

Metal-insulator transition in $NiS_{2-x}Se_x$ system – volume effect

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It was found that an abrupt volume change occurs associated with metal-to-insulator transition, and that there exists a clear relation between the temperature dependences of the electrical resistivity (ρ) and the thermal expansion coefficient (α) near the transition temperature.

A NiS_{2-x}Se_x system with the pyrite structure shows interesting magnetic and electrical properties from a view point of electron correlations. NiS₂ (x = 0) is a Mott insulator and has a complicated magnetic structure at low temperatures. For a narrow range of x(0.5-0.6), it exhibits a metal-to-insulator transition (MIT) as the temperature is raised. At low temperarures, it is an antiferromagnetic (AF) metal and the MIT occurs in the AF phase. For x > 0.6, it is metallic at all temperatures. There are many substances which exhibit an MIT as the temperature is varied, and they have a volume change of several percent associated with the MIT. So, it is worthwhile to study the relation between the MIT and the volume change. However, since many of them suffer a structural distortion in addition to the volume change, the theoretical interpretation is not so simple. In the present system, associated with the MIT, only a small volume change $(\sim 0.6\%)$ occurs, and neither a structural distortion nor a local crystal distortion occur there [1]. Therefore, the $NiS_{2-x}Se_x$ system is one of the most appropriate substances for the investigation of the MIT. Here, we shall report the observed relation between the temperature dependences of the electrical resistivity and the thermal expansion coefficient.

The samples used here were prepared by sintering the constituent elements (powder, all 99.99% in purity) in an evacuated silica tube at about 700°C for one week. S and Se were added in excess by about 5-10% in order to avoid their decrease due to evaporation during sintering. In some cases, sintering was done two times in order to obtain a homogeneous sample. All samples were examined by X-ray diffraction measurements and confirmed to be of single phase. The composition (x) was determined by the measured lattice parameter. The thus determined value of x was slightly smaller than the nominal value ($\Delta x \sim 0.02$). The electrical resistivity (ρ) was measured by the usual dc four-terminal technique. The thermal expansion was measured by a strain gage (Kyowa KFL-1-C1-11). As an active gage, a quarz plate was used to cancel the temperature variation of the gage resistance.

Some of the experimental results are shown in figs. 1 and 2. As seen in fig. 1, samples with 0.5 < x < 0.6

exhibit a clear MIT as the temperature is raised, the transition temperature (T_1) increasing with x. The change in the resistivity at T_t ($\Delta \rho$) decreases with x and, at the same time, the transition becomes more gradual. The obtained activation energy for the insulating (high-temperature) phase decreases with x and vanishes near $x \sim 0.6$. This fact indicates that the critical concentration for an MIT to occur is equal to 0.6. Fig. 2 shows the relative linear expansion with temperature, which is normalized at RT. As seen, those samples which exhibit an MIT, experience an abrupt volume change near T_1 . It is noted that the amount of volume change depends scarcely on x. Although it seems difficult to determine the definite T_{t} , it was found that if one defines T_t as the temperature at which the derivative d log ρ/dT has a maximum, then thus determined T_t agrees well, within experimental errors, with the temperature at which d log L/dT (= α) has a maximum. That is, the MIT is considered to correspond to the abrupt change in volume. Further, it



Fig. 1. Temperature dependences of the electrical resistivity for samples with various x's.



Fig. 2. Linear thermal expansion for samples with various x's.

was found that the relation

$$d \log \rho / dT = k\alpha^2 \tag{1}$$

holds well near T_t . Here, k is ~ 1.2×10^7 K and common for different samples. Fig. 3 shows the log-log plot of the maximum of d log ρ/dT against the maximum of α for various samples. Fig. 4 shows an example of the temperature variations of d log ρ/dT and α^2 for the x = 0.52 sample around T_t (the temperature scale for α^2 is shifted by 3 K for comparison).



Fig. 3. Log-log plot of the maximum value of the thermal expansion coefficient ($\alpha = dL/dT/L$) and that of $d \log \rho/dT$ for various samples exhibiting an MIT.



Fig. 4. Temperature dependences of d log ρ/dT and α^2 around T_1 for the x = 0.52 sample.

The above mentioned results imply that the MIT is closely related to the volume change. Kawabata [2] proposed a theory which involves a coupling between the bare-band width and the sample volume. And he showed that an MIT can occur in the first order for some range of parameters included in the theory. The above obtained relation (1) may give a key to the form of the coupling between band width and volume, or more generally to the relation between MIT and volume change. Recently, Fujimori [3] suggested, from his XPS measurements, that the band gap in NiS₂ is of the charge transfer type rather than of the Hubbard type. In this case, the volume change will occur so as to open the charge transfer gap as the temperature is raised.

In conclusion, it was found that there exists a clear relation between the MIT and the volume change for the NiS_{2-x}Se_x system with x = 0.5-0.6. This relation may give a key to the theoretical interpretation.

The present authors are much indebted to Prof. A. Fujimori for valuable discussions, and also thank T. Oguchi for measurements.

References

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