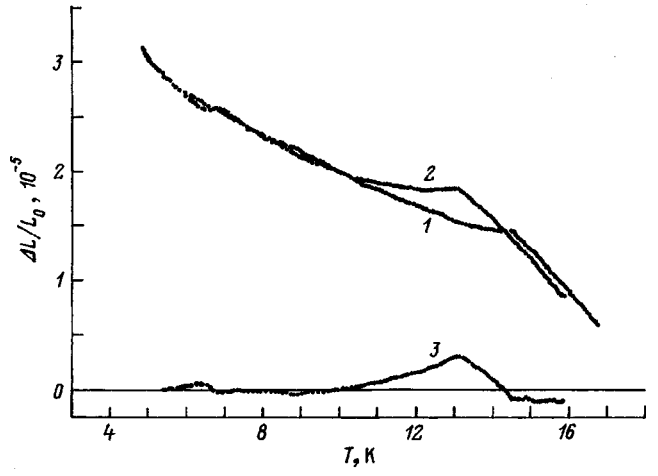

FIG. 2. The same as Fig. 1, but the strain and magnetic field are directed along the *c* axis.

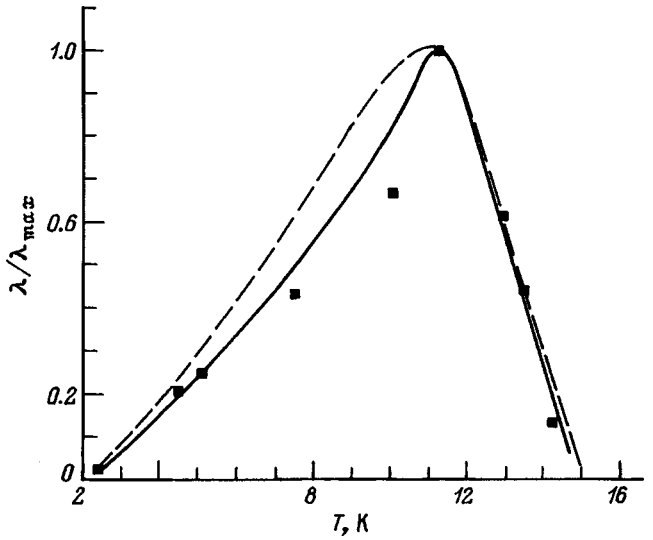

FIG. 3. Calculated and experimental graphs of the temperature dependence of the longitudinal magnetostriction. The dashed curve represents the calculated dependence, and the black squares represent the experimental results with the magnetic field along the *b* axis. The curves are normalized to the maximum values of the magnetostriction.

where Δ is the energy gap in the spectrum of singlet-triplet excitations, and w_M is the maximum value of the energy $w(k)$. The following values of the parameters were determined from the spectrum at low temperatures (1.8 K) in experiments on the inelastic scattering of neutrons by a $CuGeO_3$ crystal: $\Delta=23$ K; $w_M=180.5$ K (Ref. 8). Measurements in strong magnetic fields have shown that the energy gap Δ and the transition temperature T_{sP} of the system to the spin-Peierls state depend on the magnetic field.[9,10] The gap Δ decreases linearly as the magnetic field H increases: $\Delta=23[1-0.077H]$ (Δ in kelvins, and H in teslas). The temperature T_{sP} also decreases as the field increases and is equal to 12.5 K in a field of 10 T. It is also important to bear in mind the strong temperature and pressure dependence of Δ (Refs. 8 and 10).

We analyze the temperature dependence of the magnetostriction of the spin-Peierls magnet on the basis of an investigation of the strain dependence of the internal energy:

$$U=U_{\rm el}+U_{\rm mag}=\frac{1}{2}Eu^2+\frac{2v_0^{-1}}{(2\pi)^3}\int_0^{\pi/2}\frac{w(k)d^3k}{e^{w(k)/T}-1}, \tag{2}$$

where E is Young's modulus, u is the strain of the crystal, and $v_0=abc$. The minimization of the energy (2) with respect to the strain u gives its equilibrium value for a fixed energy gap Δ. The difference in the equilibrium strains for different values of Δ with and without an external magnetic field H determines the temperature and magnetic-field dependence of the magnetostriction. Bearing in mind the experimentally measured temperature and field dependences of Δ, we have used a numerical method to find the temperature dependence of the magnetostriction, which is represented by the dashed curve in Fig. 3. Also shown in this figure is the experimentally measured temperature dependence of the magnetostriction when the magnetic field is directed along the *b* axis. All the results are given in values normalized to

the maximum magnetostriction. In the calculations it has been assumed that the governing magnetostriction mechanism is the strain dependence of Δ. The temperature dependence of w_M is not taken into account. Satisfactory agreement is observed between the calculations and experiment. Qualitative agreement is preserved for a field directed along the c axis of the crystal but, at temperatures below the temperature of the maximum, the experimental temperature dependence of the magnetostriction is sharper.

The qualitative agreement of the magnetostriction-temperature curves calculated on the basis of the proposed model and determined experimentally indicates that the proposed magnetostriction mechanism based on a strong dependence of the energy gap Δ on the lattice strain and on the magnetic field, on the one hand, and based on the Δ dependence of population of the band of triplet states, on the other, is the principal mechanism in the region of the spin-Peierls magnetic state of a $CuGeO_3$ magnet. The root cause of magnetostriction is the strain dependence of the exchange interactions. Anisotropy of the magnetostriction is induced both by the elastic anisotropy of the crystal and by the complex influence of various strains on the exchange interactions. One possible cause of the imperfect correspondence between the calculated and experimentally measured temperature dependences of the magnetostriction is the disregard of the temperature dependence of the spectral bandwidth of magnetic singlet-triplet excitations.

The mechanism underlying the evolution of antiferromagnetic exchange interaction in the chains of Cu^{2+} spins of $CuGeO_3$ is not entirely clear at the present time. For example, Geertsma and Khomskii[11] have proposed an explanation of why the Goodenough–Kanamori rules are violated in terms of the influence of Ge^{4+}–O^{2-} side groups on 90° Cu^{2+}–O^{2-}–Cu^{2+} exchange. On the other hand, it has been shown[12] that marked distortion of the CuO_6 oxygen octahedra under certain conditions can generate an orbital superlattice and, in keeping with the Goodenough-Kanamori rules, produce antiferromagnetic exchange interaction in the chains of copper ions. There is a need for more precise calculations from first principles of exchange interactions to quantitatively account for the results of measurements of exchange and magnetoelastic interactions in $CuGeO_3$.

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