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The low-temperature specific heat of FeS and $M_{0.875}X$ (M = Fe, Co; X = S, Se) with a NiAs-like structure

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Abstract. We have measured the specific heat of FeS, $Fe_{0.875}X$, and $Co_{0.875}X$ (X = S, Se) compounds with a NiAs-like structure over the temperature range from 2 to 30 K. It was found that the ground state of FeS has an insulating character. The opening up of a gap in the density of states is probably caused by electron correlation. Two types of superstructure are known to occur due to ordering of vacancies at iron sites in $Fe_{0.875}X$; one is a 3c structure and the other a 4c structure. The γ-values obtained for 3c structure are about 10% larger than those of 4c structures. Accordingly, this result indicates that the electronic structure of $Fe_{0.875}X$ should be sensitive to the ordered structure of the vacancies. Since the γ-values obtained for non-stoichiometric compounds are larger than the calculated ones, there is electron effective-mass enhancement in non-stoichiometric compounds. Moreover comparison of the observed and calculated electronic contributions to the low-temperature specific heat suggests that the mass enhancement in Pauli-paramagnetic $Co_{0.875}X$ is larger than that in ferrimagnetic $Fe_{0.875}X$.

1. Introduction

The 3d-transition-metal chalcogenides and pnictides with a NiAs-like structure exhibit wide varieties of magnetic and electrical properties. Recently, the electronic states of 3d-transition-metal chalcogenides have been intensively studied by means of Mössbauer spectroscopy and neutron diffraction under pressure [1–4], and photoemission and inverse-photoemission spectroscopy [5, 6]. We have measured the de Haas–van Alphen (dHvA) effect for Pauli-paramagnetic NiAs and CrP using high-quality single crystals [7–9]. The electronic band structures were calculated using a linearized augmented-plane-wave (LAPW) method [8–12]. There is a good correspondence between the results of the dHvA effect measurements and theoretical calculation. On the other hand, a comparison between the observed photoemission spectra and the calculated band structures suggests the importance of electron correlation. Zaanen, Sawatzky, and Allen (ZSA) have developed a general framework for 3d-transition-metal chalcogenides and oxides [13] where the electron correlation plays an important role in the electronic properties. According to the ZSA scheme, the electronic ground states of these compounds may be classified into four types according to the relative magnitudes of the ligand-to-metal charge-transfer energy, the on-site Coulomb energy, and the bandwidth—that is, the p- or d-type metallic state and the Mott–Hubbard or charge-transfer-type insulating state.

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Under ambient conditions, the stoichiometric FeS compound has a troilite crystal structure which is closely related to the NiAs-type one, and it is an antiferromagnetic semiconductor. The phase transition from the troilite to the NiAs-type structure occurs at about 420 K [14,15]. The 3d-transition-metal chalcogenides have a substantial deficiency in metal sites and form various kinds of superstructure due to the ordering of the vacancies. One of single phases in the $Fe_{1-\delta}S$ system was found in a range around ($\delta\sim$) 0.25. $Fe_{0.875}X$ (X = S and Se) compounds are ferrimagnetic with $T_c = 578$ and 450 K, respectively [16] and the fundamental crystal structure is the NiAs-type one, where a quarter of the iron sites in alternative c-planes are vacant and the composition can be represented as Fe_7X_8. Two types of superstructure are known to occur due to ordering of the vacancies. One is a 3c-type Fe_7X_8 structure with a hexagonal symmetry [17, 18] and the other is a 4c-type Fe_7X_8 structure where the symmetries of Fe_7S_8 and Fe_7Se_8 are monoclinic and triclinic, respectively [19,20]. Resistance measurements on $Fe_{0.875}S$ using natural crystals showed that the resistance remains almost constant as temperature varies [21]. According to the electrical resistivity measurements for single-crystal 3c- and 4c-type $Fe_{0.875}Se$ compounds [22], the resistivity in 4c-type $Fe_{0.875}Se$ shows metallic behaviour and decreases rapidly below about 50 K along both the b- and c-axes. The temperature dependence of the resistivity for 3c-type $Fe_{0.875}Se$ along the b-axis is similar to those of 4c-type $Fe_{0.875}Se$, but that along the c-axis indicates a minimum at around 50 K. $Co_{0.875}X$ compounds are Pauli-paramagnetic metals and the c-values are about 10% smaller than those of the iron compounds.

It was indicated that the FeS, $Fe_{0.875}X$, and $Co_{0.875}X$ compounds belong at the boundary between the metallic and insulating states in the ZSA scheme [13]. We have measured the low-temperature specific heat for these compounds and we discuss these ground states and the effects of electron correlation caused by the electronic contribution to the low-temperature specific heat.

2. Experimental procedure

Polycrystalline samples were prepared using the following procedure. Appropriate amounts of the starting materials Fe, Co (99.998% purity) and S, Se (99.9999% purity) were sealed in an evacuated silica tube and then were heated to 900 °C for several days; the product was ground in an Ar atmosphere and kept at 900 °C for several more days. Sulphur or selenium vapour reacted with the iron or cobalt block completely during these processes. The stoichiometric FeS and $Co_{0.875}X$ (X = S, Se) compounds were produced by slow cooling from 800 °C. The $Fe_{0.875}X$ (X = S, Se) compounds were yielded by two different procedures. One was a slow cooling from 800 °C and the other was a quenching from 500 °C.

The samples obtained were analysed by means of x-ray diffraction using Cu Kα radiation. The specific heat measurements were carried out over the temperature range from 2 to 20 K at a rate of increase of about 3 K h^{-1} using an adiabatic method with a mechanical heat switch [23]. The samples used have bulk form, with about 6 mm diameter and 4 mm thickness.

3. Experimental results and discussion

The samples, except $Co_{0.875}Se$, were confirmed to be single phase, by powder x-ray diffraction. Figure 1 shows typical x-ray diffraction patterns of the 3c- and 4c-type structures. The diffraction lines indicated by arrows are fundamental ones arising from the NiAs-type structure and all other lines are caused by the superstructures due to the ordering of the vacancies. As seen in figure 1, the symmetry of the 3c structure is hexagonal and that of the 4c structure
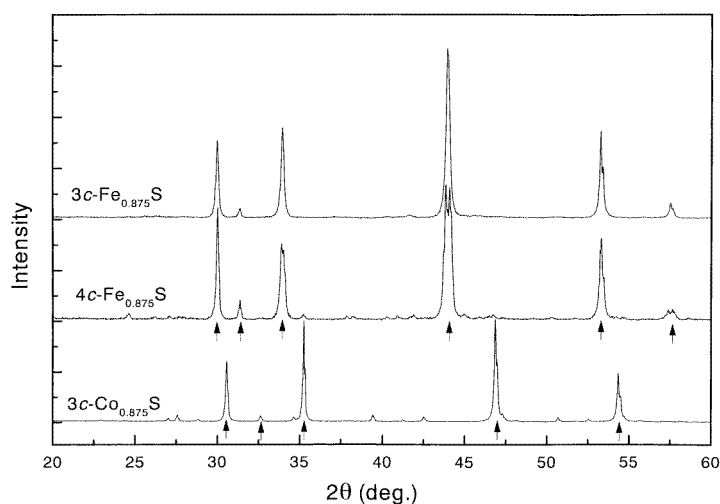
Figure 1. Three typical x-ray diffraction patterns for the 3c- and 4c-type structures obtained using Cu Kα radiation. The diffraction lines indicated by arrows are fundamental ones arising from the NiAs-type structure and all other lines are caused by the superstructures due to the ordering of the vacancies.

is lower than hexagonal symmetry, since it was observed that the fundamental lines split. $Fe_{0.875}S$ and $Fe_{0.875}Se$ samples produced by the quenching method have the 3c-type structure, and $Fe_{0.875}S$ and $Fe_{0.875}Se$ samples produced by the slow-cool procedure have the 4c-type structure. $Co_{0.875}S$ was found to have a 3c-type structure with a hexagonal symmetry which is similar to the structure of 3c-$Fe_{0.875}S$. It was established that the 3c and 4c structures are mixed in the $Co_{0.875}Se$ sample. The diffraction patterns of three compounds with the 3c structure were analysed on the basis of the $P3_121$ space group. The lattice parameters obtained for 3c-$Fe_{0.875}S$ and 3c-$Fe_{0.875}Se$ are in good agreement with those in previous reports [17, 18]. The diffraction patterns of 4c-$Fe_{0.875}S$ and 4c-$Fe_{0.875}Se$ were analysed on the basis of monoclinic and triclinic symmetries, respectively, which were indicated for single-crystal samples by x-ray diffraction [19, 20]. Since 3c and 4c structures are mixed in $Co_{0.875}Se$ samples, only the fundamental diffraction lines were analysed on the basis of the $P6_3/mmc$ space group. The lattice parameters and inter-axis angles obtained are listed in table 1. The lattice parameter c of the NiAs-type unit cell for $Co_{0.875}X$ is about 10% smaller than that for $Fe_{0.875}X$, although the a-value of the NiAs-type unit cell for $Co_{0.875}X$ is at least 1% smaller than that for $Fe_{0.875}X$.

Table 1. The lattice parameters, A, B, and C, and inter-axis angles, α, β, and γ, obtained; the error estimates are given in parentheses.

	A (Å)	B (Å)	C (Å)	α (deg)	β (deg)	γ (deg)
FeS	5.969(1)	—	11.740(1)	90	90	120
3c-$Fe_{0.875}S$	6.975(1)	—	17.096(1)	90	90	120
4c-$Fe_{0.875}S$	11.886(2)	6.868(2)	22.831(5)	90	90.4(2)	90
3c-$Co_{0.875}S$	6.746(1)	—	15.517(1)	90	90	120
3c-$Fe_{0.875}Se$	7.244(1)	—	17.671(1)	90	90	120
4c-$Fe_{0.875}Se$	12.546(2)	7.243(2)	23.555(5)	89.8(5)	89.9(5)	90.0(5)
$Co_{0.875}Se$†	3.600(1)	—	5.267(1)	90	90	120

† Only the fundamental diffraction lines were analysed on the basis of the $P6_3/mmc$ space group.

Figure 2 shows the low-temperature specific heat, C, of FeS, $Fe_{0.875}X$, and $Co_{0.875}X$ compounds, plotted as C/T versus T^2. The magnetic excitation in the Fe compounds does not contribute to the low-temperature specific heat, since these magnetic ordering temperatures are far above the temperature range of the measurements. Thus, the specific heat of these compounds at low temperature is written as $C = \gamma T + AT^3$, where the first and second terms represent the electronic and lattice contributions, respectively. The temperatures at which the Debye T^3-approximation remains appropriate for the lattice heat capacity are quite low. It may be necessary to keep samples below about $\Theta_D/50$ to get reasonably pure T^3-dependence, where Θ_D is the Debye temperature. Since the experimental results indicate good linear relations between C/T and T^2 as shown in figure 2, the γ- and A-values are estimated for $Fe_{0.875}X$ and for FeS and $Co_{0.875}X$ over the temperature ranges from 2 to 5 K and from 2 to 8 K, respectively. The Θ_D values are obtained from the A-values using

$$A = \frac{12\pi^4}{5} \frac{nk_B}{\Theta_D^3}$$

where n is the atomic number per molecule. The results are summarized in table 2. These temperature ranges used to estimate the γ- and A-values almost satisfy the temperature condition for getting reasonably pure T^3-dependence.

Table 2. Coefficients of the electronic and lattice contributions to the low-temperature specific heat, γ and A, and the Debye temperature, Θ_D; the error estimates are given in parentheses. The γ_{cal}^n- and γ_{cal}^m-values were estimated from the calculated $D(E_F)$ values for non-magnetic and magnetic states, respectively [10–12].

	γ (mJ K^{-2} mol^{-1})	A (mJ K^{-4} mol^{-1})	Θ_D (K)	γ_{cal}^n (mJ K^{-2} mol^{-1})	γ_{cal}^m (mJ K^{-2} mol^{-1})	γ/γ_{cal}
FeS	0.2(1)	0.122(2)	317(2)	8.06 [10]	3.70 [10]	0.05
3c-$Fe_{0.875}S$	17.20(3)	0.181(2)	270(2)	5.89 [11, 12]	5.69 [11, 12]	3.02
4c-$Fe_{0.875}S$	13.95(3)	0.118(2)	313(2)	5.89 [11, 12]	5.69 [11, 12]	2.45
3c-$Fe_{0.875}Se$	10.71(3)	0.365(2)	215(2)	6.54 [11, 12]	6.97 [11, 12]	1.54
4c-$Fe_{0.875}Se$	9.24(4)	0.239(2)	248(2)	6.54 [11, 12]	6.97 [11, 12]	1.33
3c-$Co_{0.875}S$	12.40(6)	0.105(1)	326(2)	4.04 [11, 12]	—	3.07
$Co_{0.875}Se$	12.33(6)	0.158(2)	289(2)	4.45 [11, 12]	—	2.77

The γ-value obtained for FeS is 0.2 ± 0.1 mJ K^{-2} mol^{-1}, which is about two orders of magnitude smaller than those of the other six compounds. The observed heat capacities of FeS, obtained using about 2 g, are comparable with those of the sample holder of our experimental apparatus over the temperature range between 2 and 8 K. On the other hand, it was found from the temperature dependence of the conductivity for $Fe_{0.9996}S$ single crystal [15] that FeS in the troilite phase is a p-type semiconductor with a band-gap of 40 meV. The observed small finite γ-value of FeS is most probably caused by the experimental difficulty of measuring small specific heats. Thus we conclude that the correct γ-value of FeS is zero.

As shown in figure 2 and table 2, the γ-values obtained for $Fe_{0.875}X$ and $Co_{0.875}X$ lie in the range from 9 to 17 mJ K^{-2} mol^{-1}. Thus the electronic ground states have metallic characters. These results are qualitatively consistent with those from previous resistance [21, 22] and recent photoemission experiments [5]. It is noticed that there are significant differences in the values of γ and Θ_D between the 3c and 4c structures of $Fe_{0.875}X$. The γ-value obtained for 3c-$Fe_{0.875}X$ is about 10% larger than that of 4c-$Fe_{0.875}X$. It was found that there is a sharp bend in the pressure dependences of the lattice parameters for 3c- and 4c-$Fe_{0.875}S$ at 4.5 and 6.2 GPa, respectively [2, 24]. The temperature dependence of the resistivity along
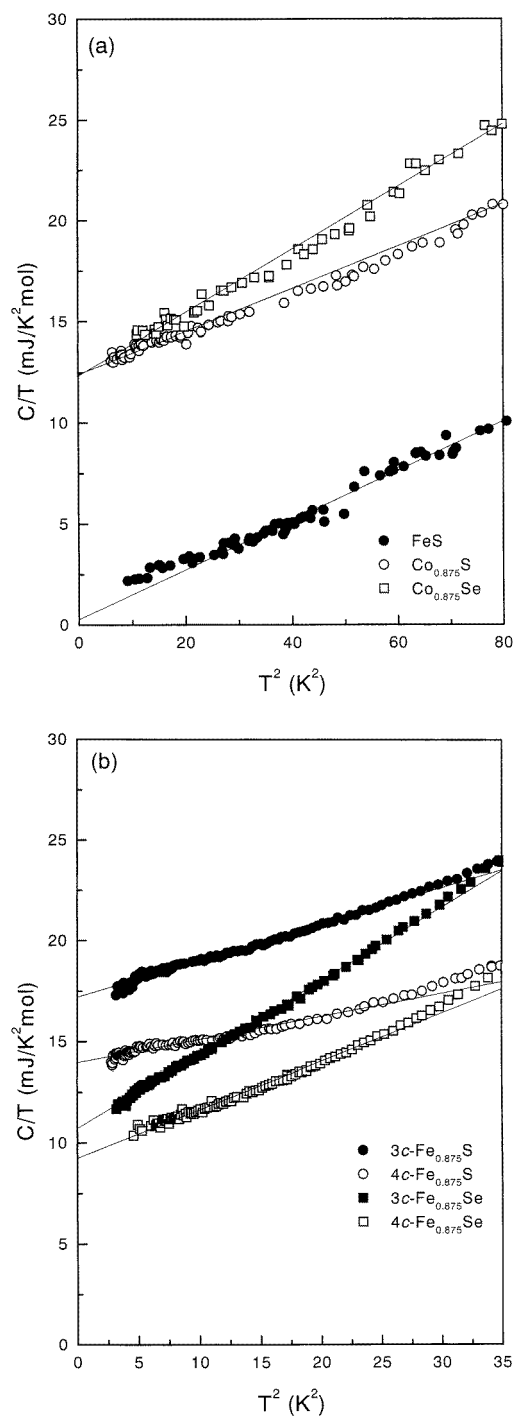
Figure 2. The low-temperature specific heat, C, of FeS and Co$_{0.875}$X (a) and Fe$_{0.875}$X (b) (X = S, Se) plotted as C/T versus T^2. The solid lines represent the results of fitting.

the c-axis of 3c-$Fe_{0.875}Se$ is quite different from that of 4c-$Fe_{0.875}Se$ [22]. Accordingly, these results indicate that the electronic structure of $Fe_{0.875}X$ should be sensitive to the ordering and periodicity of vacancies at iron sites. As summarized in table 2, the γ-value of $Co_{0.875}S$ is almost the same as that of $Co_{0.875}Se$. However, the γ-value of $Fe_{0.875}S$ is larger than that of $Fe_{0.875}Se$, which suggests that the electron correlation in $Fe_{0.875}S$ is different from that in $Fe_{0.875}Se$.

We discuss the effect of electron correlation, because the $Fe_{0.875}X$ and $Co_{0.875}X$ compounds are metallic and belong at the boundary between the metallic and insulating states. The first-principles electronic band structures obtained using the LAPW method [11,12] were calculated for $Fe_{0.875}S$, $Fe_{0.875}Se$, and $Co_{0.875}Se$ on the assumption of a hypothetical $(2a \times 2a \times 1c)$-type superstructure, where a and c denote the lattice constants of the NiAs-type structure. The γ_{cal}^{n}-values of $Fe_{0.875}S$ and $Fe_{0.875}Se$ for the non-magnetic state are estimated to be 5.89 and 6.54 mJ K^{-2} mol^{-1} from the calculated $D(E_F)$ values of 2.50 and 2.77 states eV^{-1}/formula, respectively. As shown in table 2, the γ_{cal}^{m}-values for the ferrimagnetic state are almost the same as those for the non-magnetic state; the γ_{cal}-value of $Fe_{0.875}Se$ is larger than that of $Fe_{0.875}S$. Accordingly, the ratios of the experimental and calculated γ-values, γ/γ_{cal}^{m}, for 3c- and 4c-$Fe_{0.875}S$ are about double those for 3c- and 4c-$Fe_{0.875}Se$, respectively. It is suggested that the effect of electron correlation in $Fe_{0.875}S$ is stronger than that in $Fe_{0.875}Se$. This stronger electron correlation effect in $Fe_{0.875}S$ was also observed in the high-resolution photoemission spectrum, where the broadening of the spectrum near E_F is more significant for 3c-$Fe_{0.875}S$ than for 4c-$Fe_{0.875}Se$ [5].

The values of γ/γ_{cal}^{n} are evaluated to be 3.07 for $Co_{0.875}S$ and 2.77 for $Co_{0.875}Se$, for which the ground states are Pauli paramagnets. Moreover, these values are larger than those of $Fe_{0.875}S$ and $Fe_{0.875}Se$, respectively. These facts suggest that the electron effective-mass enhancements in $Co_{0.875}S$ and $Co_{0.875}Se$ are larger than those in $Fe_{0.875}S$ and $Fe_{0.875}Se$. This result is in agreement with the results of a recent photoemission study of $Fe_{0.875}Se$ and $Co_{0.875}Se$ [6] where the effective-mass enhancements of $Fe_{0.875}Se$ and $Co_{0.875}Se$ were evaluated to be about 1.7 and 2.1, respectively.

The electronic band structure of FeS was also calculated using the LAPW method for the NiAs-type structure [10], which is a high-temperature phase of FeS [14]. The calculated $D(E_F)$ value for the non-magnetic and antiferromagnetic states is finite; the corresponding γ_{cal}-values are listed in table 1. Above 420 K, FeS has the NiAs-type structure and the conductivity is high, like that of a metal [15]. This fact is consistent with the calculated result. Although the electron correlations could possibly account for the opening up of a gap in $D(E)$ in the troilite-structure phase of FeS, we wish to calculate the electronic band structure with the troilite structure.

In conclusion, we have measured the specific heat of FeS, $Fe_{0.875}X$, and $Co_{0.875}X$ (X = S, Se) compounds over the temperature range from 2 to 30 K. Since the electronic contribution to the low-temperature specific heat of FeS is almost zero, the ground state has an insulating character. The opening up of a gap in $D(E)$ is probably caused by the electron correlation. In other non-stoichiometric compounds, there is a finite electronic contribution to the specific heat and thus their ground states have metallic character. In $Fe_{0.875}X$ compounds, the γ-values obtained for 3c structures are about 10% larger than those for 4c structure. Accordingly, the electronic structure of $Fe_{0.875}X$ should be sensitive to the ordering and periodicity of vacancies at iron sites. There are electron effective-mass enhancements in non-stoichiometric compounds owing to the electron correlation, since the γ-values obtained for non-stoichiometric compounds are larger than the calculated ones. In spite of the fact that $Co_{0.875}X$ is a Pauli paramagnet, the mass enhancement in $Co_{0.875}X$ is larger than that in $Fe_{0.875}X$.

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