Dechanneling Anomalies of High-Energy Ions at the Charge-Density-Wave Transition in $1T$-TaS_2

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Backscattering yields of 1.00-MeV He^+ ions on $1T$-TaS_2 are reported from room temperature to 120 K. The temperature dependence of the backscattering yield exhibits the softening of an acoustic mode and an optical mode. An anomalously large peak in the backscattering yield with large hysteresis was observed around the nearly commensurate to commensurate transition temperature, indicating existence of a disordered state. A small peak around 280 K was observed on heating, indicating existence of a new transition in this material.

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For the past several years, charge density waves (CDW) accompanied by periodic lattice distortions in transition-metal dichalcogenides have been extensively investigated.[1] Among the group-V*B* transition-metal dichalcogenides, $1T$-TaS_2 exhibits complex structural phase transitions due to the existence of a nearly commensurate CDW (NCDW) state which is unique to this material.[2] The NCDW becomes the commensurate CDW (CCDW) near 200 K and the details of this transition are still not fully understood. In this paper we report experimental results on the backscattering yield of high-energy He^+ ions for $1T$-TaS_2, with particular interest in the NCDW-CCDW transition.

The $1T$-TaS_2 single crystals used in the present experiment were grown by an iodine-vapor transport method. Typical dimensions of the specimens were $3\times3\times0.1$ mm^3. A standard Rutherford backscattering (RBS) arrangement with an annular backscattering detector was used in this experiment. The specimen was mounted on a three-axis goniometer in the scattering chamber and the positions were controlled digitally. He^+ ions were accelerated to 1.00 MeV by a Van de Graaff accelerator and the beam energy was stabilized by using feedback from slits in the beam line. The diameter and the divergence of the He^+ beam were 1.0 mm and 0.03°, respectively.

The specimen was positioned so that the c axis was precisely aligned parallel to the beam direction at room temperature. The specimen was slowly cooled down to 120 K (below the NCDW-CCDW transition temperature) and the temperature dependence of the backscattering yield was measured. The cooling rate was maintained within 1 K/min in the vicinity of the transition and the temperature was stabilized within ±0.05 K. After the temperature reached 120 K, the specimen was heated slowly toward room temperature in order to check the existence of hysteresis in the yield.

Typical RBS spectra of $1T$-TaS_2 in the NCDW state are shown in Fig. 1. In order to minimize the radiation damage of the specimen, we have adopted the large energy window designated in the figure. Along the c axis, the He^+ ions will traverse through the axial channel of rhombic

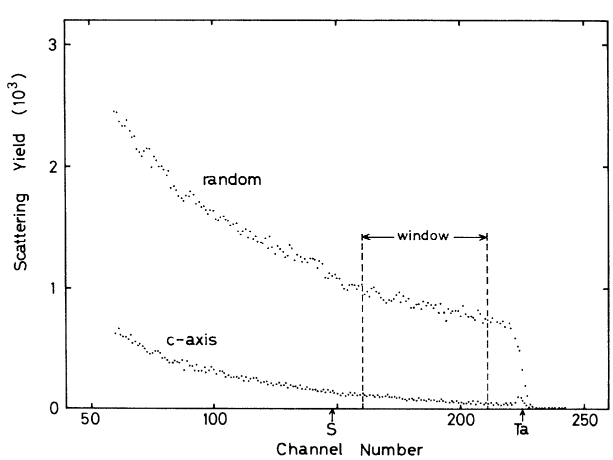

FIG. 1. Typical He^+ RBS spectra in $1T$-TaS_2 at room temperature.

shape with pairs of Ta and S atoms at the corners.

The temperature dependence of χ_{min} is shown in Fig. 2, where χ_{min} is the backscattering yield along the c axis normalized by the yield among the random directions. The figure shows the following features: (1) χ_{min} increases as temperature approaches the transition temperature in cooling and heating processes; these regions are designated by A and B in the figure. (2) In the vicinity of the transition temperature, this rise in χ_{min} changes discontinuously to a large dechanneling peak both in cooling and heating processes. The temperature difference between the two peaks is about 45 K, which corresponds to the hysteresis in the transition temperature observed previously in other properties.[1] (3) Just before the large peak in the cooling process, a small dip is observed. However, this dip is strongly sample dependent. In fact we failed to observe this dip for some specimens, while they exhibited all the other features. (4) The small peak around 280 K is observed only in the heating process starting from the CCDW state.

In general, the absolute magnitude of χ_{min} depended on the specimen quality and on the history of thermal cycles. It has already been pointed out by x-ray analysis[3] that the transformation from the NCDW state to the CCDW state introduced some irreversible damage. The difference between χ_{min} at room temperature in the cooling process and that in the heating (Fig. 2) is due to this irreversible damage. Therefore the absolute magnitude of χ_{min} is of no quantitative meaning.

Let us examine the experimental results qualitatively.

(A) The strain associated with the phase transition seems to be the probable origin of the observed anomalies. We have measured the angular dependence of the backscattering yields (channeling dip curves) at a few points in the regions A and B in order to check the above possibility. However, they did not exhibit the spread of angular half-width and fluctuations of the yields due to a formation of macroscopic domains in these regions.[4] A mosaic spread and the tilting of the c axis may play a dominant role in the first-order lock-in transition which will be discussed in section B. In the following, we will consider another possible mechanism for the anomalies in regions A and B.

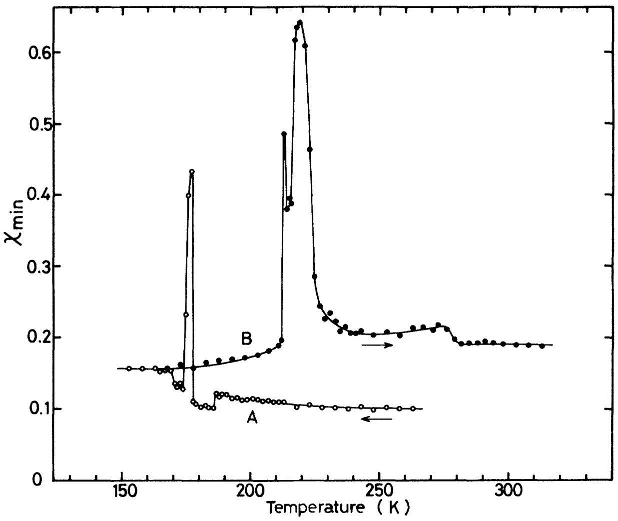

FIG. 2. The normalized backscattering yield as a function of temperature in $1T$-TaS_2.

χ_{min} reflects the softening of particular phonon modes in the following way: χ_{min} for a simple monoatomic lattice is expressed as[4,5]

$$\chi_{min} = C\sum \langle |u_{\vec{q}}|^2\rangle , \tag{1}$$

with $C = 3.0\pi Nd$, where N is the density of atoms, $(\langle |u_{\vec{q}}|^2\rangle)^{1/2}$ is the root mean square displacement of lattice vibrations of wave-vector q in the plane normal to the channeling axis, and d is the distance between atoms in an atomic string. Equation (1) indicates that χ_{min} is proportional to the Debye-Waller factor of the specimen.

Let us consider a simplified example of the softening of some particular phonon modes which start to soften at $T = T_0$ and become unstable at $T = T_c^*$; their frequencies change from $\omega^2(\vec{q}) = \omega_0^2(q')$ to $\omega^2(\vec{q}) = D_1(T - T_c^*) + D_2|\vec{q} - \vec{q}'|^2$ for $|\vec{q} - \vec{q}'| < q_c$, where $\vec{q}'$ is the wave vector of the soft mode, $\omega_0^2(\vec{q}')$ and q_c are temperature-independent constants, $D_1 = \omega_0^2(\vec{q}')/(T_0 - T_c^*)$, and $D_2 = \omega_0^2(\vec{q}')(T_0 - T)/(T_0 - T_c^*)q_c^2$. χ_{min} in this case is given by the sum of the term χ_{min}^* due to the soft phonons and the term A^* due to the other phonons which are independent of temperature; $\chi_{min} = \chi_{min}^* + A^*$, where χ_{min}^* is expressed as

$$\frac{\chi_{min}^*}{T} = \text{const}\left\{\frac{1}{1-x} - \frac{1}{3} - \left(\frac{x}{(1-x)^3}\right)^{1/2}\tan^{-1}\left(\frac{1-x}{x}\right)^{1/2}\right\}. \tag{2}$$

Here, we put $x=(T-T_c^*)/(T_0-T_c^*)$.

The actual expression of χ_{min} for $1T-TaS_2$ is more complex because of the finite contribution of the S atomic potential to χ_{min}, besides that of the Ta atomic potential.[6] However, this modification does not alter the essential feature of χ_{min} for the response of soft phonons.

In Fig. 3, the comparison of Eq. (2) with the experimental results is shown, which suggests a reasonable agreement between the theory and the experiment. The increase in χ_{min} with decreasing temperature in region A may be due to the softening of certain longitudinal acoustic modes. It is conjectured that these modes are the oscillation modes of the domain walls.[7] The increase in χ_{min} with increasing temperature in region B is considered to be related to the softening of two A_g modes[8] (c-axis modes). However, it is more likely that this increase is largely due to the softening of some shear mode (E_g mode) since the atomic displacements of this mode are in the plane normal to the channeling axis. At present, however, there is no other experiment supporting the softening of the E_g mode.

χ_{min} ($\approx A^*$) at room temperature is equal to 0.1, which is an order of magnitude larger than the theoretical value for the ideal, nondistorted state in $1T$-TaS_2. This discrepancy is explained by the effects of periodic distortions in the NCDW state and of lattice defects inherent in this quenched material.

(B) The magnitude of χ_{min} at the first-order lock-in transition has reached the value 0.5,

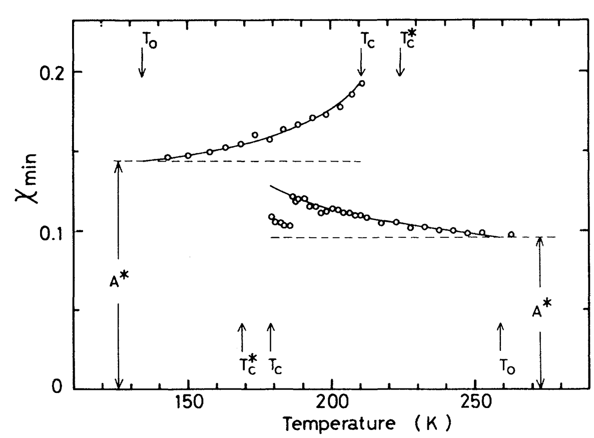

FIG. 3. The temperature dependence of χ_{min} in the regions A and B in Fig. 2. The solid lines indicate the estimates from Eq. (2). A^* in the figure is χ_{min} which consists of temperature-independent terms including the contribution from the lattice defects.

which indicates the existence of a strongly disordered lattice state in the relatively narrow region around the transition. The widths of the peak scatter from 2 to 14 K among the specimens. One of the crude speculations for the above result is as follows: The large increase in χ_{min} may be due to the spontaneous formation of macroscopic domains with random buckling of the c axis of these domains caused by the strong strains resulting from the transition.[9] The metastable nature of these distorted states indicates that in the vicinity of the lock-in transition the relaxation time is very long because of the complexity of the lattice transformation, where the periodicity of the c axis changes from $3C$ to $13C$ (C is the lattice constant of the c axis) and the lattice spacing of the c axis expands by $\Delta c/c \sim 1\times 10^{-3}$.[9] Random impurities and defects may be responsible for the unstable distorted states causing temporary pinning of the distortions.

There is another experiment closely related to our experiment. Jericho, Simpson, and Frindt[10] have observed a large peak in the sound attenuation of the order of 30 dB/cm and steplike stiffening (softening) of sound velocity at the NCDW-CCDW transition in the cooling (heating) process. The sound attenuation and behavior of χ_{min} in Fig. 2 have many similar features but the following difference is present: The width of the sound attenuation peak in the cooling process is wider than that in the heating process, whereas in our experiment the width of the peak in the cooling process is narrower than that in the heating.

Another mechanism might apply in the presence of a strongly disordered lattice. Recently, Coppersmith *et al.*[11] have shown that incommensurate phases are unstable with respect to the spontaneous creation of dislocations in the two-dimensional lattice under certain conditions. However, the CDW state in $1T$-TaS_2 is three dimensional rather than two dimensional even if the interlayer interaction is weak and the CCDW have a large number of different domains. Also, the present NCDW-CCDW transition is first order. Thus we have no definite proof of the applicability of the above theory in the present case.

(C) The small dip observed in the vicinity of the transition is closely related to the small contraction of the c axis at this temperature,[9] but the details of the physical origin of the contraction still remain unclear.

(D) The small increase in χ_{min} with increasing temperature around 280 K reveals the possible existence of a new transition in this material.[9] The new transition might be due to a transformation analogous to that in $2H$-$TaSe_2$, where the stripe discommensuration structure changes to the honeycomb structure.[12]

The discussions of this report are largely qualitative, but they do suggest that a new lattice instability exists in $1T$-TaS_2, which has not been observed yet by x-ray or electron diffractions. Detailed theoretical studies of this problem are urgently desired.

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[1]J. A. Willson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).

[2]Y. Yamada and H. Takatera, Solid State Commun. 21, 41 (1977).

[3]C. S. Scrusy, P. M. Williams, and G. S. Parry, Philos. Mag. 31, 255 (1975).

[4]T. Haga, K. Shimizu, Y. Abe, and Y. Kino, Solid State Commun. 38, 187 (1981).

[5]J. H. Barrett, Phys. Rev. B 3, 1527 (1971).

[6]D. S. Gemmell and R. C. Mikkelson, Phys. Rev. B 6, 1613 (1972).

[7]W. L. McMillan, Phys. Rev. B 16, 4655 (1977).

[8]S. Sugai, K. Murase, S. Uchida, and S. Tanaka, Physica (Utrecht) 105B, 405 (1981).

[9]O. Sezerman, A. M. Simpson, and M. H. Jericho, Solid State Commun. 36, 737 (1980).

[10]M. H. Jericho, A. H. Simpson, and R. F. Frindt, Phys. Rev. B 22, 4907 (1980).

[11]S. N. Coppersmith, D. S. Fisher, B. I. Halperin, P. A. Lee, and W. F. Brinkman, Phys. Rev. B 25, 349 (1982).

[12]K. Nakanishi and H. Shiba, J. Phys. Soc. Jpn. 44, 1465 (1978); P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B 19, 1610 (1979); R. M. Fleming, D. E. Moncton, D. B. McWhan, and F. J. DiSalvo, Phys. Rev. Lett. 45, 576 (1980).