Neutron-Scattering Study of the Structural Phase Transition in the One-Dimensional Conductor $K_2Pt(CN)_4Br_{0.3}\cdot 3D_2O$

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(Received 19 February 1974)

We report a study of the temperature dependence of the $2k_F$ instability in the one-dimensional conductor $K_2Pt(CN)_4Br_{0.30}\cdot 3D_2O$ using a neutron scattering technique. Whereas the extra scattering at room temperature has a one-dimensional character corresponding to a periodicity along the c axis of 6.66 Pt-Pt spacings, below 220 K it indicates the development of a three-dimensional superlattice structure with a new unit cell $2a\times 2a\times 6.66c$. However, this transition seems to be incomplete, in the sense that the coupling between adjacent chains does not achieve long-range order.

The mixed-valence platinum compound $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$ (KCP) has been of great interest recently because it exhibits a high room-temperature electrical conductivity of almost one-dimensional (1D) character.[1] In KCP, which has a tetragonal structure, the platinum atoms indeed form linear chains with a Pt-Pt spacing c of 2.89 Å, whereas the distance between adjacent chains $a = 9.87$ Å at room temperature.[2]

Diffuse x-ray scattering experiments[3] gave evidence of a 1D distortion along the platinum chains, corresponding to a period of about $6c$, which was attributed to a Peierls distortion or a giant Kohn anomaly. Independent coherent inelastic-neutron-scattering measurements of the longitudinal acoustic phonon dispersion in the direction of the platinum chains at room temperature revealed a pronounced anomaly at the wave number $q_0 = 0.3\pi/c = 2\pi/c - 2k_F$ (k_F is the Fermi wave number) which undoubtedly showed the existence of a giant Kohn anomaly.[4] Further x-ray scattering measurements[5] performed down to 77 K showed that the scattering due to the $2k_F$ instability loses its 1D character at temperatures lower than 120 K, announcing a phase transition to a larger unit cell, $2a\times 2a\times(\sim 6c)$ ($a = 9.87$ Å, $c = 2.89$ Å), which was not completed at 77 K and was therefore assumed to occur at a temperature somewhat lower than 77 K. This phase transition, considering the electrical properties, was interpreted as due to the condensation of the sofest phonons of the giant Kohn anomaly, corresponding to an antiparallel coupling of the Kohn-Peierls waves in neighboring chains in agreement with theoretical predictions by Barišić.[6] These earlier measurements were performed on crystals containing hydrogen, and the neutron scattering measurements were therefore restricted to inelastic scattering. With deuterated single crystals of KCP, because of the reduction of incoherent scattering, the experimental conditions could be improved considerably, and the neutron scattering measurements extended around zero energy transfer.

It is the purpose of this Letter to report the first results of neutron scattering measurements performed down to 6 K, in order to elucidate the origin of the low-temperature phase transition in KCP. As will be seen, most of the present results deal with the quasielastic part of the neutron scattering. The details of the measurements of the inelastic $2k_F$ anomaly in the phonon spectra are still under progress and will be reported later.

The measurements were made with the standard triple-axis–spectrometer neutron scattering technique. We used spectrometers at the reactor FR2 in Karlsruhe and at the high-flux reactor in Grenoble. Besides a few "constant-Q" scans, mainly constant-energy–type scans were made. Two single crystals of about 1 cm^3 were studied, one grown at the Brown Boveri Research

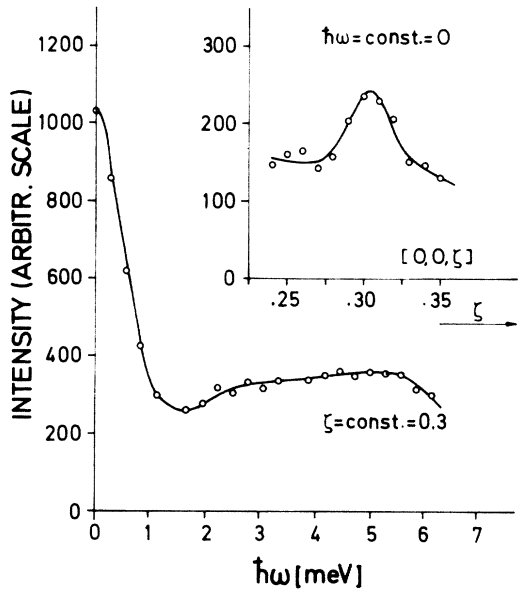

FIG. 1. Central peak in KCP at room temperature ($\zeta = cq/\pi$). The inelastic part of the constant-Q scan shows a phonon ridge which is due to the Kohn anomaly at $a_z = 2k_F$.

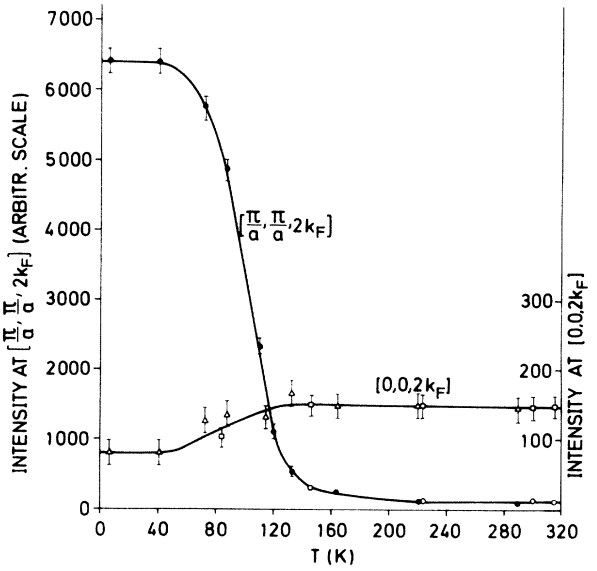

FIG. 2. Temperature dependence of critical scattering in KCP.

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Figure 1 shows a typical "constant-Q" scan at the point $(0, 0, 2k_F)$ in the reduced zone of the reciprocal lattice of KCP where the Kohn anomaly has been observed previously. The inset to Fig. 1 shows the result of a "constant-E" scan with $\hbar\omega = 0$. Both measurements were at room temperature.

Besides the phonon ridge which corresponds to the extremely sharp Kohn anomaly in the phonon dispersion, there is clearly an extra intensity around $\hbar\omega = 0$ at $q_z = 2k_F$. This "central peak" is observed in all off-symmetry directions studied at wave-vector $\vec{q}$ values having a component $q_z = 2k_F$ parallel to the platinum chains, and constitutes a new feature which could not be observed in previous neutron scattering measurements (as a result of the high incoherent scattering of hydrogen). This proves the existence, in addition to the giant Kohn anomaly, of a 1D periodic distortion of $6.66c$ at room temperature and considerably complicates the very simple picture which had emerged from the previous neutron and x-ray measurements.

If the extra scattering is truly elastic, we would have to assume uncorrelated static distortions of the platinum chains. This would imply the coexistence of a Kohn anomaly and a Peierls distortion already at room temperature.[7] However, the finite ω and q resolution of the instruments always allows the assumption of dynamical fluctuations, and the central peak can then be interpreted as critical scattering.[8,9]

The clearest experimental evidence obtained from the low-temperature measurements at the reciprocal point $(0, 0, 2k_F)$ and at the superlattice point $(\pi/a, \pi/a, 2k_F)$ was that the 3D ordering around 77 K (observed in the x-ray measurements) essentially concerned the intensity of the "central quasielastic peak."

The results are summarized in Fig. 2, where the peak intensities of the elastic scans at these two points are plotted as a function of temperature. From 315 down to about 220 K the intensities at both points are essentially the same. In this temperature range the superlattice distortion is thus 1D. Measurements at higher temperatures are impossible because of the decomposition of the compound. The intensity at the superlattice point $(\pi/a, \pi/a, 2k_F)$ increases rather rapidly below 140 K and saturates at about 40 K. In the same temperature range the intensity at the point $(0, 0, 2k_F)$ decreases but does not go to zero as would be expected for a long-range ordered superstructure. A few elastic scans at different temperatures in the reciprocal plane $q_z = 2k_F$ and along the direction $(\zeta, \zeta, 2k_F)$ are shown in Fig. 3. It may be worthwhile to mention that the peak intensities are 3 to 4 orders of magnitude smaller than those of neighboring Bragg reflexes. If a

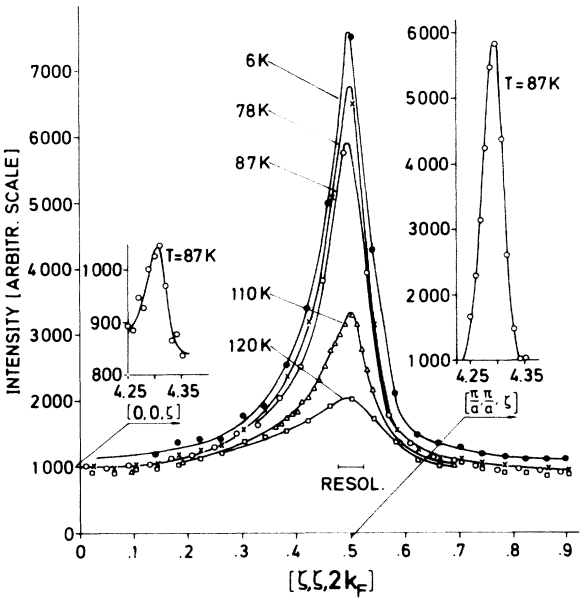

FIG. 3. T dependence of critical scattering in the $(\zeta,\zeta,2k_F)$ direction $(\zeta = aq/2\pi)$. The insets show scans in the $(0,0,\zeta)$ and $(\pi/a,\pi/a,\zeta)$ directions $(\zeta = cq/\pi)$. The half-width of the peak in these scans is given by the resolution of the spectrometer and remains constant over the whole temperature range.

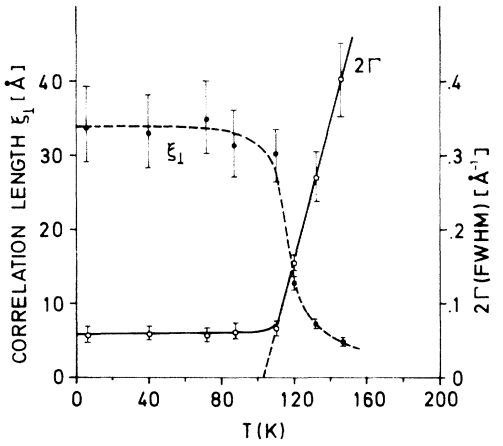

FIG. 4. T-dependent linewidth 2Γ (full width at half-maximum) of the intensity distribution in the $(\zeta,\zeta,2k_F)$ direction $(\zeta = aq/2\pi)$. The correlation length is defined as $\xi_\perp = \Gamma^{-1}$.

slight asymmetry in the q dependence of the intensity distributions is neglected, they can be described approximately by Lorentzians. The widths at half-maximum of these curves are considerably larger than the resolution of the spectrometer, whereas the elastic scans perpendicular to the plane $q_z = 2k_F$ show no broadening compared to the spectrometer resolution over the whole range of temperature. This leads us to the conclusion that even at the lowest temperatures (6 K in the present experiment) the long-range order perpendicular to the platinum chains is not established and that the locally ordered superlattice structure described for the vicinity of 77 K from the x-ray measurements is essentially valid down to 6 K.

If we take the half-width of the Lorentzians of Fig. 3, corrected for the instrument resolution, as the inverse of a correlation length for the interchain order, we get the results shown in Fig. 4. There seems to be a fairly sharp transition between 120 and 110 K; at 120 K the interchain correlation has reached one interchain distance a, increasing rapidly with decreasing temperature to about $3a$, and then it remains constant down to 6 K.

The reason for the absence of the long-range order for the interchain coupling is not clear. Too little is known about the organization of the Br ions (0.6 per unit cell), the disorder of the potassium atoms (two sites per atom), and the effect of statistical disorder on the coupling between chains.

The situation is completely different if one considers the correlation length in the direction of the platinum chains. Investigating the influence of 1D fluctuations on the transition temperature T_P of the Peierls transition, Lee, Rice, and Anderson[10] found that T_P is suppressed to about one quarter of the mean field value T_P^{mf}. From the observed transition in KCP around 110 K they concluded that T_P^{mf} is approximately 400 K and estimated the correlation length parallel to the chains to be equal to $7c$ at room temperature. The q resolution of the neutron spectrometer used in the present investigation gives a lower limit of the correlation length of $20c$. The smaller value of $7c$ predicted by Lee, Rice, and Anderson would have been observed as a broadening of the elastic scans parallel to the chain direction, but no such broadening was found.

It has further been assumed that the transition from a 1D system, from a high-temperature conducting state to a low-temperature Peierls distorted state, coincides with the temperature of the 3D superlattice structure.[10-13] This concept would imply that the observed extra quasielastic scattering at $q_z = 2k_F$ up to 315 K is of dynamical nature and due to thermodynamic fluctuations. With our present energy resolution of 0.15 THz, it was not possible to observe at any temperature

a finite energy width of the central peak which would give direct support to these ideas. Since a small static distortion and thermodynamic fluctuations also correspond to the same structure factor, intensity measurements around different reciprocal lattice points do not help to clarify the nature (static or dynamic) of the $2k_F$ quasielastic scattering. It is therefore impossible to conclude whether the true Peierls transition in KCP occurs at low temperature and coincides with the 3D local ordering (dynamical interpretation of the quasielastic scattering), or if the Peierls distortion already exists at room temperature (static interpretation of the quasielastic scattering). It should be emphasized that a small Peierls gap at high temperature would make only very small changes in the electrical properties as well as in the phonon spectrum at room temperature.[7]

We expect a more precise answer to this question from the measurements of the temperature dependence of the truly inelastic part of the $2k_F$ anomaly in the phonon spectrum. If, for instance, the phonon frequencies in the range of the Kohn anomaly increase with decreasing temperature, this would prove the existence of a Peierls distortion already at room temperature.

We should like to thank our colleagues from the Brown Boveri Research Center Baden (A. Beck, P. Brüesch, M. J. Rice, S. Strässler, and H. R. Zeller) for several valuable discussions. We also thank our colleagues at the Institut Laue-Langevin in Grenoble, especially R. Currat, for their assistance during the measurements at the High Flux Reactor.

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p-^{4}He Elastic Scattering at 1.05 GeV

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(Received 16 October 1973)

The angular distribution of the elastic-scattering differential cross section of 1.05-GeV protons by ^{4}He has been measured from 3 to 47° lab. The main features of this measurement are that the first minimum is much less deep than previously measured and that, at the point where a second minimum is predicted by calculations, there is just a slight change of slope.

Since the appearance of the first experimental results on 1-GeV proton scattering from nuclei,[1] considerable theoretical effort[1-4] has been focused on an explanation of p-^{4}He elastic-scattering differential cross section data. In particular, Lambert and Fesbach[3] studied the influence of short-range correlations and Ikeda[4] the effects of N^* production during the multiple scattering process. The theories show how cross sections are quite sensitive to those aspects,