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Neutron diffraction study of the compressibility of the quasi-one dimensional conductor KCP(Br) under hydrostatic pressures

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Résumé. — Nous présentons des mesures de compressibilités de KCP[K₂Pt(CN)₄Br_{0.3}·2,7 D₂O] par diffraction de neutrons sous hautes pressions hydrostatiques jusqu'à ~ 21 kbar à la température ambiante. Les valeurs observées sont, respectivement, suivant les axes *a* et *c*, $k_a = 1,51$ et $k_c = 1,61 \times 10^{-12}$ cm²/dyne. Les constantes de Grüneisen le long des axes sont, respectivement, $\gamma_a = 7,9$ et $\gamma_c = 7,1$. Ces résultats indiquent que KCP est essentiellement tridimensionnel en ce qui concerne la liaison du cristal.

Abstract. — In this paper, we report the first comprehensive measurements of the compressibility of KCP[K₂Pt(CN)₄Br_{0.3}·2,7 D₂O] by neutron diffraction at room temperature under hydrostatic pressures up to 21 kbar. The linear axial compressibilities of the tetragonal lattice are, respectively, $k_a = 1.51$ and $k_c = 1.61 \times 10^{-12}$ cm²/dyne. The corresponding Grüneisen parameters are, $\gamma_a = 7.9$ and $\gamma_c = 7.1$. The results indicate that KCP is essentially a three-dimensional, almost isotropic material as far as crystal binding is concerned.

1. Introduction. — The mixed-valence planar compound, KCP[potassium cyano-platinide,

has been the focus of considerable interest in the past few years. The interest in this material originated because of its unusual quasi-one-dimensional electronic transport properties [1], and later on, was spurred by the discovery of structural instabilities associated with its nearly 1-D metallic character [2]. There are two interesting findings about KCP and both of them have defied clear understanding : 1) In spite of the fact that this material shows a giant Kohn anomaly already at room temperature [3], no long-range three-dimensional structural phase transition develops at the lowest temperature examined (6 K) [4]. The final low-temperature state of KCP can be described in terms of elongated volumes about $300 \times 50 \times 50 \text{ \AA}^3$ in size in which the 3-D distortion giving rise to the insulating properties are correlated, but there is no long-range order. 2) The $2 k_F$ phonon anomaly observed at room temperature persists,

though in an altered form, down to the lowest temperature of 6 K [5]. One thus does not observe a soft mode which condenses at the *phase transition* giving rise to a low-temperature insulating 3-D modulated structure. In contrast, TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) displays a sequence of long-range collective phase transitions at low temperatures [6].

It is known that a 1-D metallic system is inherently unstable against a Peierls transition [7] in which the lattice distorts to a new periodicity with the opening of a band gap at the Fermi level. However, a purely 1-D system with short-range interactions cannot undergo a real phase transition for any temperature $T \neq 0$. The establishment of long-range order, necessary for a phase transition, is prevented by thermodynamic fluctuations [8]. To undergo a real phase transition, there has to be present a finite amount of interchain coupling. In a real system, this is provided by Coulomb interaction between the chains and by interchain hopping or tunnelling of electrons. This makes feasible phase transitions at finite temperatures as indeed observed in TTF-TCNQ. The magnitude of the fluctuations and ordering temperatures depend on the interchain interactions [9]. The absence of a genuine phase transition in KCP might then be

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attributed to an interchain coupling too weak to suppress the 1-D thermodynamic fluctuations. This conjecture seems to be supported by the observation of a sharp metal-insulator transition in this material induced by high pressure [10]. Pressure is expected to enhance the 3-D interchain coupling.

It is common knowledge that compressibilities, together with their pressure derivatives, can provide valuable information on the strength and nature of intrachain and interchain binding in quasi-one-dimensional materials. In a recent paper [11], we have reported the linear axial compressibilities of a deuterated sample of TTC-TCNQ. The results indicated a strong interchain interaction. In this paper, we present the results of the first comprehensive measurements of the compressibility of a deuterated sample of KCP by neutron diffraction under hydrostatic pressures. The aim of this work was to get a feeling for the strength of the interchain coupling. The surprising finding of our results is that, mechanically speaking, KCP is a fully three-dimensional almost, isotropic material.

There are two earlier X-ray measurements [12, 13] of the compressibility of KCP, the former to 100 kbar in a nonhydrostatic medium and the latter to only 1.5 kbar. Interrante and Bundy [12] followed only one Bragg peak to determine the pressure dependence of the c -parameter, and their measurement of the a -parameter at the lowest pressure value (~ 10 kbar) appeared spurious. Kuse [13] could measure only one Bragg spot from which he determined the a -axis compressibility. The results of these two authors differ by a factor of two for the compressibility along the a -axis. Thus it seemed important to us to remeasure the compressibility of KCP in a hydrostatic pressure environment with a reasonably high precision up to 20 kbar.

2. Experimental. — A polycrystalline sample of deuterated KCP(Br) was prepared by standard technique. The experimental approach for neutron diffraction measurements under pressure has been discussed previously [11, 14]. Deuterated ethyl alcohol was used as the pressure transmitting medium to insure hydrostatic sample environment. The pressure was measured by monitoring the resistance of a manganin wire coil placed directly in the transmitting liquid. The linear response of the manganin gauge to applied pressure showed that the pressure developed was hydrostatic in the entire range of measurements. Neutron diffraction patterns were taken at ambient temperature using the conventional two-axis diffractometer H12 at the C.E.N. de Saclay with incident neutron wavelength of $1.14 \text{ \AA}$. The intensities and angular positions of six nuclear Bragg peaks were followed as a function of pressure between zero and 21 kbar. The lattice parameters a and c of the tetragonal unit cell of KCP [15] were determined by

least-square fitting of the six Bragg peaks by Gaussian functions.

3. Results and discussion. — As an illustration of the change in diffraction spectra brought about by applied pressure, we have shown in figure 1 a selected

Fig. 1. — Pressure dependence of the nuclear (221), (002) and (301) Bragg angles of deuterated KCP (Br). The solid lines represent least-square Gaussian fits.

region of Bragg angles (2θ) for spectra taken at two different pressures. The effects of compression are evidenced by the shift of the diffraction peaks toward larger angles as the pressure is increased. The relative positions and the intensities of the peaks are observed to remain basically unaffected by the application of pressure. In figure 2, we display the pressure dependence of the a and c lattice parameters. They are normalized with respect to their extrapolated ambient-pressure values in order to readily compare the relative compression along these principal directions. The data were fitted by a least-square technique to a parabolic function in pressure. From the fitting parameters we obtained the following linear axial compressibilities $\left[= \left(\frac{\Delta l}{l} \frac{1}{P} \right)_{P \rightarrow 0} \right]$, where P is the pressure and l the appropriate lattice parameter] : $k_a = 1.51 (12)$ and $k_c = 1.61 (15) \times 10^{-12} \text{ cm}^2/\text{dyne}$. The linear Grüneisen parameters were calculated

Fig. 2. — Linear compression along the a - and c -axes of deuterated KCP (Br) as function of pressure. Solid lines are least-square fits to the experimental data. Note that the uncertainty associated with the experimental points is ± 0.0015 .

from $\gamma_l = \frac{1}{2}(\partial^2 l / \partial P^2) / (\partial l / \partial P)^2$ and the volume Grüneisen parameter followed from

$$\gamma = \frac{1}{2} V (\partial^2 V / \partial P^2) / (\partial V / \partial P)^2 - \frac{2}{3} \quad [16].$$

The respective zero-pressure values are :

$$\gamma_a = 7.9 \pm 2.2, \quad \gamma_c = 7.1 \pm 1.5$$

and

$$\gamma = 2.0 \pm 0.4.$$

The observed lattice parameters at ambient pressure are, respectively, $a = 9.870(8)$ and $c = 5.774(5)$ Å. The lattice parameters at zero pressure are in good agreement with those observed by neutron diffraction for a deuterated sample of KCP containing 2.7 D₂O per formula unit [17].

This material most closely corresponds to the sample used in this study. Our measurement of the c -axis compressibility agrees with that of Interrante and Bundy [12], but the a -axis compressibility confirms the work of Kuse [13] and indicates that the value obtained by the formers is too small by nearly a factor of two. The value of the volume Grüneisen parameter, γ , reported by Thielemans *et al.* [10] from low-temperature resistivity measurement under pressure is much smaller than the value obtained by us. It is difficult to comment on this discrepancy since

one is not sure of the assumptions made by these authors in arriving at the Grüneisen parameter from the pressure dependence of the electron-phonon coupling constant.

The elastic stiffness constants, c_{ij} 's, for a tetragonal lattice can be computed from the three following relations [18] :

$$(c_{11} + c_{12})k_a + c_{13}k_c = 1$$

$$2c_{13}k_a + c_{33}k_c = 1$$

$$E = 1/s_{33} = c_{33} - 2c_{13}^2/(c_{11} + c_{12})$$

where k_a and k_c are the compressibilities along the a - and c -axes, respectively, and E is the Young's modulus along the c -axis. The value of E is reported to $267 \pm 54 \times 10^9$ dynes/cm² by a vibrating reed experiment [19]. Use of the above equations and the measured values for k_a , k_c and E yields $c_{11} + c_{12} = 508 \pm 36$, $c_{13} = 145 \pm 22$ and $c_{33} = 350 \pm 68 \times 10^9$ dynes/cm², respectively. The value of c_{33} so obtained compares favourably with that deduced from the velocity of longitudinal acoustic waves, measured by inelastic neutron scattering experiments [20], namely

$$c_{33} = 380 \times 10^9 \text{ dynes/cm}^2.$$

From the results discussed above one can arrive at the following important and significant conclusion. Though quasi-one-dimensional in its electrical transport properties, KCP is a fully three-dimensional, almost isotropic material as far as crystal binding is concerned. This is evidenced by the very similar values of the axial compressibilities and the corresponding Grüneisen parameters. The interchain binding is thus quite strong.

This, however, does not necessarily mean a strong coupling between electrons on neighbouring chains. To suppress the 1-D thermodynamic fluctuations and render possible a long-range 3-D structural phase transition, what is needed is an interchain interaction between the 1-D electron gases or charge-density waves along the platinum chains. It is not possible to comment on the strength of this interaction from compressibility data which are a measure of the overall structural coupling. Nevertheless, our results indicate the presence of 3-D phonons and, hence, an effective electron-electron interchain coupling *via* the electron-phonon interaction can not be ruled out.

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