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Electron transport in Chevrel phase superconductors, $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $0 \leqslant y \leqslant 8$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$, $0 \leqslant y \leqslant 4$— Fit to Cote-Meisel theory

V SANKARANARAYANAN, G RANGARAJAN and R SRINIVASAN
Department of Physics, Indian Institute of Technology, Madras 600 036, India

Abstract. Normal state electrical resistivity of the Chevrel phase compounds of the type $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $0 \leqslant y \leqslant 8$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$, $0 \leqslant y \leqslant 4$ is analysed on the basis of the generalized diffraction model which incorporates a postulate on electron-phonon interaction, *viz* phonons with wavelength exceeding the electron mean-free path are ineffective electron scatterers. Fit obtained by this model was found to be superior to other models based on the interband *s–d* scattering of electrons.

Keywords. Chevrel phase superconductors; electrical resistivity; Cote-Meisel theory.

1. Introduction

Sankaranarayanan *et al* (1984) measured the electrical resistivity of the Chevrel phase compounds $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$ ($0 \leqslant y \leqslant 8$) in the form of sintered pellets from 300 K down to the super-conducting transition temperature. The temperature variation of electrical resistivity, normalised to the value at 300 K, showed systematic variation with the composition y. In all these compounds, below about 30 K, the normalised electrical resistivity varies linearly with the square of the absolute temperature and shows a tendency towards saturation at high temperature. The results were analysed in terms of the models of Woodard and Cody (1964), Milewits *et al* (1976) and Morton *et al* (1978). It was observed that the Morton's model in which the lower limit, θ_0/T, of the transport theory integral

$$J_r(T) = \int_{\theta_0/T}^{\theta_D/T} \frac{y^r \, dy}{(e^y - 1)(1 - e^{-y})}, \tag{1}$$

was taken to be non-zero, gave a physically meaningful fit to the resistivity data. Here, θ_D is the Debye temperature and θ_0 is a measure of the minimum phonon energy needed for *s–d* scattering of electrons. Both θ_D and θ_0, obtained from a fit to the resistivity data, decreased as more and more selenium was substituted for sulphur. The values of θ_D obtained from the above fit agreed with the value for $Cu_{1\cdot8}Mo_6S_8$ determined by Morohashi *et al* (1981) and for $Cu_{1\cdot8}Mo_6S_1Se_7$ determined by Vasudeva Rao (1983) from specific heat measurements. The RMS deviation between the calculated and experimental values was less than 2% in all the cases. However, systematic deviations were observed at low temperatures, the experimental values being more than the calculated values. This could indicate an additional scattering mechanism, which in view of the T^2 dependence of the normalised electrical resistivity at low temperatures may be due to the electron-electron scattering mechanism suggested by Baber (1937).

In the present paper, we report the resistivity measurements on $Cu_{1.8}Mo_6S_{8-y}Te_y$, $0 \leqslant y \leqslant 4$. None of the above models is able to explain the data on the above compounds. On the other hand, the Cote-Meisel (1977) model, based on the diffraction model due to Ziman with the inclusion of the Ziman-Pippard condition, not only gives a satisfactory explanation for the results of the tellurium substituted compounds; but also gives a better fit than the model proposed by Morton *et al* (1978) for the selenium substituted compounds.

2. Experimental results

The preparation and the technique used to measure the electrical resistivity of the Chevrel phase compounds have already been described in an earlier paper (Sankaranarayanan *et al* 1982, 1984). Figure 1 shows the electrical resistivity of $Cu_{1.8}Mo_6S_{8-y}Te_y$ for $0 < y \leqslant 4$. The resistivity in each case is normalised to the value at 300 K. Figures 2 and 3 show plot of normalised resistivity as a function of T^2 at low temperature. The linear relation between resistivity and T^2 is apparent from the figures and is similar to the behaviour observed in the selenium substituted compounds

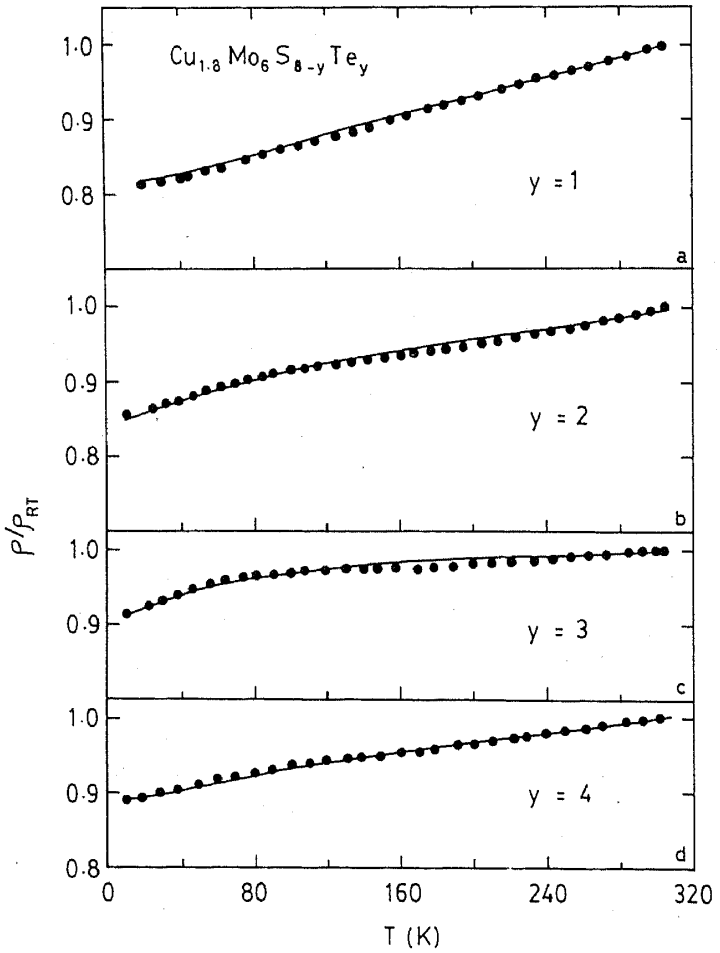

Figure 1. Variation of normalised electrical resistivity of $Cu_{1.8}Mo_6S_{8-y}Te_y$, $1 \leqslant y \leqslant 4$ as a function of temperature, points-experimental, continuous curve-fitted to Cote-Meisel theory.

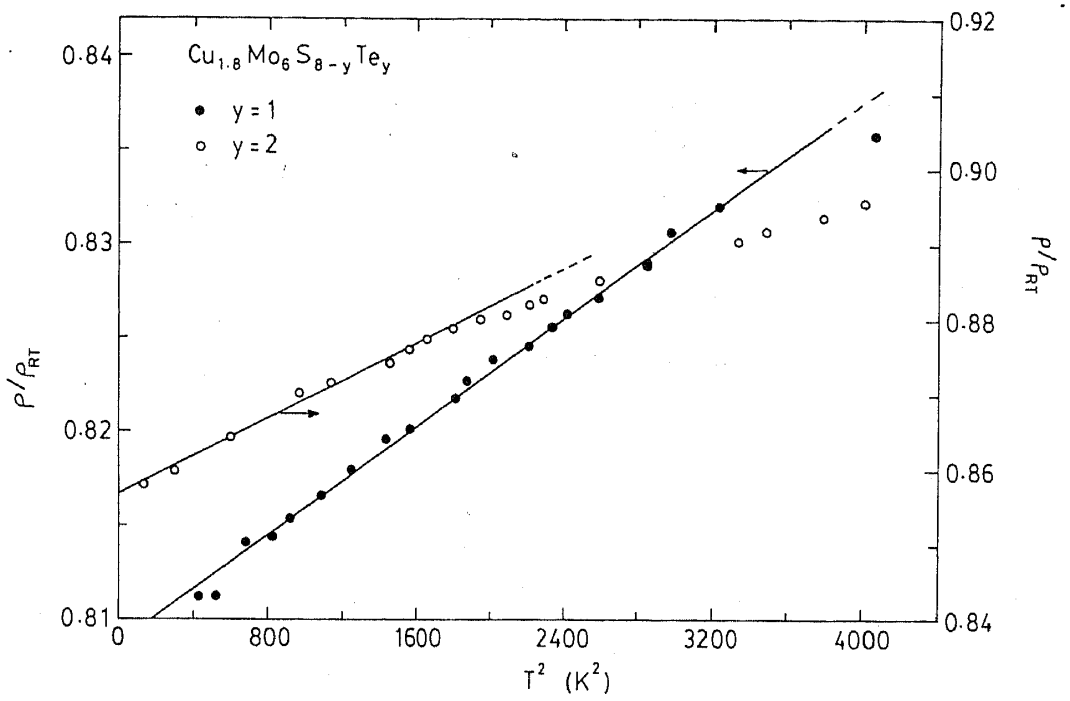

Figure 2. Variation of normalised electrical resistivity of $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$ as a function of square of the temperature for $y = 1$ and 2.

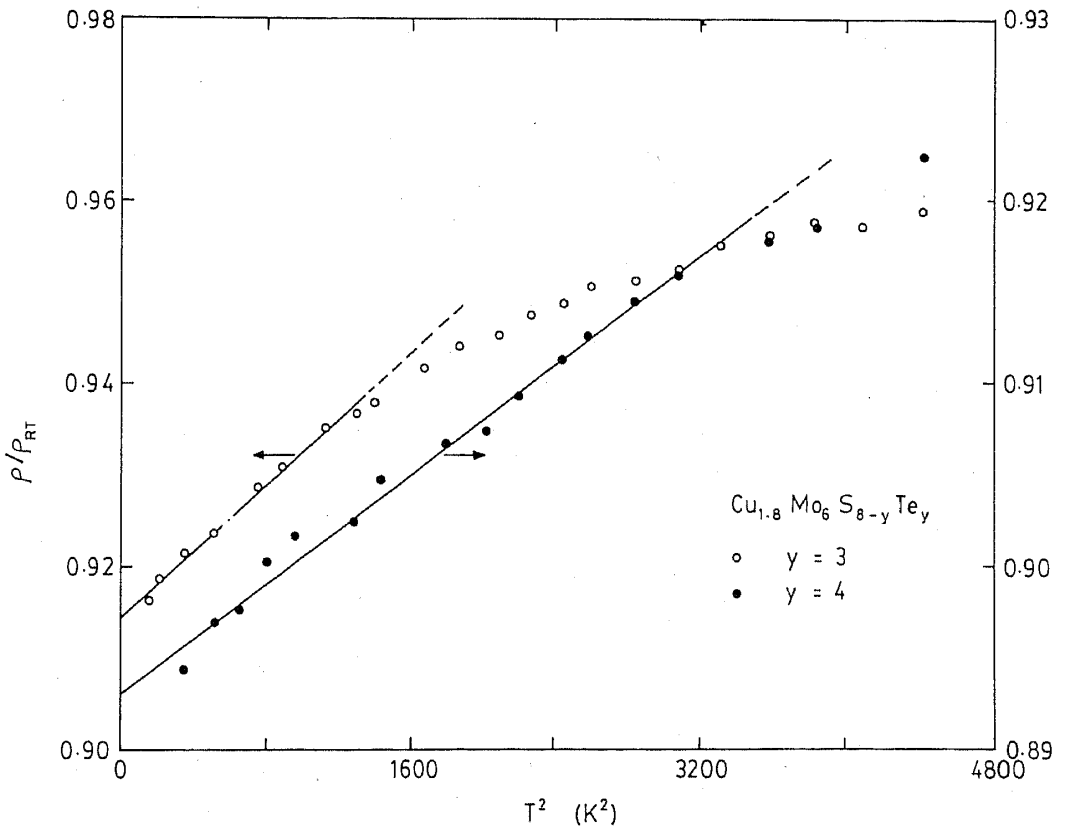

Figure 3. Variation of normalised electrical resistivity of $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$ as a function of square of the temperature for $y = 3$ and 4.

(Sankaranarayanan *et al* 1984). An attempt was made to fit the experimental data on the tellurium-substituted compounds to the models suggested by Woodard and Cody (1964), Milewits *et al* (1976) and Morton *et al* (1978). However, no physically meaningful fit could be obtained as the electron-phonon interaction constant for intra and interband scattering in the resistivity expression on these models came out to be negative. Hence, it was thought that to try out a different model for resistivity proposed by Cote and Meisel (1978) from the Ziman (1961) diffraction model for liquid metals. This model was observed to be applicable to amorphous and disordered crystalline materials. Later, Cote and Meisel were able to fit the electrical resistivity of the A-15 superconductors such as Nb_3Sn on the basis of the above theory.

3. Electron transport in high resistivity metals

Mooij (1972) studied a wide variety of amorphous and crystalline materials containing transition metals and found that there exists a correlation between the temperature coefficient of electrical resistivity and the electrical resistivity. The main outcomes of the Mooij correlation are: (i) in high resistivity materials with electrical resistivity, $\rho > 100$ μohm cm, ρ is found to be insensitive to the details of the electronic structure and atomic arrangements, (ii) the compounds having $\rho > 150$ μohm cm, have a negative temperature coefficient for the electrical resistivity; and (iii) all alloys, irrespective of the value of electrical resistivity, exhibit a temperature-independent electrical resistivity at high temperature and this property is known as 'saturation' of electrical resistivity.

Most of the features, observed by Mooij, have been successfully explained in the framework of the theory developed by Cote and Meisel (1977). Using the above theory, Cote and Meisel were able to account for the temperature dependence of electrical resistivity of amorphous transition metals. According to their theory, the expression for electrical resistivity can be written as the sum of the 'structure scattering' term and 'thermal scattering' term. This is given by

$$\rho = \rho_1 + \rho_2, \tag{2}$$

where ρ_1 is the structure scattering component given by

$$\rho_1 = C \int_0^1 \mathrm{d}(\mathbf{K}/2k_f)(\mathbf{K}/2k_F)^3 a(\mathbf{K}) |t(\mathbf{K})|^2 \exp[-2W(\mathbf{K})], \tag{3}$$

and ρ_2 is the thermal scattering term given by

$$\rho_2 = CD(T/\theta_D)^2 \int_0^1 \mathrm{d}(\mathbf{K}/2k_F)(\mathbf{K}/2k_F)^3 \times A^{\rho}(\mathbf{K}) |t(\mathbf{K})|^2 J_2(\theta_D/T) \exp[-2W(\mathbf{K})], \tag{4}$$

where $C = 12\pi\Omega_0/e^2\hbar v_F^2$ and $D = 3\hbar^2K^2/Mk_B\theta_D$. Here $\exp(-2W(\mathbf{K}))$ represents the Debye-Waller factor, $A^{\rho}(\mathbf{K})$ is the averaged electrical resistivity structure factor, θ_D is the Debye temperature v_F is the Fermi velocity and M is the ionic mass. The integral

$J_2(T)$ is given by

$$J_2(x) = \int_0^x \frac{x^2\,dx}{(e^x-1)(1-e^{-x})}. \tag{5}$$

At high temperature, $T \gg \theta_D$, $J_2(x)$ tends to behave as x and the electrical resistivity should vary as T/θ_D^2. On the other hand, in the low temperature range, $T \ll \theta_D$, $J_2(x)$ attains a constant value of 3·29 and the electrical resistivity varies as T^2/θ_D^3. Hence, according to this theory, the electrical resistivity of amorphous and disordered crystalline materials should vary as T at high temperature and as T^2 at low temperature. This behaviour is observed only in the materials with $\rho < 50$ μohm cm. However, when ρ exceeds this limit the electrical resistivity tends to saturate at high temperature instead of having linear temperature dependence.

Cote and Meisel (1978) were also able to explain this property of saturation of electrical resistivity in the high resistivity materials by invoking an important postulate due to Pippard and Ziman. According to this interaction postulate, phonons with wavelengths exceeding the electron mean free path, Λ, are ineffective in electron scattering. The effect of this postulate is to have a low frequency cut-off in the integral over the phonon spectrum which occurs in the diffraction model. According to this postulate, for a Debye spectrum of phonons, the electron-phonon interaction becomes zero for $\Lambda \geqslant 2\pi/q_D$, q_D being the Debye wavenumber. This is due to the fact that the electron mean-free path becomes comparable to the interatomic spacing. Hence once this limit is attained further scattering of electrons by phonons does not occur. Then the electrical resistivity *vs* temperature exhibits a saturation at high temperature. On the above basis the expression for electrical resistivity in high resistivity metal is given by

$$\rho/\rho^* = [\rho_{ip}/\rho^* + \rho_0 \exp(-2W^*)/\rho^*]\,(\rho_{ip}/\rho^* + 1)^{-1}, \tag{6}$$

where ρ^* is the saturation resistivity and $\exp(-2W^*)$ is the averaged Debye-Waller factor and ρ_{ip} is the ideal one-phonon resistivity given by,

$$\rho_{ip} = \beta(T/\theta_D)^2 \int_0^{\theta_D/T} (x^2/(e^x-1)(1-e^{-x}))\,dx$$

$$= \beta f(T), \tag{7}$$

where β is a constant. According to (6), the electrical resistivity tends to saturate at high temperature and varies as T^2 at low temperature $T \ll \theta_D$.

3. Applicability of the Cote-Meisel theory to the Chevrel phase compounds under study

It has been observed that in these solid solutions the substitutional disorder plays the same role as the disorder due to radiation damage which causes the temperature coefficient of electrical resistivity to decrease. In figure 4 is shown the temperature coefficient of electrical resistivity at 250 K as a function of normalised residual electrical resistivity for the compounds, $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $0 \leqslant y \leqslant 8$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$, $0 \leqslant y \leqslant 4$. The correlation obtained is very similar to that obtained by Mooij. In addition to all the above facts both selenium and tellurium-substituted compounds exhibit a T^2 dependence of electrical resistivity at low temperature. Since this T^2

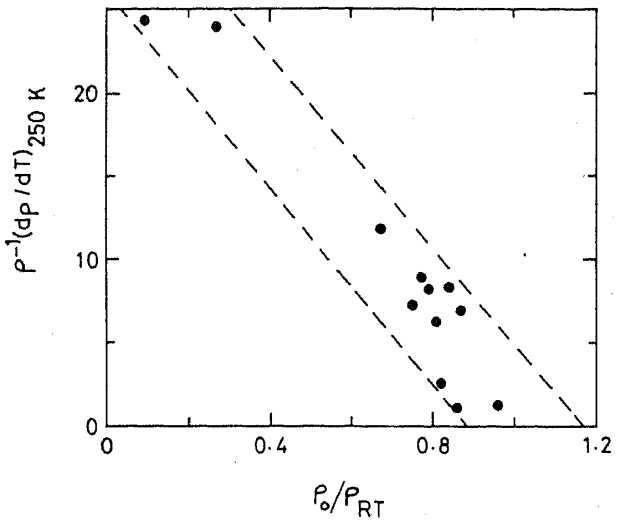

Figure 4. Plot of ρ^{-1} (dρ/dT) at 250 K as a function of residual resistivity ratio ρ_0/ρ_{RT}.

dependence follows as a natural consequence of the Cote-Meisel theory, it was decided to analyse the electrical resistivity data on these compounds on the basis of this theory.

4. Analysis of electrical resistivity of $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$ on the basis of the Cote-Meisel theory

Equation (6) was used in the following analysis. As a first approximation the Debye-Waller factor was assumed to be unity and (6), after substituting for ρ_{ip}, can be rewritten as

$$\rho = (\beta f(T)+\rho_0)/(1+\beta f(T)/\rho^*)$$
$$= [(\beta'/\theta_D^2)f(T)+\rho_0]/[1+\beta' f(T)/\rho^*\theta_D^2], \quad (8)$$

where $\beta' = \beta\theta_D^2$.

Equation (8) can be reduced to the form

$$(\rho-\rho_0)/\rho f(T) = (\beta'/\theta_D^2)[(1/\rho)-(1/\rho^*)]. \quad (9)$$

Hence, if the Cote-Meisel model is valid for these compounds, the plot of $(\rho-\rho_0)/\rho f(T)$ *vs* $1/\rho$ should be a straight line and from the slope and the intercept of the graph β' and ρ^* can be determined. In the present analysis for selenium-substituted compounds, the θ_D values were assumed to be the same as that used in the transport theory integral in the model proposed by Morton *et al* (1978). In figures 5 and 6, are shown the variation of $(\rho-\rho_0)/\rho f(T)$ with ρ_{RT}/ρ for the compounds, $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $y = 0$, 0·5, 1 and 8, where the overall electrical resistivity variation with temperature is relatively more. In all the above cases the plot obtained was linear. In the case of compounds with $y = 0$, 0·5 and 8 which exhibit a structural transformation at about 270, 240 and 170 K respectively (Sankaranarayanan *et al* 1984), the linear plot was obtained only upto the structural transformation temperature. From the straight line fit to the observed data, the values of β' and ρ^* were obtained.

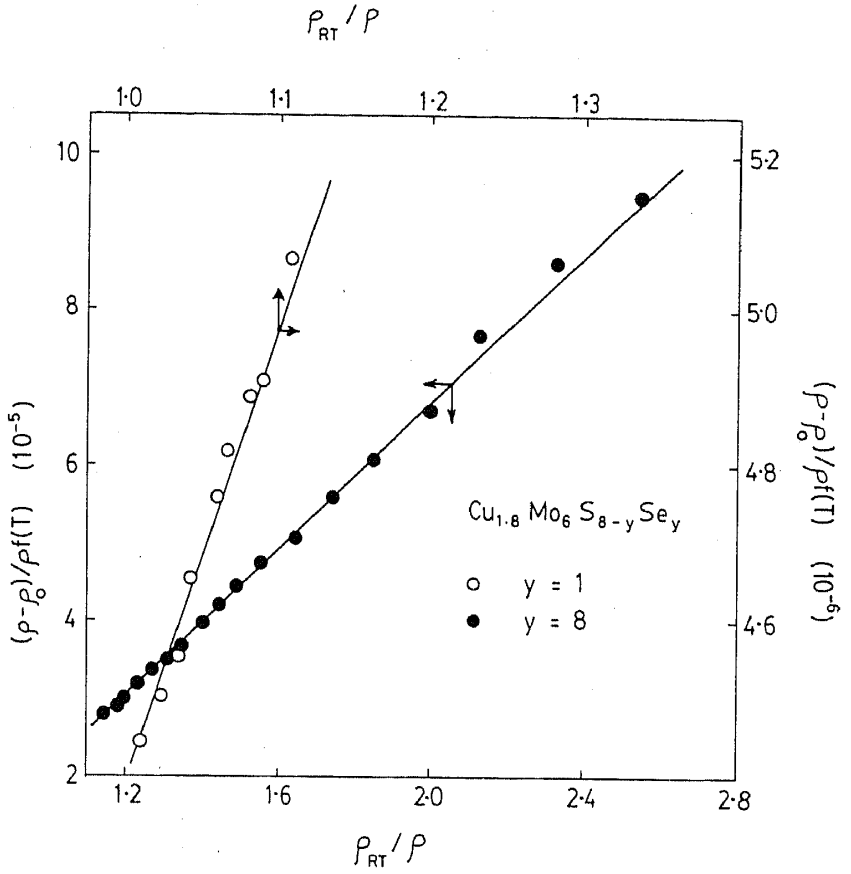

Figure 5. Variation of $(\rho-\rho_0)/\rho f(T)$ as a function of ρ_{RT}/ρ for the compounds $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $y = 0$ and 0·5.

In the rest of the selenium and tellurium-substituted compounds, the above procedure could not be adopted since the overall variation of normalised electrical resistivity with temperature is small in these cases. Hence, a computer fit has been made to fit the electrical resistivity data of the above compounds. In the case of tellurium-substituted compounds θ_D was also taken as a parameter to fit equation (9). Figures 7 and 8 give the experimental data points along with the fitted curves for the selenium-substituted compounds. The continuous lines in figure 1 represent the fitted curves for the tellurium-substituted compounds. In all the cases the RMS deviation of the fit obtained was less than 1%. Hence, the normal state electrical resistivity data of both $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$ could be fitted to the model proposed by Cote and Meisel for the amorphous and disordered crystalline materials.

The values of the parameters ρ^*, β' and θ_D obtained from the fit are shown in table 1. It is found that in the case of $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $0 \leqslant y \leqslant 8$ the value of the parameter β' decreases as y increases from zero, reaches a minimum corresponding to $y = 4$ and then increases with further increase in y. In the case of $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$, though the fit obtained was satisfactory, no systematic variation of the parameters, β' and ρ^*, with the composition y was observed. In the above analysis the Debye-Waller factor, $\exp(-2W^*)$ was assumed to be unity throughout the temperature range which may not be valid strictly in these cases. This may be the reason why no systematic variation of the parameters with y is observed in tellurium-substituted compounds.

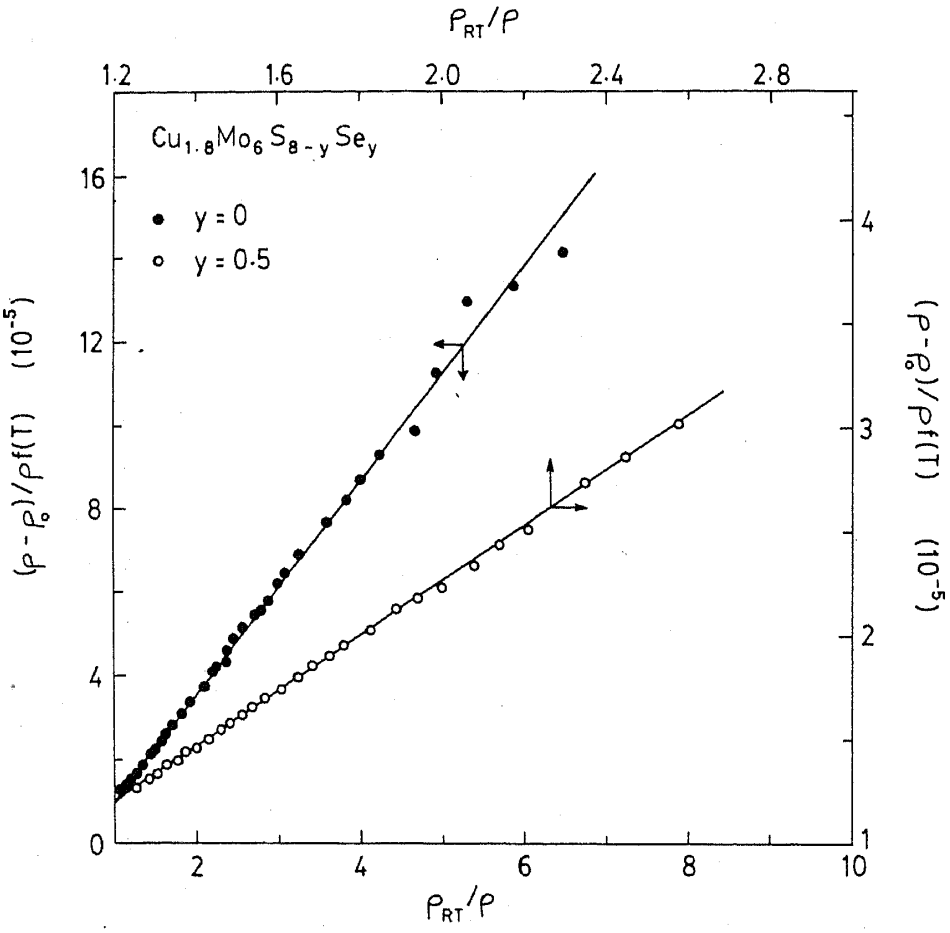

Figure 6. Variation of $(\rho-\rho_0)/\rho f(T)$ as a function of ρ_{RT}/ρ for the compounds $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $y = 1$ and 8.

Table 1. Values of the parameters β', ρ^* and θ_D for the compounds $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $0 \leqslant y \leqslant 8$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$, $0 \leqslant y \leqslant 4$.

Compound	$\beta'(K^{-2})$	ρ^*	θ_D (K)
$Cu_{1\cdot8}Mo_6S_8$	2·59	1·62	265
$Cu_{1\cdot8}Mo_6S_{7\cdot5}Se_{0\cdot5}$	1·31	3·65	260
$Cu_{1\cdot8}Mo_6S_7Se_1$	0·49	10·51	250
$Cu_{1\cdot8}Mo_6S_5Se_3$	0·34	3·94	240
$Cu_{1\cdot8}Mo_6S_4Se_4$	0·11	7·1	230
$Cu_{1\cdot8}Mo_6S_3Se_5$	0·28	5·5	225
$Cu_{1\cdot8}Mo_6Se_8$	4·85	1·72	200
$Cu_{1\cdot8}Mo_6S_7Te_1$	0·28	7·32	245
$Cu_{1\cdot8}Mo_6S_6Te_2$	1·52	1·16	220
$Cu_{1\cdot8}Mo_6S_5Te_3$	6·03	1·02	200
$Cu_{1\cdot8}Mo_6S_4Te_4$	0·87	1·31	180

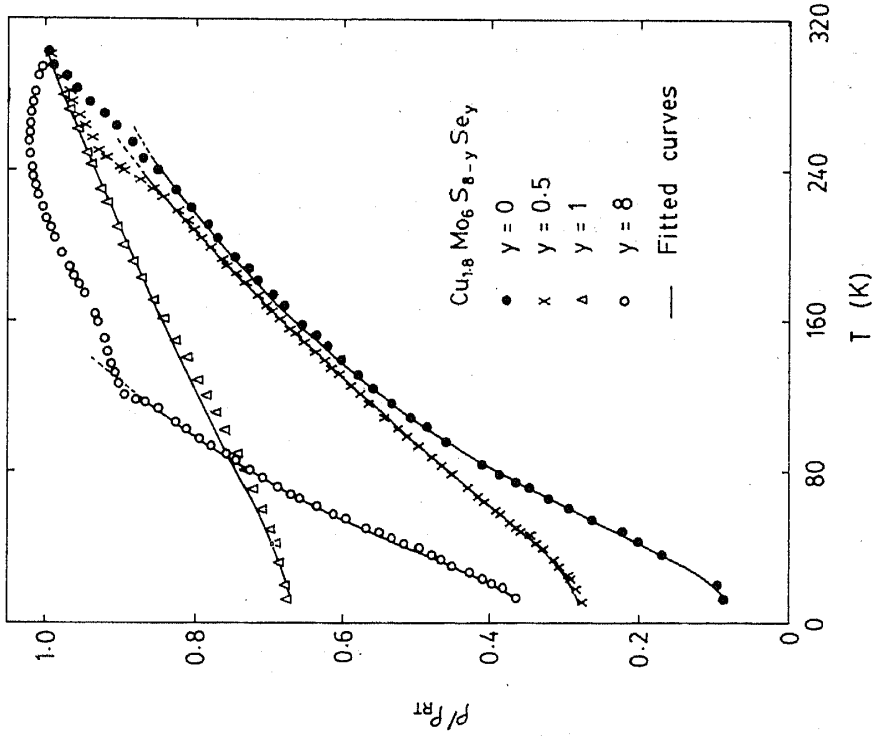

Figure 7. Electrical resistivity *vs* temperature data of $Cu_{1.8}Mo_6S_{8-y}Se_y$ ($y = 0$, 0·5, 1 and 8) fitted to Cote-Meisel theory.

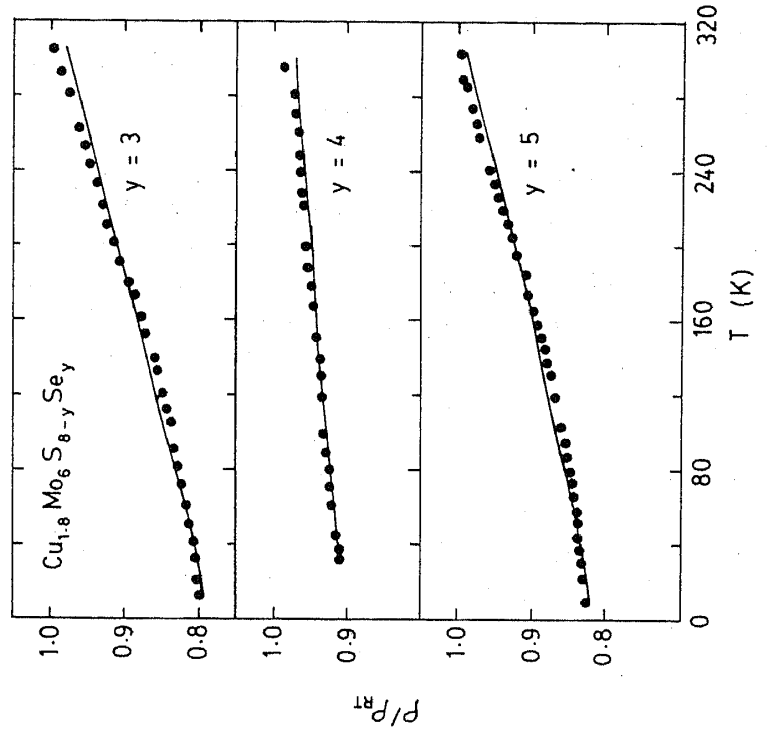

Figure 8. Electrical resistivity *vs* temperature data of $Cu_{1.8}Mo_6S_{8-y}Se_y$ ($y = 3$, 4 and 5) fitted to Cote-Meisel theory.

5. Conclusions

The Cote-Meisel theory, proposed to explain the origin of saturation of electrical resistivity at high temperature in amorphous and disordered crystalline materials, satisfactorily fits the electrical resistivity data on both $Cu_{1\cdot8}Mo_6S_{8-y}Se_y$, $0 \leqslant y \leqslant 8$ and $Cu_{1\cdot8}Mo_6S_{8-y}Te_y$, $0 \leqslant y \leqslant 4$. On the other hand, the model proposed by Morton *et al* on the basis of *s–d* scattering could not explain the electrical resistivity behaviour in the tellurium-substituted compounds. Besides this the low temperature T^2 dependence of electrical resistivity follows as a natural consequence of the Cote-Meisel model, whereas in the *s–d* scattering model an additional contribution due to electron-electron scattering had to be taken into account to explain this temperature dependence. Thus the Cote-Meisel theory appears to be superior to any other models based on interband *s–d* scattering of electrons.

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