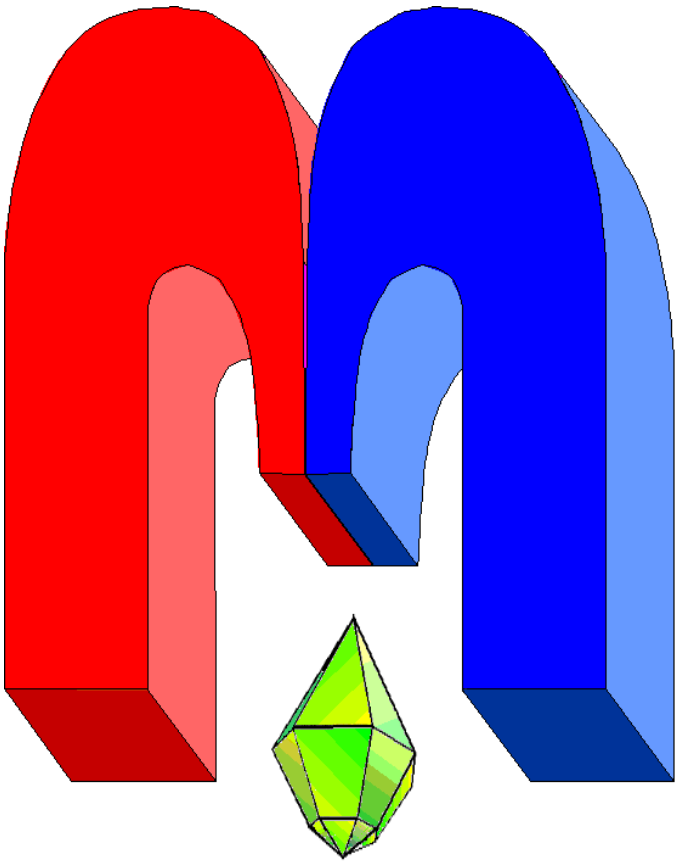
ISSN 2072-5981
doi: 10.26907/mrsej



Magnetic Resonance in Solids

Electronic Journal

Volume ***26***
Issue ***1***
Article No ***24104***
1-7 pages
April, ***19***
2024
doi: **10.26907/mrsej-24104**

http://mrsej.kpfu.ru
https://mrsej.elpub.ru

Established and published by Kazan University*
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140), August 2, 1996
First Issue appeared on July 25, 1997

"***Magnetic Resonance in Solids. Electronic Journal***" (**MRS*ej***) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (*ESCI*, Clarivate Analytics, from 2015), *Scopus* (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*, *DOAJ*, *ROAD*, *CyberLeninka* (from 2006), *SCImago Journal & Country Rank*, etc.

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Short cite this: *Magn. Reson. Solids* **26**, 24104 (2024) doi: 10.26907/mrsej-24104

Berezinskii-Kosterlitz-Thouless correlations in $BaNi_2X_2O_8$[†]

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(Received April 14, 2024; accepted April 15, 2024; published April 19, 2024)

In this report, we compare the analysis of electron spin resonance (ESR) studies of Berezinskii-Kosterlitz-Thouless (BKT) correlations in the spin $S = 1$ Ni^{2+}-based layered honeycomb antiferromagnets $BaNi_2X_2O_8$ with X = V, P and As. Moreover, we investigate the effect of doping on the BKT correlations by the substitution of Ni^{2+} by spin $S = 1/2$ Cu^{2+} ions in $BaNi_2V_2O_8$.

PACS: 76.30.–v, 73.90.+f, 75.30.Kz

Keywords: quasi-2D antiferromagnets, electron spin resonance, spin relaxation, Berezinskii-Kosterlitz-Thouless transition

1. Introduction

Physical properties of low-dimensional systems such as surfaces, thin films, multilayers and low-dimensional magnets are in the focus of basic condensed matter research. Many of those properties are not observed in three dimensional systems, but are exclusive of the reduced dimensionality of those structures. The study of such systems has substantially advanced our fundamental knowledge of physics, apart from the important technological applications.

Physicists in the last fifty years became interested in defect-mediated phase transitions. These defects have been introduced in terms of non-linear excitations. Depending on the problem at hand, these excitations can take different topological types of defects. Berezinskii [1,2] suggested that vortices can be a kind of topological defects. Kosterlitz and Thouless [3, 4] formulated a new theory based on a vortex-mediated phase transition in the two-dimensional XY model, and this important theory has initialized intense activities in the study of two-dimensional systems.

During the last three decades, a great deal of experimental efforts has been invested to study the Berezinskii-Kosterlitz-Thouless (BKT) phase transition in the antiferromagnetic honeycomb-layer compounds $BaNi_2X_2O_8$ (X = P, As, V). With Ni^{2+} (electronic configuration $3d^8$ in octahedral ligand field), these systems serve as ideal candidates for the spin $S = 1$ XY-model. Careful analysis of the experimental results, which were obtained by inelastic neutron scattering (INS) and nuclear magnetic resonance (NMR) in $BaNi_2P_2O_8$, indicated that the observed electronic spin dynamics can be well described in the framework of a BKT scenario [5, 6]. Electron spin resonance (ESR) data obtained on single crystals of the isostructural compound $BaNi_2V_2O_8$ satisfied the BKT scenario even better [7]. Therefore, further intense theoretical and experimental studies have been devoted to the magnetic phase diagram of $BaNi_2V_2O_8$ [8–12]. Especially, recent neutron diffraction and myon spin rotation results [13] as well as quantum Monte-Carlo simulations of the spin $S = 1$ Heisenberg antiferromagnet on a honeycomb lattice with easy-plane anisotropy and weak in-plane easy-axis anisotropy [14] prove the BKT scenario of magnetic vortex formation to be essential for the understanding of the temperature dependence of the magnetic correlation length above the Néel temperature T_N.

[†]This paper is dedicated to Professor Boris I. Kochelaev on the occasion of his 90th birthday.

2. Theoretical Background

The two dimensional XY-model describes exchange coupled spins which can rotate and interact (exchange coupling $J_x = J_y = J$ and $J_z = 0$) in the xy-plane, only. It has been theoretically analyzed independently by Berezinskii [1,2] and Kosterlitz and Thouless [3,4], (for a review see Ref. [15]). For small difference in the angles $\Phi_i - \Phi_j$ between neighboring spins, the Hamiltonian can be expressed in terms of a spin orientation field $\tilde{\Phi}$ following

$$\mathcal{H}_{xy} = JS^2 \sum_{i,j=nn} \cos(\Phi_i - \Phi_j) \approx E_0 + \frac{1}{2} JS^2 \int d^2r \left(\nabla\tilde{\Phi}(\mathbf{r})\right)^2. \tag{1}$$

Using the condition that on a closed curve the integral over the angle differences attains multiples of 2π and after separation from spin-wave contributions, one obtains so called vortex solutions $\tilde{\Phi}(\mathbf{r}) = q\,\varphi + \alpha$, where the polar coordinates r, φ are measured from the vortex center (x_0, y_0)) and the parameter α rotates all spins by the same angle. The vorticity q is a full number, with $q > 0$ for a vortex and $q < 0$ for an antivortex. The corresponding energies are obtained inserting the vortex solutions into Eq. 1:

$$E - E_0 \approx \frac{1}{2} JS^2 \int d^2r \left(\frac{q}{r}\mathbf{e}_\varphi\right)^2 = \pi|J|S^2q^2 \ln\frac{R}{a}. \tag{2}$$

Here a is the lattice constant and R the spatial extension of the system. As the vorticity q appears quadratically, thermal excitations with $|q| > 1$ are practically negligible. The vortex energy as well as the vortex entropy $S_\mathrm{v}(q = \pm 1) = k_\mathrm{B} \ln N = k_\mathrm{B} \ln(R/a)^2$ diverge logarithmically with the magnitude of the system. $N = (R/a)^2$ is the number of lattice sites, i.e. all possible positions of the vortex center.

Below a certain critical temperature T_KT the vortices and antivortices are bound in vortex-antivortex pairs. This so called Kosterlitz-Thouless temperature can be estimated from the zero point of the free energy F

$$F(T) = U - TS_\mathrm{v} = (\pi|J|S^2 - 2k_\mathrm{B}T)\ln(R/a) \tag{3}$$

yielding $k_\mathrm{B}T_\mathrm{KT} = \pi|J|S^2/2$. However, the exact value depends on the peculiar properties of the model system (e.g. square or honeycomb lattice). The temperature dependence of the correlation length $\xi(T)$, which denotes the average half distance between two free vortices, does not reveal a critical law like $(T - T_\mathrm{KT})^{-\gamma}$, but exhibits an exponential divergence at T_KT following

$$\xi(T) = \xi_0 \exp\left(\frac{b}{(T/T_\mathrm{KT} - 1)^\nu}\right) \tag{4}$$

with $\nu = 0.5$ and $b = \pi/2$. Note that b may be weakly dependent on temperature and experimentally smaller values have been already found, e.g. $b = 0.91$ in $BaNi_2P_2O_8$ [6].

In real quasi two dimensional systems the inter-layer coupling $J_\perp \ll J_\parallel$ gives rise to three dimensional order at T_N, where both the interaction to z' nearest neighbors of adjacent layers as well as the interaction to z nearest neighbors within the same layer resembles the thermal energy

$$k_\mathrm{B}T_\mathrm{N} \approx z'|J_\perp|S^2 \frac{\xi^2(T_\mathrm{N})}{\xi_0^2} \approx zJ_\parallel S^2 \tag{5}$$

accounting for the number $(\xi(T_\mathrm{N})/\xi_0)^2$ of correlated spins in each layer [16]. With the correlation length from Eq. 4 this yields

$$\frac{T_\mathrm{N}}{T_\mathrm{KT}} \approx 1 + \left(\frac{2b}{\ln\frac{zJ_\parallel}{z'J_\perp}}\right)^2 \tag{6}$$

i. e. $T_N > T_{KT}$ and, thus, the three dimensional order masks the Kosterlitz-Thouless transition.

Regarding real systems it is also important to mention that detailed theoretical investigations revealed the existence of vortices and the BKT transition not to be confined to the pure XY model, but even a weak planar anisotropy is enough to provide for vortex excitations in a two-dimensional magnet [17–20].

3. Review of ESR in undoped $BaNi_2X_2O_8$ with X =V, P, As

On the search for two dimensional spin systems, which allow to study vortex dynamics by ESR, the honeycomb-layer compounds $BaNi_2X_2O_8$ (where X = V, P, As) turned out to be ideally suited materials. They crystallize within a rhombohedral unit cell containing magnetic layers of edge-sharing NiO_6 octahedra (Ni^{2+}: spin $S = 1$) arranged on a honeycomb lattice and separated by nonmagnetic layers of $X^{5+}O_4$ tetrahedra and Ba^{2+} ions. The large ratio between intra-layer Ni–Ni distance d_1 and inter-layer distance d_2 of about $d_2 = 2.57d_1$ provides a strong two-dimensionality. In $BaNi_2V_2O_8$ the antiferrromagnetic (AFM) intra-layer exchange interaction $J/k_B = -96\,K$ is much stronger than in the isostructural phosphate and arsenate compounds [21]. Above $T > 100\,K$ the magnetic susceptibility is isotropic with a broad maximum near 125 K indicating short range AFM correlations. At lower temperatures it becomes anisotropic for magnetic fields parallel and perpendicular to the NiO_6 layers. 3D AFM ordering occurs at $T_N = 50\,K$ with the Ni spins aligned antiferromagnetically within the planes and between adjacent layers [22]. The specific heat exhibits a small feature at about T_N showing that most of the entropy is released already at higher temperatures. These properties indicate $BaNi_2V_2O_8$ to be a weakly anisotropic 2D Heisenberg AFM [19, 20]. Although $BaNi_2As_2O_8$ ($J/k_B = -7\,K$, $T_N = 19\,K$) and $BaNi_2P_2O_8$ ($J/k_B = -8\,K$, $T_N = 24.5\,K$) exhibit a larger XY-type anisotropy in their susceptibility than the vanadate, the temperature regime of dominant two dimensional correlations between the maximum of the susceptibility and the ordering temperature is by far smaller than in $BaNi_2V_2O_8$.

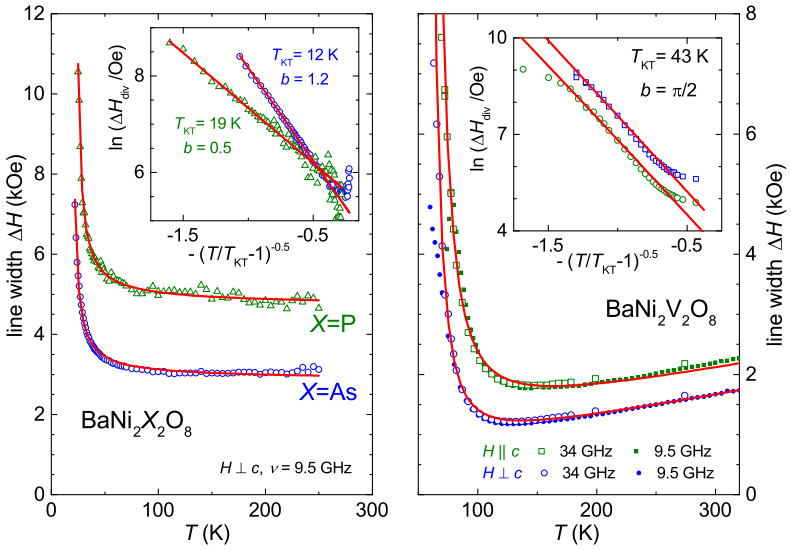

Figure 1. Temperature dependence of the linewidth in $BaNi_2P_2O_8$ and $BaNi_2As_2O_8$ (left frame) and in $BaNi_2V_2O_8$ (right frame). The red lines indicate the fit curves in terms of the BKT scenario. The insets show the divergent part of the linewidth after subtraction of the high-temperature contribution in a BKT plot.

At high temperatures the ESR spectra in $BaNi_2V_2O_8$ consist of a broad resonance line of Lorentzian shape at $g \approx 2.23$ as typical for Ni^{2+} in octahedral ligand field. On decreasing temperature the resonance strongly broadens, shifts to higher fields, and finally vanishes on approaching the magnetic ordering transition at T_N [7]. The right frame of Figure 1 shows the temperature dependence of the ESR linewidth for $50 < T < 300$ K measured at X-band and Q-band frequencies. The results for both frequencies nearly coincide except for the temperature range in which the line becomes very broad. In that region, the values obtained at 34 GHz are more precise and can be analyzed up to a value of about 8 kOe due to the higher resonance field. For temperatures $120 < T < 300$ K, the linewidth increases linearly with increasing temperature, which is probably due to single-phonon absorption and emission processes like in the 2D $S = 1/2$ AFM $Cu(HCOO)_2$: $4H_2O$ [23, 24]. The constant residual linewidth results from the zero-field splitting of the spin $S = 1$ state due to the crystal electric field. The divergent behavior on approaching T_N contains the relevant information on the spin dynamics. After subtraction of the linear high-temperature contribution, the divergence can be reasonably described by the BKT model following $\Delta H_{div} \propto \xi^3$ with the vortex correlation length given in Eq. 4 [25]. For $b = \pi/2$, we obtain $T_{KT} = 43.3$ K, which is resulting in $J_\parallel/J_\perp \approx 3000$ (cf. Eq. 6) [7]. Previous estimations of $J_\parallel/J_\perp$ in both $BaNi_2P_2O_8$ and $BaNi_2As_2O_8$ yielded similar values of the order of $10^3 - 10^4$ [21].

The ESR data of the related phosphate and arsenate compounds are more difficult to evaluate, because already at high temperatures their linewidth is about five times larger due to the smaller exchange interaction and correspondingly weaker exchange narrowing of the signals. Nevertheless, as shown in the left frame of Fig. 1, the temperature dependence of the ESR linewidth of both quasi-2D antiferromagnets [25, 26] has been described in terms of a BKT scenario, but with a parameter b smaller than the theoretical value $b = \pi/2$. This is in fair agreement with the NMR results in $BaNi_2P_2O_8$. However, for a deeper quantitative analysis high-field ESR at frequencies at least 10 times larger than X-band would be necessary to compensate for uncertainties due to the fact that at X-band the linewidth is equal or even larger than the resonance field.

4. $Ba(Ni_{1-x}Cu_x)_2V_2O_8$

In order to study the effect of doping in $BaNi_2V_2O_8$, one substitutes Cu^{2+} ions for Ni^{2+} into the hexagonal honeycomb layers. With $3d^9$ electronic configuration, the Cu^{2+} ions exhibit one hole with spin-1/2 in the $3d$ orbitals, which is Jahn-Teller active, giving rise to local distortion. The polycrystals of $Ba(Ni_{1-x}Cu_x)_2V_2O_8$ ($x = 0, 0.03, 0.05$) were prepared by solid-state reaction technique as was reported by Nath *et al.* [27]. For the ESR measurements the powdered samples were fixed in quartz tubes with paraffin. The measurements were performed at frequencies of 9.4 GHz (X-band) and 34 GHz (Q-band) between 50 K and 300 K. The g-values are found to be $g \approx 2.22$, like in the undoped system.

Typical ESR spectra are shown in the left frame of Fig. 2. Like in the single crystals of the pure compound they are well described by the field derivative of a Lorentzian line. Note that in the powder average the field-in-plane orientation of the crystal predominates. On decreasing temperature, the spectra of all copper concentrations under consideration broaden rapidly, shift to higher resonance fields, and disappear during the transition to three-dimensional order at the Néel temperature. The ESR intensities follow the temperature dependence of the susceptibility proving the proper origin of the signal from all Ni^{2+} and Cu^{2+} ions. There is no significant difference of the spectra for different copper doping.

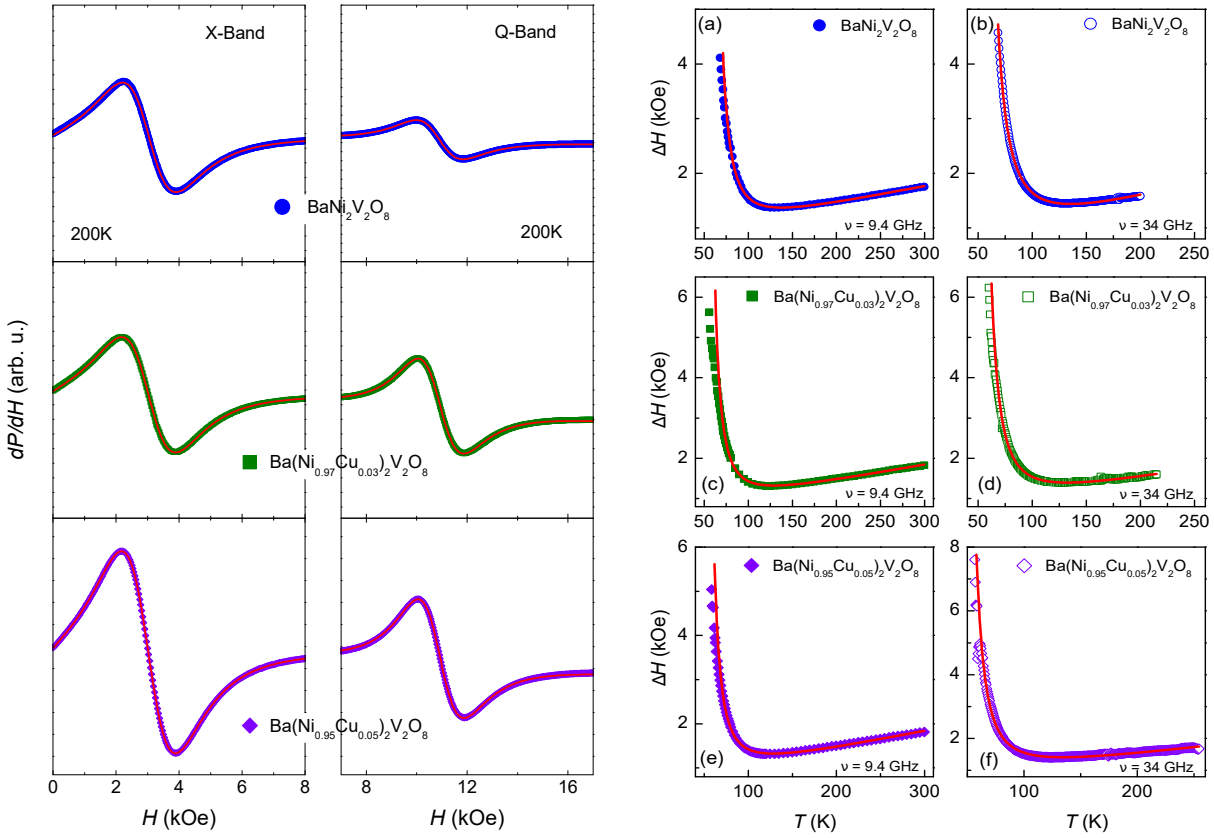

Figure 2. (Left frame) ESR spectra of different concentrations of $Ba(Ni_{1-x}Cu_x)_2V_2O_8$ (x = 0, 0.03, 0.05) at 200 K for both X- and Q-band frequencies. The red solid lines indicate the fit with the field derivative of the symmetric Lorentz line. (Right frame) Temperature dependence of the linewidth in $Ba(Ni_{1-x}Cu_x)_2V_2O_8$ (x = 0, 0.03, 0.05) measured at the X-band ($\nu = 9.4$ GHz) and Q-band ($\nu = 34$ GHz) and fit in terms of the BKT scenario.

The temperature dependence of the ESR linewidth of $BaNi_2V_2O_8$ between 50 K and 300 K for X- and Q-band frequencies are shown in the right frame of Figure 2 (Fig. 2(a,b)). In the X-band, a linear adjustment for $T > 150$ K results in a slope of about 3.6 Oe/K and residual linewidth of $\Delta H_0 = 650$ Oe. Below 120 K, the linewidth passes a minimum of approximately 1300 Oe. Comparable values were found in the Q-band data. Generally, the data of the polycrystalline $BaNi_2V_2O_8$ are in very good agreement with the single-crystal data shown in Fig. 1 proving the high quality of the powder sample. By further cooling the line broadens very fast and cannot be detected below 55 K any more. To characterize the divergent behavior on approaching T_N, the temperature dependence of the linewidth in polycrystalline $BaNi_2V_2O_8$ was again analyzed in the context of the BKT scenario. Similar to the single crystal, one obtains $T_{KT} \approx 43$ K and $\xi(T_N) \approx 284$ Å. The ratio $J_\parallel/J_\perp \approx 3000$. For Q-band, $T_{KT} \approx 40$ K, which leads to a small deviation of both ξ and $J_\parallel/J_\perp$. Turning to the copper-doped samples, ΔH exhibits the same temperature behaviour as shown in the right frame of Figure 2 (see Fig. 2(c-f)). As doping lead to the decrease of T_N [27], one also expects a decrease of T_{KT}. Following the BKT model, one obtains $T_{KT} \approx 40$ and 39 K for X- and Q-band measurements, respectively. The corresponding value of $\xi(T_N) \approx 479$ Å. This indicates that the vortices in the xy-plane are still robust. By further increasing the amount of Cu^{2+}, the respective values of $T_{KT} \approx 39$ K and 36 K for X- and Q-band. The spin-spin correlation length is $\xi(T_N) \approx 674$ Å, which is approximately three times larger than in the undoped one. However, this does not mean that the ratio $J_\parallel/J_\perp$ strongly

increases as a result of doping. But these results show that the decrease of the Kosterlitz-Thouless temperature T_{KT} on copper doping is weaker than the decrease of the AFM ordering temperature T_{N}. This means that the magnetic vortices are more robust against doping than the three-dimensional long-range AFM order. This could motivate further doping experiments to suppress AFM order such that the pure BKT transition of vortex-antivortex pairing becomes accessible and is not masked by conventional AFM order.

5. Summary

We presented an overview of the BKT correlations in the layered honeycomb antiferromagnets $BaNi_2X_2O_8$ with X = V, P, and As. Among these compounds, $BaNi_2V_2O_8$ appears to be the most ideal system to study the BKT scenario and related magnetic properties. It reveals stable and robust vortex dynamics behavior with a well defined KT transition temperature below T_{N}. Moreover, systematic doping of small amounts of Cu^{2+} ions onto the Ni^{2+} site of $BaNi_2V_2O_8$ results in a gradual suppression of T_{N} and T_{KT}. But T_{N} is stronger suppressed on doping than T_{KT}. This indicates a quite strong robustness of the BKT scenario against perturbations.

Acknowledgments

We thank R. J. Cava, Princeton University, J. P. Boucher, Université Grenoble Alpes, and A. V. Mahajan, Indian Institute of Technology Bombay, for providing the samples. This work was financially supported by the German Research Foundation (DFG) within the Transregional Collaborative Research Center TRR 360 "Constrained Quantum Matter", project no. 492547816 (Augsburg, Munich, Stuttgart, Lepzig).

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