Specific heat of a single-crystalline $3d^1$ perovskite, $Ca_{1-x}Sr_xVO_3$

Specific heat of a single-crystalline 3d^1 perovskite, Ca$_{1-x}$Sr$_x$VO$_3$

I H Inoue†+, N Shirakawa‡, I Hase‡, O Goto§, H Makino‖ and M Ishikawa¶

† PRESTO-JST and Electrotechnical Laboratory, Tsukuba 305-8568, Japan
‡ Electrotechnical Laboratory, Tsukuba 305-8568, Japan
§ Department of Electronics and Communications, Meiji University, Kawasaki 214-8571, Japan
‖ Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan
¶ ISSP, University of Tokyo, Tokyo 106-8666, Japan

Abstract. The electronic specific heat coefficients γ for single crystals of a perovskite-type 3d^1 vanadate system, Ca$_{1-x}$Sr$_x$VO$_3$, are reported. Wilson's ratio R_W has been determined by comparing the data to the Pauli-paramagnetic susceptibility; the value $R_W \simeq 2$ indicates a strong electron correlation in this system. Nevertheless, the effective masses are not so large as expected from the critical-mass-enhancement picture near the Mott transition.

1. Introduction

The most important feature of 3d-transition-metal oxides is that simple one-electron band theory is no longer sufficient to give a good account of the electronic states, since the electron correlations are much larger than expected for the one-electron bandwidth.

A metallic 3d^1 alloy system, Ca$_{1-x}$Sr$_x$VO$_3$, has recently given us a great incentive to examine how much we can control the electron correlation and concomitant electronic properties [1–3]. In the Ca$_{1-x}$Sr$_x$VO$_3$ system, one can control the bandwidth W systematically through a buckling of the V–O–V bond angle by means of an isovalent chemical substitution of a Ca^{2+} ion for a Sr^{2+} ion, so the ratio of the electron correlation U to W can be controlled. In fact, significant and systematic spectral weight redistribution has been reported already on the basis of photoemission spectroscopy and optical conductivity measurements [1, 4, 5]. These have elucidated a strong electron correlation and its systematic evolution in this system.

The purpose of this study is to clarify how the effective mass of Ca$_{1-x}$Sr$_x$VO$_3$ actually changes as we control the bandwidth. We report thermodynamic and magnetic properties of single-crystalline Ca$_{1-x}$Sr$_x$VO$_3$, which eventually reveal intriguing behaviours of the effective mass of this system.

2. Experiments

We grew single crystals of Ca$_{1-x}$Sr$_x$VO$_3$ by the floating-zone method [2], and the crystals obtained were annealed in air at ∼200 °C for around 24 hours, which reduces the departure

+ Present address: Electrotechnical Laboratory, Tsukuba 305-8568, Japan; e-mail: inoue@etl.go.jp.

of the oxygen from stoichiometry to less than ∼0.1 [2]. The ratio Ca:Sr:V = $1 - x$:x:1 was confirmed using an inductively coupled plasma atomic emission spectrometer (the departure from stoichiometry was less than 1%). The constant-pressure specific heat C_p was measured down to ∼0.5 K using a semi-adiabatic heat-pulse method. We also measured the dc susceptibility using a commercial rf-SQUID magnetometer.

3. Results and discussion

The measured values of C_p for $Ca_{1-x}Sr_xVO_3$ below ∼10 K are shown in figure 1. It is valid to compare this result to the constant-volume specific heat C_v, since these two quantities are almost identical in a solid.
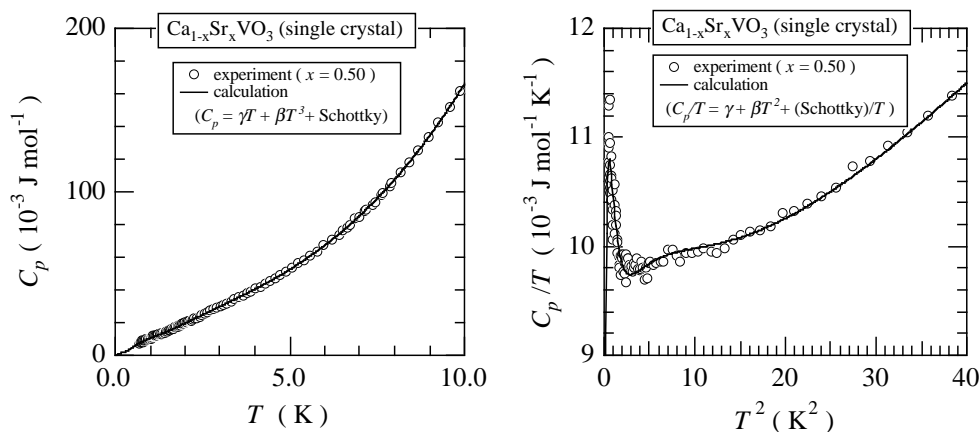
Figure 1. Left: $C_p \simeq C_v$ for $Ca_{1-x}Sr_xVO_3$ ($x = 0.5$) plotted against T. Right: C_p/T plotted against T^2. In both parts, open circles stand for measured data and solid lines are the result of fittings using equation (1).

Sufficiently below the Debye temperature Θ, C_v/T can be plotted against T^2, i.e., as

$$C_v/T = \gamma + \beta T^2$$

where γ is called the electronic specific heat coefficient. Using this identity, in general, we separate out the contribution of the ionic degrees of freedom (βT^3) dominant at high temperatures. The coefficient β is inversely proportional to Θ^3 for $T \ll \Theta$. However, in the temperature range displayed in figure 1, the data do not behave simply as described by the above equation. Therefore, we have tried to fit the observed specific heat $C_p \simeq C_v$ to the formula

$$C_v = \gamma T + \beta T^3 + k_B \sum_{i=1,2} \frac{N_i x_i^2 e^{x_i}}{(1 + e^{x_i})^2} \tag{1}$$

(where $x_i \equiv \Delta E_i/(k_B T)$) where the last term corresponds to the Schottky contributions of N_i ($i = 1, 2$) 'impurities' per mole with the excitation energies ΔE_i. As shown in figure 1 (right-hand side), we can fit the data fairly well using equation (1). The two bumps at around 3 K and 1 K can be attributed to the two Schottky terms, except for the upturn below ∼1 K. The excitation energies ΔE_i are ∼0.2 and ∼0.8 meV, which are almost independent of sample and Sr content x. Typical amounts of the Schottky impurities per V ion are $N_1 \sim 0.1\%$ and $N_2 \sim 0.2\%$; these values are comparable to those of the local

moments estimated using a Curie–Weiss term [2]. The Debye temperatures obtained, Θ, vary according to the Sr content as shown in figure 2 (right-hand side). The values of Θ are comparable to $\Theta \sim 300$ K deduced from the temperature of the phonon-drag peak of the Seebeck coefficient of CaVO$_3$ [6], substantiating the result of our least-squares fit to the specific heat data. We then deduced the effective mass from γ as described below.

All of the magnetic susceptibility data are well reproduced by the formula

$$\chi = \chi_{\text{spin}} + \chi_{\text{core}} + \chi_{\text{orb}} + \frac{C}{T - \vartheta} + \alpha T^2$$

where χ_{spin} is the paramagnetic spin susceptibility, χ_{core} comes from the diamagnetic contribution of the core levels, and χ_{orb} is due to the orbital Van Vleck paramagnetism. For χ_{core} and χ_{orb}, we have used the values given in the literature [7, 8]. The Curie–Weiss term is attributed to a very small amount of oxygen defects; the estimated amount of local impurity moments due to V^{3+} ions is $\sim$0.2% per Ca$_{1-x}$Sr$_x$VO$_3$, which is almost equal to that of the Schottky impurities. The last term is considered to originate in the higher-order temperature-dependent term in the Pauli paramagnetism.
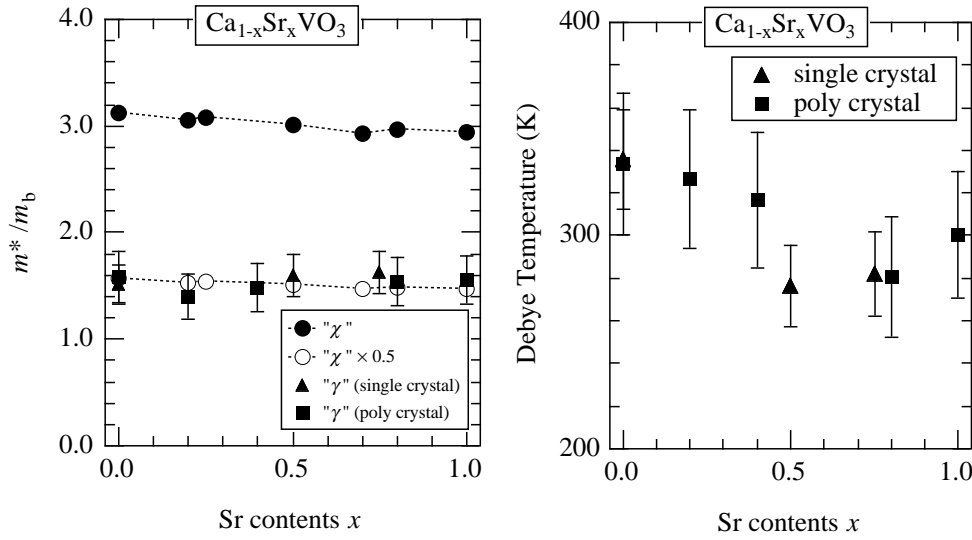
Figure 2. Left: m^*/m_b obtained by comparing the observed γ with the calculated one (filled squares, denoted by 'γ'). 'χ' stands for m^*/m_b deduced from χ_{spin} (filled circles, denoted by 'χ') and the half-values of 'χ' (open circles) also plotted for comparison. Right: Debye temperatures plotted against x.

The effective mass compared to the band mass m^*/m_b is defined as the ratio of the measured density of states (DOS) at the Fermi energy, E_F, to that of a band calculation, $D(E_F)$. We have performed an augmented-plane-wave band calculation with the local density approximation (LDA), and compared the result to that of the experiments. From the paramagnetic spin susceptibility, which consists of the terms for the Pauli paramagnetism and the Landau diamagnetism, m^*/m_b can be deduced using the relation

$$\chi_{\text{spin}} = \left(\frac{m^*}{m_b} - \frac{m_b}{3m^*}\right) N\mu_B^2 D(E_F).$$

(Note that the expression for this diamagnetism term is exact only for a free-electron band. However, the diamagnetism term is actually proportional to $(m^*/m_b)^2$; the deviation from

this expression is not very significant for this system.) In contrast, m^*/m_b can also be deduced from the electronic specific heat coefficient, using the identity

$$\gamma = \frac{m^*}{m_b} \frac{\pi^2}{3} k_B^2 N D(E_F)$$

where N is the number of itinerant electrons per mole in the unit formula. The values deduced for m^*/m_b against x are plotted in figure 2 (left-hand side).

From figure 2, we can estimate Wilson's ratio [9]:

$$R_W = \left(\frac{m^*}{m_b}\right)_\chi \Bigg/ \left(\frac{m^*}{m_b}\right)_\gamma.$$

The value of R_W for $Ca_{1-x}Sr_xVO_3$ estimated from our experiments is ~ 2, as seen in figure 2, where the half-values of m^*/m_b given by the magnetic measurements are plotted for comparison. For a non-interacting Bloch-electron system, R_W is equal to unity, whilst, for strongly correlated electron systems, it has been argued that the value of R_W becomes equal to 2 at $U/W = \infty$ [9, 10]. The observed $R_W \approx 2$ may indicate the importance of electron correlations in this system. However, this is rather too peculiar to be naively understood, because R_W is generally modified to $R_W(1 + \lambda)^{-1}$, where λ comes from the electron–phonon interaction. Moreover, R_W should decrease towards unity in the limit of large orbital degeneracy [11]. Since the degeneracies of the t_{2g} orbitals of the vanadium 3d electrons are not completely lifted in this $Ca_{1-x}Sr_xVO_3$ system, R_W is not necessarily equal to 2.

A more interesting result is that the values of m^*/m_b obtained from the thermodynamic measurement are around 1.5; we could not recognize any signs of mass enhancement, even though there is a lot of evidence of strong electron correlation in the $Ca_{1-x}Sr_xVO_3$ system. Photoemission spectra have shown a systematic evolution of the spectral weight; however, m^*/m_b increases moderately in going from $SrVO_3$ to $CaVO_3$. These points are at variance with the diverging behaviour expected from the Brinkman–Rice picture.

We consider that a key to elucidating some shortcomings which are involved in the above confusion will be found in a problem inherent to the LDA. Near the Mott transition, the screening effect becomes weaker and thus the non-local exchange interaction should not be neglected. However, in the LDA, the exchange potential is approximated by a local potential, which certainly leads to underestimation of the bandwidth [12], and thus also to overestimation of $D(E_F)$. Therefore, the value of m^*/m_b does not show a large enhancement, whilst an apparent large spectral weight transfer compared to the LDA DOS is observed. This scenario supports the idea of 'k-mass' advocated in reference [1].

Although the experimental error bars for the estimation of γ-values may hide other intrinsic properties, especially in the lower-temperature region, and we need further theoretical investigation of how the Wilson ratio should behave in the system with such long-range exchange correlation, the above argument will give us a clue as to how to understand the anomalous metallic behaviours in the very close vicinity of the Mott transition.

References

[1] Inoue I H, Hase I, Aiura Y, Fujimori A, Haruyama Y, Maruyama T and Nishihara Y 1995 *Phys. Rev. Lett.* **74** 2539
[2] Inoue I H, Goto O, Makino H, Hussey N E and Ishikawa M 1998 *Phys. Rev.* B **58** 4372
[3] Makino H, Inoue I H, Rozenberg M J, Hase I, Aiura Y and Onari S 1998 *Phys. Rev.* B **58** 4384
[4] Morikawa K, Mizokawa T, Kobayashi K, Fujimori A, Eisaki H, Uchida S, Iga F and Nishihara Y 1996 *Phys. Rev.* B **52** 13 711

[5] Rozenberg M J, Inoue I H, Makino H, Iga F and Nishihara Y 1996 *Phys. Rev. Lett.* **76** 4781
[6] Zhou J-S and Goodenough J B 1996 *Phys. Rev.* B **54** 13 393
[7] Van Vleck J H 1932 *The Theory of Electronic and Magnetic Susceptibilities* (Oxford: Oxford University Press)
[8] Pouget J P, Launois H, Rice T M, Derrier P, Gossard A, Villeneuve G and Hagenmuller P 1974 *Phys. Rev.* B **10** 1801
[9] Wilson K 1975 *Rev. Mod. Phys.* **47** 773
[10] Nozières P 1974 *J. Low Temp. Phys.* **17** 31
[11] Yoshimori A 1976 *Prog. Theor. Phys.* **55** 67
[12] Ashcroft N W and Mermin N D 1987 *Solid State Physics* HRW International edn (Hong Kong: Saunders College/CBS Publishing Asia Limited) p 334