Diffusive energy transport in the S=1 Haldane chain compound AgVP₂S₆

A. V. Sologubenko, S. M. Kazakov, and H. R. Ott

Laboratorium für Festkörperphysik, ETH Hönggerberg, CH-8093 Zürich, Switzerland

T. Asano and Y. Ajiro

Department of Physics, Kyushu University, Fukuoka 812-8581, Japan

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We present the results of measurements of the thermal conductivity κ of the spin S=1 chain compound AgVP₂S₆ in the temperature range between 2 and 300 K and with the heat flow directed either along or perpendicular to the chain direction. The analysis of the anisotropy of the heat transport allowed for the identification of a small but non-negligible magnon contribution κ_m along the chains, superimposed on the dominant phonon contribution κ_{ph} . At temperatures above about 100 K the energy diffusion constant $D_E(T)$, calculated from the $\kappa_m(T)$ data, exhibits similar features as the spin diffusion constant $D_S(T)$, previously measured by NMR. In this regime, the behavior of both transport parameters is consistent with a diffusion process that is caused by interactions inherent to one-dimensional S=1 spin systems.

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I. INTRODUCTION

Anomalous features of transport properties of onedimensional Heisenberg antiferromagnetic (1D HAFM) spin S = 1/2 systems were predicted decades ago. In particular, it was argued that both the spin and thermal conductivity are not expected to be of diffusive character as is typical for classical systems without long-range order,^{1,2} but instead are based on ballistic transport of spin and energy, at least in the case of ideal 1D systems.³⁻⁶ On theoretical grounds it was recently demonstrated that this difference is due to the conservation of spin and energy currents in integrable models which apply for 1D S = 1/2 spin systems.^{7–11} The situation is much less clear with respect to the theory of transport properties of 1D S = 1 systems. Contrary to half-integer spin, 1D HAFM systems with isotropic exchange, for which the spin excitations are S = 1/2 spinons and the corresponding spectrum is gapless,¹² the integer-spin chains exhibit gapped excitation spectra and S=1 magnon excitations.¹³ Numerical calculations for S = 1, 1D HAFM systems relate the gap Δ to the exchange integral J, such that $\Delta = 0.41J$.¹⁴ Early theoretical work predicted that the transport in ideal 1D HAFM S = 1 systems must be diffusive.³ More recent discussions of Sachdev and Damle,^{15,16} considering the spin transport in Heisenberg S=1 chains in terms of the nonlinear σ -model (NL σ M), also concluded with the claim of diffusive spin transport. However, Fujimoto,¹⁷ based on the integrability of NL σ M, suggested that in a perfect 1D S = 1 system, the spin transport is ballistic. The author noted, however, that external perturbations, unavoidable in real S=1 chain compounds and leading to the destruction of integrability, may restore diffusive transport. In this respect, Fujimoto refers to a previous experimental observation of spin diffusion in the S =1 chain compound AgVP₂S₆, by Takigawa *et al.*,¹⁸ and suggests that the spin-phonon interaction might provide this type of perturbation.

Energy transport via spin excitations, which can be probed by measurements of the thermal conductivity, has not yet been investigated in S=1 chain compounds. It seems natural to expect that its features are similar to those of spin transport. In a recent paper by Alvarez and Gros,¹⁹ relations between the spin and thermal conductivities in 1D spin systems, similar to the famous Wiedemann-Franz law for the ratio between the electrical and thermal conductivities in metals, were discussed. In the present work, we report the results of an experimental investigation of the thermal conductivity of $AgVP_2S_6$, a compound which is considered as one of the best physical realizations of an S=1 1D AFM Heisenberg model system. $AgVP_2S_6$ crystallizes with a monoclinic crystal structure of type P2/a.²⁰ Each V^{3+} ion with spin S=1 is located inside a distorted octahedron of sulfur ions. The zigzag chains formed by these vanadium ions run along the *a* axis. Evidence for an energy gap in the spin excitation spectrum was found by measurements of the magnetic susceptibility²¹⁻²⁴ and inelastic neutron-scattering experiments.^{25,26} The magnetic properties of the compound are well described by the isotropic nearest-neighbor Heisenberg Hamiltonian and weak single-ion anisotropy:

$$H = J \sum_{i} \mathbf{S}^{i} \mathbf{S}^{i+1} + D \sum_{i} (S_{z}^{i})^{2}, \qquad (1)$$

with the intrachain exchange constant $J/k_B = 780$ K and $D/J = 5.8 \times 10^{-3}$.²⁷ The interchain interaction $J' \le 10^{-5}J$ is very weak.²⁵ The dynamics of the V³⁺ spins in AgVP₂S₆ was studied by NMR experiments by Takigawa *et al.*¹⁸ The data are compatible with spin diffusion at temperatures exceeding ~ 100 K and above a temperature-dependent frequency of the order of $10^{11}-10^{12}$ s⁻¹. Using these results, the temperature dependence of the spin diffusion constant $D_S(T)$ was established. Below we compare the experimental results for the temperature variation of the spin diffusion constant $D_S(T)$, probed by NMR, and the energy diffusion parameter $D_E(T)$, which is obtained from the results of our thermal-conductivity measurements.

II. SAMPLES AND EXPERIMENT

For the measurements of the thermal conductivity $\kappa(T)$, we grew several single crystals of AgVP₂S₆ by solid-state reaction of stoichiometric amounts of Ag, V, P, and S, as described in Ref. 20. The largest crystals had dimensions of several millimeters along the *a* axis (the spin chain direction), a maximum of 0.5 mm along the *b* axis, and, at most, 0.2 mm along the *c* axis. A single crystalline specimen with dimensions of $2 \times 0.5 \times 0.15$ mm³ (denoted as S1) was used for the thermal-conductivity measurements along the chain direction. Another sample from the same batch served to measure the dc magnetic susceptibility χ .

A standard method for separating the spin-mediated thermal conductivity $\kappa_m(T)$ from other, less anisotropic, contributions to $\kappa(T)$ is based on measurements of this quantity both along and perpendicular to the chain direction. Unfortunately, the dimensions of our crystals only allowed for measurements of $\kappa(T)$ along the chains. For this reason we investigated the heat transport also on grain-aligned specimens. Some of these samples were previously used for measurements of the magnetic susceptibility²¹ and for NMR experiments.^{18,27} All the specimens with typical sizes of 4 $\times 2 \times 0.2$ mm³ were single pieces consisting of many equally oriented flakelike single crystals. On one such piece (denoted as sample J1), the thermal conductivity was measured along the a axis. Another sample, denoted as J2, with the largest spatial extension along the b axis, was cut out from the central part of sample J1. Sample J2 was subsequently used for experiments with the heat flow perpendicular to the chain direction.

The thermal conductivity was measured using a standard uniaxial heat flow method, where the constant heat flux along a rectangular-bar-shaped sample was produced by a heater attached to one end of the sample. The opposite end of the sample was attached to a copper heat sink. The temperature gradient was monitored by a system of 25 μ m diameter Chromel-Au+0.07% Fe thermocouples. We estimate the uncertainty of the absolute value of κ to be of the order of 10%, because of the uncertainty of the sample geometry. The relative error of the measured thermal conductivity, however, is only about 0.5%. The magnetic susceptibility was measured between 4.5 and 240 K, employing a commercial superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

The magnetic susceptibility data are shown in Fig. 1. The measurements were taken in a magnetic field of H = 40 kOe oriented along the *a* axis. The data are in good agreement with results of Mutka *et al.*,²² also shown in Fig. 1. In particular, the nonlinear χ versus 1/T dependence at low temperatures, noticed in Ref. 28 and attributed to the weak coupling between finite-length segments of spin chains, is well reproduced in our data (see the inset of Fig. 1). The $\chi(T)$ data can be fit to the equation²²



FIG. 1. Magnetic susceptibility χ as a function of temperature. Our results are represented by the solid circles. For comparison, previous data reported in Ref. 22 and obtained for a powder and a single-crystalline sample are displayed by the open diamonds and triangles, respectively.

$$\chi(T) = \frac{A}{T^{1/2}} \exp\left(-\frac{\Delta}{k_B T}\right) + \frac{B}{T^{\alpha}} + \chi_0, \qquad (2)$$

where the first term on the right-hand side represents the contribution from the Haldane-gapped S=1 chains, the second term reflects the above-mentioned finite segment interaction contribution, and the last and constant term is due to the diamagnetic orbital susceptibility. The best fit, shown as the solid line in Fig. 1, is achieved with the fit parameters $A=1.77\times10^{-2}$ emu mol⁻¹ K^{1/2}, $\Delta/k_B=244$ K, $B=3.60\times10^{-3}$ emu mol⁻¹ K^{0.55}, $\alpha=0.55$, and $\chi_0=-2.5\times10^{-4}$ emu mol⁻¹. The resulting value for the energy gap Δ/k_B is consistent with estimates of 228 K (Ref. 22) and 250 K (Ref. 21) from the analyses of magnetic susceptibilities, but somewhat lower than the results obtained from NMR (Ref. 27) (320 K) and the neutron-scattering²⁵ (300 K) measurements. The power-law exponent $\alpha=0.55$ is within the range $0.5 < \alpha < 0.8$ established in Ref. 22.

The temperature dependences of the different thermal conductivities are shown in Fig. 2. Each curve exhibits a maximum at temperatures around 10 K and a region with a positive slope $\partial \kappa / \partial T$ at temperatures above about 200 K. The latter feature is presumably due to unaccounted heat losses via radiation, typical in standard steady-state thermal-conductivity experiments probing materials with low values of κ at high temperatures. Our numerical estimates suggest that for our AgVP₂S₆ samples, these effects are negligible only below about 170–200 K and therefore, our data analysis presented below is restricted to temperatures below 170 K.

By rapidly reducing the temperature of the grain-aligned samples (J1 and J2) from values in the region between 170 and 300 K to temperatures between 80 and 170 K with a cooling rate of ≈ 1 K/s, subsequent slow relaxations of κ with time were observed. As illustrated in the inset of Fig. 2, even upon a slow variation of the temperature (as slow as



FIG. 2. Thermal conductivity vs temperature for two samples along the chain direction and one sample in a perpendicular direction. The inset demonstrates the slightly irreversible behavior at high temperatures.

0.01 K/s), a small hysteresis of $\kappa(T)$ was observed at intermediate temperatures above the maximum of $\kappa(T)$. We believe that these effects are not related to intrinsic properties of the material. Since they were not observed when probing the single-crystalline specimen, they are most likely due to the multigrain nature of these samples.

By inspecting the $\kappa(T)$ curves at temperatures below 60 K, we note that they all exhibit the same qualitative features. At higher temperatures, a shoulder-type feature in $\kappa_a(T)$, which is absent in the $\kappa_b(T)$ curve, may be identified. Similar high-temperature features emerging as a shoulder or a second maximum were observed for $\kappa(T)$ if measured along the chain or ladder direction of spin-chain and spin-ladder compounds.^{29–36} An obvious interpretation of this high-temperature feature is to ascribe it to a spin-mediated thermal conductivity κ_m , in addition to the common heat conduction via phonons, which is reflected in a contribution $\kappa_{\rm ph}$ to the total thermal conductivity.

In order to isolate the spin contribution $\kappa_m(T)$, accurate evaluations of other contributions to the total measured $\kappa(T)$ need to be made. Since AgVP₂S₆ is an insulator, no heat conduction by free charge carriers is expected, and only heat transport via lattice excitations needs to be considered. Because of the extremely weak interaction between spins of neighboring chains, no sizable heat transport via the spin system is expected for directions perpendicular to the *a* axis. Hence only phonons contribute to $\kappa_b(T)$, shown in Fig. 2. The shape of the $\kappa_h(T)$ curve, typical for phonon heat transport, results from the competition between different phononscattering mechanisms, most notably phonon scattering by sample or grain boundaries at the lowest temperatures and by phonons, defects and magnons at more elevated temperatures. In contrast to the boundary and defect scatterings which are usually sample dependent, the scattering of phonons by quasiparticles in general is expected to be sample independent because it is related to intrinsic scattering processes.

At temperatures much less than Δ/k_B , the number of spin excitations that participate in the heat transport reflected in $\kappa_a(T)$ is decreasing exponentially with decreasing tempera-



FIG. 3. Magnon thermal conductivity along the *a* axis of AgVP₂S₆, extracted from $\kappa_a(T)$ for the two samples S1 (a) and J1 (b).

ture. Therefore, at $T \ll \Delta/k_B$ the phonon heat transport is expected to also dominate $\kappa_a(T)$. While the different temperature dependences of κ for different samples on the left of the $\kappa(T)$ maxima in Fig. 2 can be accounted for by differences in the boundary scattering conditions, it is remarkable that at temperatures above the maxima, up to about 40 K, the ratio between the κ values for different samples is practically independent of temperature. This implies that the temperature dependences of these $\kappa(T)$ curves are identical and that in this temperature region, the intrinsic processes of phonon scattering dominate. As we have already argued in Ref. 29, the anisotropy of the purely phononic heat transport is not likely to change at high temperatures. This is why we assume that at high temperatures, the phonon thermal conductivity along different directions and for different samples merely differs by a constant factor. With this assumption, we calculated the magnon contribution

$$\kappa_{m,a} = \kappa_a - K \kappa_b \tag{3}$$

with K=2.7 and K=2.3 for samples S1 and J1, respectively. The K values were calculated as the averaged ratio κ_a/κ_b in the temperature interval between about 20 and 35 K. The phonon contributions $K\kappa_b$ for samples S1 and J1 are shown by the broken lines in Fig. 2.

The resulting values of $\kappa_m(T)$ are presented in Fig. 3. The uncertainties caused by the subtraction of two experimentally measured curves, each with a relative error of about 0.5%, are also displayed in Fig. 3. Because of the relatively large uncertainties inherent to the evaluation procedure below about 40 K, it is impossible to draw any conclusions about $\kappa_m(T)$ in that temperature region. Therefore, only data at temperatures above 50 K were considered for the following analysis. In the accessible regime, $\kappa_m(T)$ first increases with increasing temperature but tends to pass through a maximum or to reach saturation at higher temperatures. The maximum absolute values of $\sim 1 \text{ Wm}^{-1} \text{ K}^{-1}$ for the magnon thermal conductivity are one to two orders of magnitude smaller than the corresponding values for κ_m in S = 1/2 two-leg spinladder compounds (La,Sr,Ca)₁₄Cu₂₄O₄₁ (Refs. 30–32) and



FIG. 4. The energy diffusion constant $D_E(T)$, calculated from the thermal conductivity data of sample S1 (open circles), and the spin diffusion constant $D_S(T)$ from Ref. 18 (solid circles) are shown in the left panel. In the right panel, the corresponding data for the S = 1/2 spin chain compound Sr_2CuO_3 are shown.

various S = 1/2 spin-chain materials, $^{29,33,35-37}$ where the enhanced spin-mediated thermal conductivity is thought to be the consequence of a quasiballistic energy transport.

In view of the implicit interpretation that heat may be transported via spin excitations, it seems natural to compare the energy transport with spin transport. The temperature dependence of the spin diffusion constant $D_S(T)$ in AgVP₂S₆ was measured by Takigawa *et al.*¹⁸ Based on our $\kappa_m(T)$ data, we calculated the spin-related energy diffusion constant D_E from $D_E(T) = \kappa_m(T)/[C_s(T)a^2]$, where $C_s(T)$ is the specific heat of the spin system and a = 2.96 Å is the distance between neighboring spins along the chains. The low-temperature specific heat of Heisenberg-type S=1 spin chains was analyzed by Jolicoeur and Golinelli³⁸ employing the quantum nonlinear σ -model. The energy ε versus the wave vector k, measured from the AFM wave vector π/a , is given by the equation

$$\varepsilon(k) = [V^2(ka)^2 + \Delta^2]^{1/2}, \tag{4}$$

and the results of numerical calculations at T=0 are Δ_0 =0.41J and V=2.49J.¹⁴ The energy diffusion constant $D_E(T)$, calculated for the single-crystalline sample S1 as outlined above and using $C_s(T)$ as calculated by Jolicoeur and Golinelli,^{38,39} is shown in the left panel of Fig. 4; the data for the second sample, not shown here, are very similar. The spin diffusion constant $D_{S}(T)$ from Ref. 18 is also displayed in the same figure. The absolute values of the two parameters are similar in magnitude at high temperatures and they exhibit very similarly shaped temperature dependences. This is true although, in comparison with the corresponding feature of $D_{S}(T)$, the maximum value of $D_{F}(T)$ is about two times larger and slightly shifted to lower temperatures. The only other spin-chain compound, for which data on both the spin and the energy transports are available, is the Heisenberg S = 1/2 chain compound Sr_2CuO_3 . In the right panel of Fig. 4, we present both $D_S(T)$ data from Ref. 40 and $D_E(T)$ data calculated from the results of our previous thermal-conductivity measurements on $\mathrm{Sr_2CuO_3}^{29}$ It is again obvious that both quantities vary similarly with temperature and $D_E \sim 2D_S$ in the covered temperature interval. The only other material for which D_E and D_S have been compared up to now is solid ³He in the region 0.05 < T < 0.12 K, where the ratio $D_E/D_S \approx 2.1$ is, again, close to $2.^{41}$ It is remarkable that indeed the difference of factor 2 between D_E and D_S is expected to be a general property of any Bravais lattice with identical spins on each lattice point.⁴² The fair agreement of our results with this expectation thus confirms the reliability of our calculation of the spin-mediated thermal conductivity.

The limited accessible temperature interval for the evaluation of $\kappa_m(T)$ and the increasing uncertainty with decreasing temperatures do not allow a serious analysis of its overall temperature dependence. The classical high-temperature limit of D_E for a spin system is given by³

$$D_{E,\mathrm{ht}} \sim J[S(S+1)]^{1/2}/\hbar.$$
 (5)

For AgVP₂S₆, this high-temperature limit is $D_{E,ht} \sim 10^{14} \text{ s}^{-1}$. The observed values in the temperature range covered in this study are, except at the lowest temperatures, consistently higher than $D_{E,ht}$, but tend to approach this value with increasing temperature. The enhancement is, however, much less pronounced than in S=1/2 chain and ladder compounds. A better way to demonstrate this is by invoking the average mean free path of itinerant spin excitations $\ell_m(T)$, which can be defined as $\ell_m \equiv D_E/v_m$, where $v_m(T)$ is the average group velocity

$$v_m(T) = \frac{1}{\hbar} \left[\int \frac{\partial \varepsilon}{\partial k} f(\varepsilon, T) dk \right] / \left[\int f(\varepsilon, T) dk \right], \quad (6)$$

with $f(\varepsilon,T) = [\exp(\varepsilon/k_BT) - 1]^{-1}$ and the dispersion relation $\varepsilon(k)$ as given by Eq. (4). We calculated $\ell_m(T)$ taking into account the temperature dependence of the energy gap, given by the NL σ M at low temperatures as³⁸

$$\Delta(T) \approx \Delta_0 + (2\pi\Delta_0 k_B T)^{1/2} \exp(-\Delta_0 / k_B T).$$
(7)

The calculated values of $\ell_m(T)$, shown in the inset of Fig. 4, do not exceed 60 Å. In contrast, the mean free paths of spin excitations in many S = 1/2 chains typically reach values of the order of 10^3 Å.^{29,33-35,37}

The data presented above and the subsequent comparison of S=1 and S=1/2 spin chains provoke the obvious question concerning the reasons for the much reduced spinmediated energy transport in the S = 1 system. Two possibilities may be considered. First, extrinsic causes, such as a much stronger scattering of magnons by defects and phonons might significantly reduce κ_m in the compound studied here. Second, intrinsic causes of reduced energy transport, e.g., as a result of the nonintegrability of the Hamiltonian even for the pure S=1 spin system should be considered. We argue that the influence of defects is hardly the major factor leading to low values of D_E , because the data for the two different samples of different quality that were studied in the course of this work provide very similar results for the magnon thermal conductivity (see Fig. 3). That the magnonphonon scattering is the main source for low κ_m values in $AgVP_2S_6$ cannot altogether be ruled out, but at present we cannot offer an obvious reason why this scattering should be much stronger in $AgVP_2S_6$ than in all other spin-chain compounds mentioned above.

The second and the most likely possibility is that the energy diffusion observed in our experiments on AgVP₂S₆ is intrinsic and is governed by dynamic correlations of the S =1 spin system. Unfortunately, to our knowledge, there is no calculation of $D_E(T)$ available in the literature for temperatures much less than J/k_B to compare our data with. However, a semiclassical consideration of S=1 chains by Damle and Sachdev,¹⁶ and applied to $AgVP_2S_6$, results in D_S values which are in fair agreement with the $D_S(T)$ data shown in Fig. 4. Since our values for D_E are compatible with D_S , we take this as a clear indication for the same type of behavior of both parameters. Nevertheless, the reason for the divergence between $D_E(T)$ and $D_S(T)$ at low temperatures, namely, below about 100 K is not understood. In Ref. 18, the drop of $D_{S}(T)$ at temperatures below 100 K was considered to be the result of a crossover from spin diffusion to a region of freely propagating magnons. Our results do not contradict this assumption, however a rigorous analysis of $D_F(T)$ in this temperature regime is impossible, because of the prohibitively large uncertainty in κ_m at these temperatures.

A rigorous approach to transport properties of lowdimensional quantum spin systems, based on the notion of a thermal Drude weight $D_{\rm th}(T)$ in integrable spin systems, analogous to the familiar Drude weight in the theory of metallic conductivity, has recently been developed.^{19,43–49} The spin-related thermal conductivity $\kappa_{\rm spin}$, which here corresponds to a conductivity via either magnons in the S=1 case (κ_m) or spinons in the S=1/2 case (κ_s), is given as

$$\kappa_{\rm spin}(T) = \lim_{\omega \to 0} \kappa_{\rm spin}(\omega) \tag{8}$$

with

$$\kappa_{\rm spin}(\omega) = D_{\rm th}(T)\,\delta(\omega). \tag{9}$$

For an ideal integrable system, $\kappa_{\rm spin}$ diverges if $D_{\rm th}$ is non-zero. If perturbations introduce a finite lifetime τ , the ther-

mal conductivity is also expected to be finite and can be represented as $\kappa_{spin} = D_{th} \tau$. In Ref. 49, where this approach was applied to S=1 HAFM chains, it is noted that this is true only in the case of a large and energy-independent τ or, equivalently, to a long mean free path ℓ . However, impurity scattering, for example, is shown⁴⁹ to invoke energydependent lifetimes, thus leading to a more complicated behavior of κ_m which is not simply given by a product of the thermal Drude weight and the average relaxation time. Since in our case, as reflected in the small values of ℓ_m which approach the interspin distance (see the inset of Fig. 4), the relaxation is quite strong, we do not attempt a direct application of the thermal Drude weight formalism to our result for $\kappa_m(T)$ of AgVP₂S₆. This approach seems, however, well justified for the analysis of κ_s in S = 1/2 1D spin systems, where the spinon mean free paths are often rather large.³⁷

IV. SUMMARY AND CONCLUSIONS

In conclusion, by probing the anisotropy of the thermal conductivity of the S=1 Haldane-gap HAFM compound AgVP₂S₆, we established the magnitude and the temperature variation of the spin-related energy transport in the temperature region between about 50 and 170 K. By comparing the energy and the spin diffusion parameters $D_E(T)$ and $D_S(T)$, both derived from experimental data, we note that they not only exhibit similar temperature dependences but that also their absolute values are of the same order of magnitude. We argue that the previous suggestion of an intrinsic origin of the spin diffusion at high temperatures in this system¹⁶ also applies to the energy transport that is investigated here. The character of the energy transport at low temperatures remains to be investigated.

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