MX_3 Compounds (Phase Transition・Charge Density Wave)

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MX_3 Compounds

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The structure and properties of a new class of low dimensional compounds, MX_3, are reviewed. The most interesting phenomena observed in $NbSe_3$ are the anomalous non-linear electrical conductivity below the CDW transition temperatures and the resistivity decrease below 4K under pressure as well as at the atmospheric pressure. The results of diffraction experiments are also summarized.

In the transition-metal trichalcogenides, MX_3, a variety of electronic instabilities are observed systematically, as shown below These compounds have the common structural unit. The metal atom is at

Table 1

NbS_3	TaS_3	$NbSe_3$	$TaSe_3$
triclinic	orthorhombic	monoclinic	monoclinic
$P\bar{1}$	Cmcm	P21/m	P21/m
a= 4.963	a=36.804	a= 10.009	a= 10.042
b= 6.730	b=15.177	b= 3.481	b= 3.495
c= 9.144	c= 3.340	c= 15.629	c= 9.829
β=97.17		β=109.47	β=106.26
α=γ=90			
semicond.	Peierls	CDW's	supercond.
(Peierls?)	210 K	142.58 K	2.3 K
	"$2K_f$"=0.25c*	"$2K_f$"≃0.25b*	

the center of the trigonal prism of chalcogen atoms. The prism is repeated along the direction of the shortest lattice constant (chain axis). It can be found from the table that the sulphides are more low-dimensional than the selenides, and Nb-compounds than Ta-compounds. It is interesting to compare this trend with that found in the transition metal di-chalcogenides. In general MX_3 compounds can be regarded as one-dimensional. But the strong transverse anisotropy cannot be neglected to understand these materials. The rest of this paper is devoted to $NbSe_3$, because of the "2-D" feature.

The electrical resistivity of $NbSe_3$ along the b-axis shows two anomalies at 142 K (T_1) and at 58 K (T_2), as shown in Fig. 1. The Hall coefficient shows similar anomalies at these temperatures.[1) These effects can be explained as due to the decrease of carriers by the partial vanishing of the Fermi surface (CDW formation). The result of the thermopower study supports this argument.[2) The anisotropy of the conductivity has been measured by the microwave technique.[3] The conductivity is 300 - 1200 times larger along the b-axis than perpendicular. The recent dc (Montgomery method) measurement gave a smaller value of ∿16.[4] The latter is the ratio σ_b/σ_c. It is interesting to determine whether the difference is attributed to the apparently small value of the microwave conductivity $\sigma_\perp$, which was deduced from the averaged value in the ac plane. The crystal structure of $NbSe_3$ has the "van der Waals gap" parallel to the bc plane and it is expected that $\sigma_b >> \sigma_c > \sigma_a$. In this sence $NbSe_3$ is often called as 2-D.

Tsutsumi et al. first gave the direct evidence of CDW formation at T_1.[5] From the electron and X-ray diffraction, it was found that the T_1-and T_2-anomalies correspond to the formation of incommensurate CDW's.[5-7] The $\vec{q}$'s are tabulated in Table 2, with other characteristics.

Table 2

transition temperature	CDW's $\vec{q}$	elastic anomaly	specific heat amonaly
T_1 = 142 K	q_1 = 0.244b*	yes	no
T_2= 58 K	q_2 = 0.26b* + 0.50c* (Ref. 6) 0.50a* + 0.26b* + 0.50c* (Ref. 7)	no	yes

Other interesting findings are :

i) that the two CDW's with $\vec{q}_1$ and $\vec{q}_2$ are coexisting below T_2,

ii) that the second harmonics $2\vec{q}_2$ are observed,

iii) no observable change in the $\vec{q}_1$ intensity at T_2,

iv) no change in the $\vec{q}_2$ intensity in the current carring state.[7]

There has been no experiment to observe the harmonics of the type $q_1 \pm q_2$, which are expected to offer the information how the two CDW's are coexisting.

As far as we are aware, there is only one calculation of the band structure.[8] Bullett found that the Fermi level lies between Nb d-band and Se p-band and the density of states is quite small. There has not been yet any experiment to judge his result.

As is well known, the non-linear electrical conductivity is the characteristic of many low-dimensional conductors. In $NbSe_3$ a remarkable non-linear effects have been observed just below T_1 and T_2.[3] The conductivity is expressed as $\sigma = \sigma_0 + \sigma_1 \exp(-E_0/E)$ where the activation field E_0 is temperature dependent. Ong and Monceau found that E_0 has minimum values of ca. 1 v/cm at 120 K and 0.1 v/cm at 50 K.

Furthermore, the activation field is divergent as temperature approaches the transition temperatures from below. Theories published so far have failed to explain quantitatively this unique behavior of the activation field. Ong and Monceau measured the temperature dependence of the microwave conductivity.[3] At 9.3 GHz (38×10^{-6} eV) the two anomalies are nearly vanishing. This problem is still left to be solved.

Monceau et al. found that $NbSe_3$ becomes superconducting under pressure.[9] The transition temperature rises under pressure with the rate of 0.6 K/bar, which is much larger than those found in other materials including layered compounds. Haen et al found a decrease of the resistivity below 2 K at the atmospheric pressure, without any sign of the Meissner effect.[10] On the contrary we could not find any decrease of the resistivity with the current density comparable with Haen's in undoped $NbSe_3$. While trials with several strained specimens were also negative, lightly doped $NbSe_3$ with Zr showed a large decrease of the resistivity. The complete vanishing of the dc resistivity was also observed in a specimen. The details will be published separately.

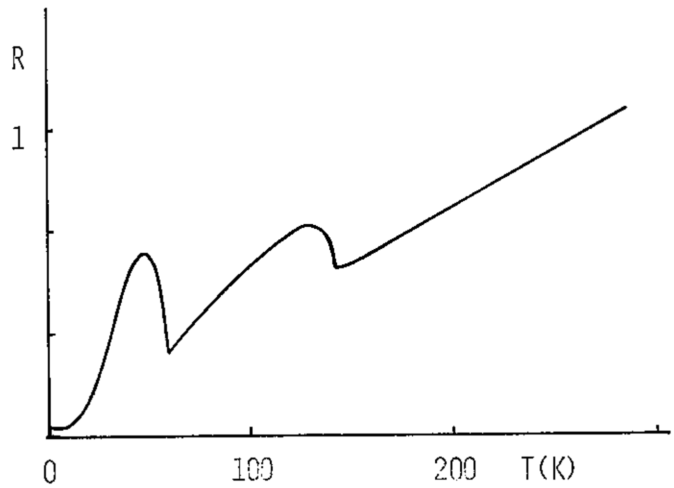

Fig. 1

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