NMR in the pseudogap- and charge-density-wave states of $(TaSe_4)_2I$

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Abstract

We have studied the ^{77}Se NMR spectrum and spin-lattice relaxation rate (SLRR) in the quasi-one-dimensional conductor $(TaSe_4)_2I$ in the temperature range of 150 to 320 K, i.e., both above and below the temperature of the charge-density wave transition, $T_c = 263$ K. Both the Knight shift and the SLRR vary strongly with temperature in the entire range investigated with no sharp feature at T_c . In particular, no critical divergence or Hebel-Slichter peak is observed. The SLRR is strongly “non-Korringa,” i.e., *not* proportional to the square of the Knight shift times temperature. All these findings are interpreted in terms of a fluctuating gap model.

Keywords: nuclear magnetic resonance spectroscopy; metal-insulator phase transitions; many-body and quasiparticle theories

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NMR has been widely employed to study the structure and excitations of charge-density waves (CDW) [1]. Most of these studies have been performed on nuclei with nonzero quadrupolar moment resulting in a coupling to the electric field gradients created by the periodic lattice distortion accompanying the CDW. It has been shown that due to this coupling, the nuclear spin-lattice relaxation rate (SLRR) in the CDW phase is dominated by the low-lying phase excitations of the order parameter. A critical divergence of the SLRR at the CDW transition temperature T_c is also attributed to the coupling to the order parameter.

In this work we study the NMR of ^{77}Se, a nucleus with spin $I = 1/2$ and zero quadrupolar moment, in the quasi-one-dimensional CDW system $(TaSe_4)_2I$ [2]. The interest of this study is twofold: First, because of the absence of quadrupolar coupling to the order parameter, we are able to test the properties of single particle excitations in the CDW phase. Second, the fluctuating gap or “pseudogap” state [3] proposed to describe the properties of the high-temperature phase [4,5] is a good test-field of similar phenomena in other systems, e.g., in high-temperature superconductors.

All measurements have been performed on a 97-mg single crystal of $(TaSe_4)_2I$ in a static magnetic field of 9 T (73 MHz) oriented perpendicular to the well-conducting *c* axis and parallel to one of the twofold symmetry axes within the tetragonal base plane. With this orientation, the spectrum in the metallic phase consists of two pairs of narrow lines (2 to 5 kHz, limited by spin-spin relaxation) corresponding to the two symmetry-inequivalent Se sites of the structure. Details of the angular- and temperature dependence of the spectrum will be published elsewhere [6].

The temperature dependencies of the Knight shift K and of the temperature-normalized SLRR $R \equiv 1/(T_1 T)$ of the four lines are similar; in Fig. 1, we show K and R for the line with the lowest Larmor frequency (Line 1). The Knight shift is in close agreement with earlier results on the spin susceptibility χ_s [4], which are also reproduced in the figure. Neither of these quantities is temperature independent in the high-temperature “metallic” phase but decrease with decreasing temperature and only show a smooth crossover at the transition to the CDW phase at $T_c = 263$ K. The presence of a sharp phase transition, however, is clearly seen in the line width as demonstrated in the inset of Fig. 1. We interpret the line broadening below T_c as due to the modulation of the chemical shift by the CDW [6].

Johnston *et al.* [4] successfully interpret the temperature dependence of the susceptibility in the fluctuating gap model by Lee, Rice, and Anderson [3]. In this model, a fluctuating order parameter ψ develops well above T_c, the onset of a static order parameter. As a result, the quasiparticle density of states is depleted near the Fermi energy and enhanced near and above $\Delta_f = |\psi|^2\ ^{1/2}$, a situation often described as the opening of a “pseudogap.” Beside the strongly temperature dependent susceptibility, optical- and

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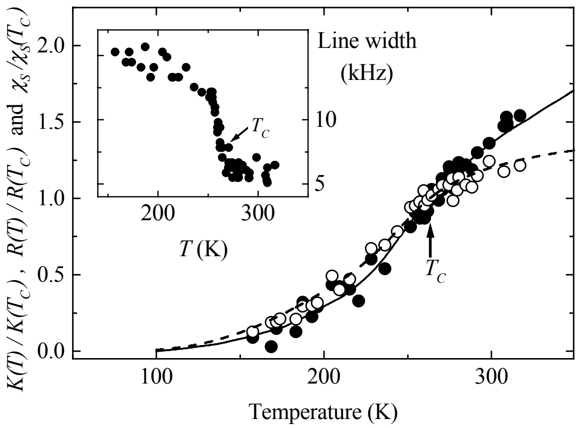

Fig. 1. Temperature dependence of the Knight shift K (full circles) and spin-lattice relaxation rate $1/(T_1T)$ (open circles) of Line 1. The continuous line is the electronic susceptibility χ_s from Ref. [4]. All quantities are normalized to their respective values at the transition temperature T_c. The dashed line is a fit to the SLRR (see text). Inset: Temperature dependence of the width of Line 4.

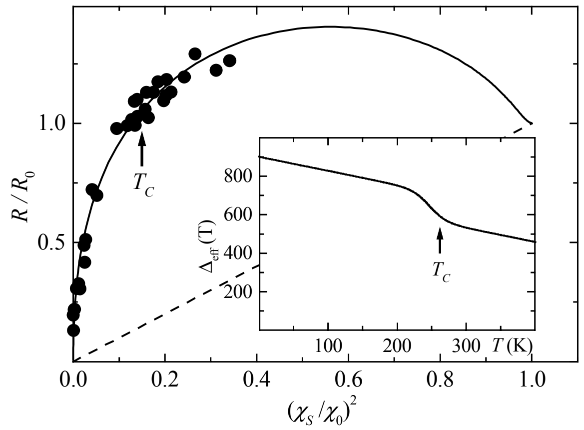

Fig. 2. Korringa plot of the relaxation rate, i.e., $R = 1/(T_1T)$ as a function of the square of the spin susceptibility, χ_s^2 (circles). Both R and χ_s are normalized to their respective metallic values in the absence of pseudogap, R_0 and χ_0. The continuous line is the result in the effective gap model Eqs. (1) to (3). The straight dashed line is Eq. (4). Inset: Temperature dependence of the effective gap.

photoemission spectroscopy provide more direct evidence of the existence of a pseudogap [5].

The susceptibility and SLRR are calculated as follows:

$$\chi_s/\chi_0 = 2\int_0^\infty n(\varepsilon)(-\partial f/\partial\varepsilon)\, d\varepsilon \;, \tag{1}$$

$$R_s/R_0 = 2\int_0^\infty n^2(\varepsilon)(-\partial f/\partial\varepsilon)\, d\varepsilon \;, \tag{2}$$

where χ_0 and R_0 are the respective "metallic" values in the absence of a pseudogap, and the density of states is $N_0\, n(\varepsilon)$ with N_0 the metallic density of states. Instead of trying to describe $n(\varepsilon)$ in details, we use—as a simple model—the density of states of a one-dimensional semiconductor:

$$n(\varepsilon) = \mathrm{Re}\left(\varepsilon \Big/ \sqrt{\varepsilon^2 - \Delta_{\mathrm{eff}}^2}\right) \;. \tag{3}$$

First we describe the measured susceptibility data using Eqs. (1) and (3) together with $\chi_0 = 2.02 \times 10^{-5}$ cm^3/mole Ta taken from Ref. [4]. The result of these calculations is an effective gap $\Delta_{\mathrm{eff}}(T)$ shown in Fig. 2. The gap in the high-temperature phase is only weakly temperature dependent but, remarkably, its magnitude is higher than T in the entire range investigated. At the transition temperature, a rather sharp step is observed in Δ_{eff}, followed by a weak increase with decreasing temperature. Together with the similar temperature dependence of the line width, this behavior may indicate a weakly first order phase transition.

Next, using $\Delta_{\mathrm{eff}}(T)$, we calculate R from Eq. (2). To remove the singularity of the integral, we introduce—as usual—a small imaginary part to Δ_{eff}: $\mathrm{Im}(\Delta_{\mathrm{eff}}/T) = 0.01$. In Fig. 1, we show the result of the fit with $R_0 = 2.5 \times 10^{-2}$ s^{-1}K^{-1}. The good agreement with the experimental data strongly supports the fluctuating gap model.

In a metal with weak electronic correlations, both R and $K \propto \chi_s$ are temperature independent, and the ratio K^2/R is called the Korringa constant. In strongly correlated metals, R and χ_s become temperature dependent and their relation is very often analyzed in terms of a "generalized Korringa relation":

$$R(T) = C\chi_s(T)^2 \tag{4}$$

with a temperature-independent constant C. To emphasize the spectacular failure of Eq. (4) in our case, in Fig. 2 we re-plot R against χ_s^2 together with the fit in the effective gap model. The deviation from Eq. (4) is a natural consequence of the pseudogap: Since the density of states varies significantly in the energy range k_BT, $n(\varepsilon)$ cannot be approximated by $n(0)$ in the integrals in Eqs. (2) and (3).

Finally we remark that in the CDW phase a coherence factor ½ $(1 + \Delta^2/\varepsilon^2)$ should be inserted into the integral in Eq. (2). Mean field theory predicts then a Hebel-Slichter peak in R in the CDW phase. Such a peak is expected at $T/\Delta \approx 1$, but in our case, due to the pseudogap, $T/\Delta \ll 1$ everywhere in the CDW phase, and the absence of the Hebel-Slichter peak is well understood. A pseudogap in the normal phase may be the explanation of the missing Hebel-Slichter peak in certain strongly correlated superconductors as well.

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[1] For a review, see: T. Butz (ed.), Nuclear Spectroscopy on Charge Density Wave Systems, Kluwer, Dordrecht, 1992.
[2] H. P. Geserich in P. Monceau (ed.), Electronic Properties of Inorganic Quasi-One Dimensional Materials, Reidel, Dordecht, 1985, p.111.
[3] P. A. Lee, T. M. Rice, P. W. Anderson, Phys. Rev. Lett. **31** (1973) 7.
[4] D. C. Johnston, M. Maki, G. Grüner, Solid State Comm. 53 (1985) 1.
[5] For a review, see N. Shannon, R Joynt, cond-mat/9806131 (1998).
[6] L. Németh *et al.* (unpublished).