Specific heat and the cooperative Jahn–Teller effect in KDy(WO$_4$)$_2$

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Abstract. The specific heat of KDy(WO$_4$)$_2$ has been measured over the wide temperature range from 3.5 K to 200 K. Only one anomaly, indicating the phase transition driven by the cooperative Jahn–Teller effect, has been found, at $T_{JT} = 6.4$ K. The phonon specific heat has been estimated and subtracted from the heat capacity measured. The Schottky anomaly originating from the population of the lowest two doublets of the dysprosium ions, and the λ-anomaly connected with the Jahn–Teller phase transition have been described theoretically using the molecular-field approximation. Satisfactory agreement between experimental points and theoretical dependences calculated using the material parameters known from the literature was obtained.

1. Introduction

As has been mentioned in several previous papers, crystals of the chemical composition MRe(XO$_4$)$_2$, where M and Re stand for alkali metal and rare-earth ions, respectively, and X denotes a molybdenum or tungsten ion, form a very interesting group of materials. Many of them show complicated structural phase transitions, driven by the cooperative Jahn–Teller effect, and magnetic phase transitions at low temperatures. Whereas double molybdates have been studied intensively, papers concerning double tungstates are considerably less numerous. Among the tungsten compounds, KDy(WO$_4$)$_2$ seems to be a particularly interesting material for the following reasons.

(1) It crystallizes in a low-symmetry monoclinic structure, characterized by the space group C$_{2h}^6$ (C2/c), the monoclinic angle $\beta = 94°13'$, and the lattice constants $a = 8.05$ Å, $b = 10.32$ Å, and $c = 7.75$ Å [1, 2]. The crystal unit cell contains four formula units.

(2) At $T_{JT} = 6.38$ K, it undergoes a phase transition driven by the cooperative Jahn–Teller effect, which is rarely observed in materials of such low symmetry. The Jahn–Teller-active Dy^{3+} ions occupy sites of C$_2$ point symmetry.

(3) Low-temperature specific heat measurements [3] showed that the relaxation time, i.e. the time that the sample needs to reach a state of thermal equilibrium, is several times greater above T_{JT} than below T_{JT}. Thus, in reference [3], the hypothesis has been made that the structural phase transition from the low-temperature to the high-temperature phase

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can go through an intermediate incommensurate phase, like in the similar molybdenum compounds $KDy(MoO_4)_2$ [4] and $CsDy(MoO_4)_2$ [5]. If this hypothesis were correct, a second anomaly in the temperature dependence of the specific heat, indicating the phase transition from the incommensurate phase to the high-temperature phase, should be observed above T_{JT}.

The main purpose of the present studies was to measure the specific heat of the $KDy(WO_4)_2$ compound over a wide temperature range, from liquid helium temperature up to 200 K, and to explain whether any additional anomalies, indicating phase transitions, can be observed in this range. The earlier specific heat investigations described in [3] were performed up to 20 K only, due to the limitations of the experimental set-up.

An additional purpose was to estimate the lattice contribution to the specific heat of $KDy(WO_4)_2$ and to perform a quantitative analysis of the anomaly observed at 6.38 K.
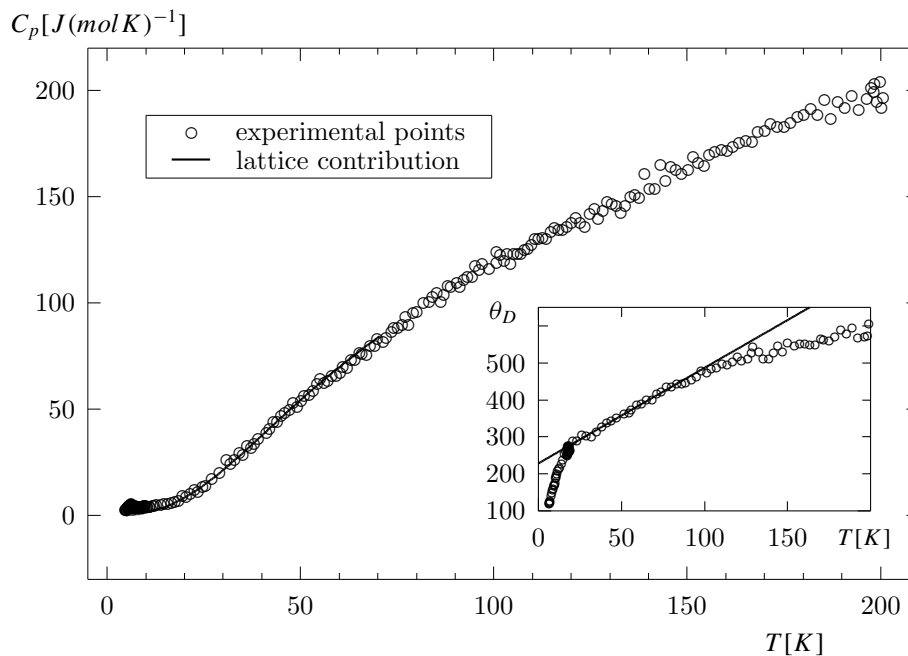

Figure 1. The specific heat of $KDy(WO_4)_2$. Circles: experimental points; solid curve: the calculated lattice contribution; circles in the inset: the Debye temperature as a function of temperature; solid line in the inset: the linear extrapolation of the $\theta_D(T)$ dependence.

2. Experiment

The specific heat was measured using a calorimeter built recently at the Institute of Physics of the Polish Academy of Sciences. In this apparatus, measurements can be carried out in the temperature range from pumped helium temperatures up to room temperature, in the presence of a magnetic field of up to 12 T. Over the whole temperature range, the quasi-adiabatic method is applied. The sample studied consisted of four pieces of the $KDy(WO_4)_2$ single crystal and its total mass was equal to 2.092 g. The $KDy(WO_4)_2$ specific heat has

been measured over the range from 3.5 K to 200 K. The results obtained are shown in figure 1 and figure 2. Over the whole range studied, only one sharp anomaly, located at $T_{JT} = 6.4$ K and associated with the second-order phase transition driven by the cooperative Jahn–Teller effect, has been observed. No indications of any other phase transition were found. In order to avoid the effects of freezing of any metastable phase, especially in the region in which considerable relaxation times were observed, the sample was cooled from room temperature down to the liquid helium temperature very slowly, over a few hours. Moreover, the temperature dependence of the specific heat, always registered during the process of heating the sample, was measured a few times, after cooling the sample to different temperatures. The same dependence was obtained irrespective of whether the starting temperature was lower or higher than $T_{JT} = 6.4$ K.
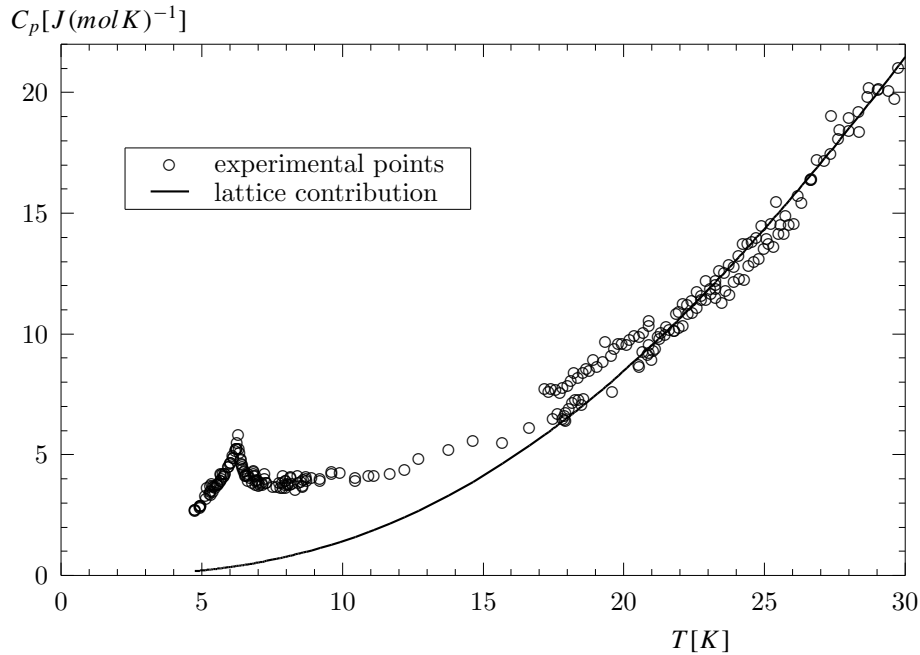

Figure 2. The low-temperature part of the temperature dependence of the KDy(WO₄)₂ specific heat. Circles: experimental points; solid curve: the calculated lattice contribution.

3. Analysis

The lattice contribution to the specific heat of KDy(WO₄)₂ was estimated following the procedure explained in reference [6] and described in appendix A, i.e. it was assumed that for each temperature T, the specific heat is given by the Debye function (A1). Next, the hypothetical Debye temperature θ_D was calculated for each experimental point by solving the entangled relation (A2). As a result, the dependence $\theta_D(T)$, shown in figure 1 in the inset, was obtained. As one can see in the figure, a steep decrease of θ_D is observed when temperature decreases to below 20 K. This is caused by the fact that in the vicinity of the Jahn–Teller phase transition temperature, below 20 K, the total specific heat measured consists of three contributions:

(i) the lattice specific heat,

(ii) the contribution connected with thermal excitations of particular dysprosium ions to the first excited doublet, i.e. the Schottky anomaly, and

(iii) the contribution associated with the second-order phase transition, in this case with the cooperative Jahn–Teller effect, i.e. the λ-anomaly.

Whereas above 20 K, the two latter effects are negligible, below 20 K, they dominate, and at 6 K, the lattice specific heat contributes only several per cent to the total specific heat measured. Thus, the θ_D-values calculated following the procedure described above can be interpreted as the Debye temperature only above 20 K. Below 20 K, θ_D is an artificial parameter only. It is evident from figure 1 that over a rather wide temperature range from 20 K to 70 K, the temperature dependence of θ_D can be approximated by a straight line. As is explained in appendix A, this considerable temperature dependence of θ_D can be attributed to the rather large values of the thermal expansion coefficient of $KDy(WO_4)_2$, which were measured in reference [3]. Following the Landau theory of second-order phase transitions, one can assume that the last of the three contributions enumerated above is absent above T_{JT}. So, in the range from T_{JT} to 20 K, only the first two effects contribute to the total heat capacity. Because they do not influence each other and there is no reason to expect any extraordinary change in the lattice dynamic properties above T_{JT}, it has been assumed that the linear temperature dependence of the Debye temperature can be extrapolated down to T_{JT}, and the lattice specific heat has been calculated, substituting the appropriate values of T and $\theta_D(T)$ into the expression (A1). Because the distance between the lowest doublets of Dy ions in $KDy(WO_4)_2$ is known from earlier optical studies [7, 8], the Schottky contribution to the specific heat can be calculated easily using the formula (B1). Thus, an agreement between the Schottky anomaly calculated and the Schottky contribution determined experimentally, by subtraction of the lattice contribution calculated from the total specific heat measured, is a good test of the validity of the method used for estimation of the lattice contribution. As is shown below, in the case of $KDy(WO_4)_2$, over the temperature range from T_{JT} to 20 K this agreement is very good. A somewhat more complicated situation arises below T_{JT}. As a result of the structural Jahn–Teller phase transition, the crystal lattice deforms, and one could expect considerable changes in the phonon spectrum. Moreover, one could expect that a few degrees below T_{JT} the crystal will behave like the majority of normal materials, and that the common increase of the Debye temperature with decrease of temperature [6] will be observed at low temperatures. Because the Raman scattering studies [9] showed that the Jahn–Teller phase transition weakly influences the $KDy(WO_4)_2$ phonon spectrum, and because over the range from 4.7 K to T_{JT} the lattice specific heat was a small fraction of the total signal measured, we have assumed that the linear temperature dependence of the Debye temperature can be extrapolated down to 4.7 K. However, to be sure that this procedure will not introduce a significant error, we also performed calculations assuming that at T_{JT} the Debye temperature starts to grow linearly and unreasonably quickly with decreasing temperature, reaching 400 K at 4.7 K. It has been found that this completely different behaviour of $\theta_D(T)$ leads at 4.7 K, where the difference is the largest, to values of the Schottky and the cooperative Jahn–Teller effect contributions higher by less than 6% than the values obtained using the linear extrapolation. This difference falls within the limits of experimental error, as is illustrated in figure 3, where the value obtained at 4.9 K assuming the fast increase of $\theta_D(T)$ is indicated by a full circle.

The lattice contribution, calculated following our procedure, i.e. assuming the linear $\theta_D(T)$ dependence over the range from 4.7 to 70 K, is shown in figure 1 and figure 2. The
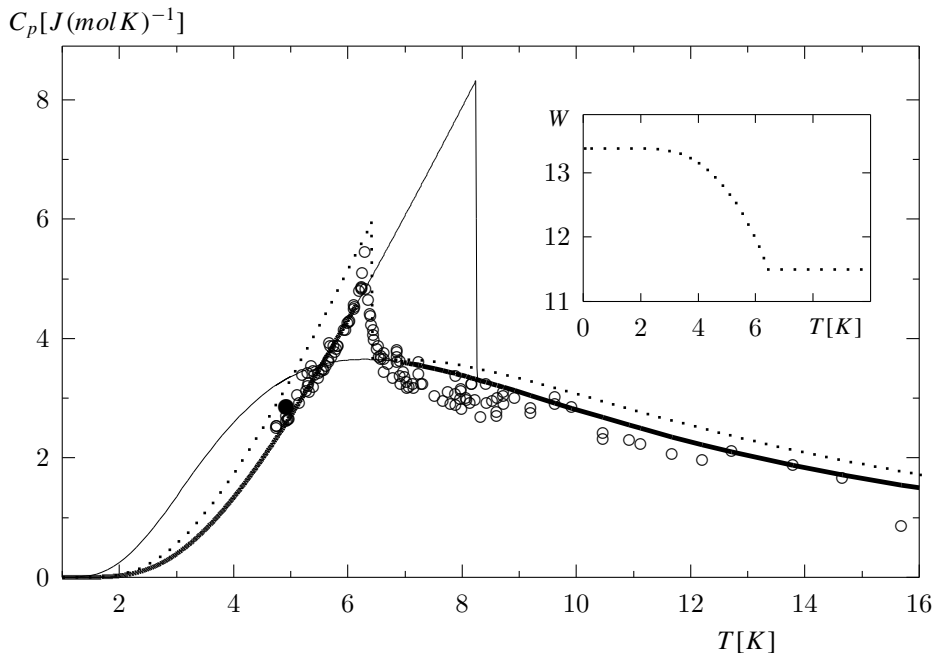
Figure 3. Schottky and cooperative Jahn–Teller effect contributions to the total specific heat of KDy(WO₄)₂. Open circles: the difference between the total specific heat measured and the lattice specific heat calculated. Full circle: the difference mentioned in the text calculated for $T = 4.9$ K assuming unreasonably fast growth of θ_D with decrease of temperature. Thick solid line above $T_{JT} = 6.4$ K and thin solid line below T_{JT}: the Schottky anomaly calculated for $\Delta = 10.5$ cm^{-1} according to (B1). Thin solid line above T_{JT} and thick solid line below T_{JT}: the specific heat calculated according to (C7) for $\Delta = 10.5$ cm^{-1} and the overestimated transition temperature $T_{JT}^{theo} = 8.25$ K. Dotted line: the theoretical specific heat calculated according to (B1) and (C7) assuming that $\Delta = 11.5$ cm^{-1} and $T_{JT} = 6.4$ K. Inset: the theoretical temperature dependence of the splitting between the lowest two doublets of the Dy^{3+} ion, W, calculated according to (C6) for $\Delta = 11.5$ cm^{-1} and $T_{JT} = 6.4$ K.

difference between the total specific heat measured and the lattice specific heat calculated is presented in figure 3.

According to [7, 8], in KDy(WO₄)₂ above T_{JT}, the distance between the lowest two Kramers doublets of the ground-state multiplet of the Dy^{3+} ion, ^{6}H$_{15/2}$, is equal to $\Delta = 10.5$ cm^{-1}. Because the next doublets are located at $\sim$140 cm^{-1} and $\sim$200 cm^{-1}, only the lowest two doublets determine the thermodynamic properties of the dysprosium ions at low temperatures. Thus, the Schottky contribution to the molar specific heat of KDy(WO₄)₂ above T_{JT} has been calculated applying the formula (B1) derived for the two-level system. This function has been plotted in figure 3 and, as can be seen, it agrees with the points measured above T_{JT} within the limits of experimental error. As was mentioned above, this agreement confirms the validity of the method applied in the present paper for estimation of the lattice specific heat. Of course, below T_{JT}, where the distance between the lowest two doublets increases as a result of the phase transition, the expression (B1), derived for $\Delta = $ constant, breaks down, and the other theoretical approach, presented below, has to be applied.

In the case of $KDy(WO_4)_2$ we deal with the so-called pseudo-Jahn–Teller effect, i.e. with the situation in which the lowest two doublets are non-degenerate and the cooperative Jahn–Teller transition increases only the distance between them. According to [3], the influence of an external magnetic field on the phase transition occurring at T_{JT} suggests that the Jahn–Teller deformation in $KDy(WO_4)_2$ has an antiferrodistortive character rather than a ferrodistortive one. To analyse the λ-anomaly appearing at T_{JT}, the pseudo-spin formalism for $S = 1/2$ and the molecular-field approximation have been used [10, 11]. Details of the theoretical approach and the methods which we applied to derive the formulae used in the further considerations are given in appendix C.

To compare the measured specific heat with predictions of the molecular-field theory, two theoretical curves have been plotted in figure 3. Each of them has been calculated using the expression (C7) below the Jahn–Teller transition temperature and the expression (B1) above this temperature. The first curve, drawn in the figure as a dotted line, has been calculated taking the Jahn–Teller transition temperature equal to the measured value 6.4 K and the Δ parameter equal to 11.5 cm^{-1}, i.e. to the value for which the best fit of the theoretical curve to the experimental points has been achieved. The value 11.5 cm^{-1}, although higher than the value 10.5 cm^{-1} determined in [8] on the basis of optical absorption measurements, falls within the limits of experimental error of those studies. The second curve, drawn as a thick solid line below T_{JT} and as a thin solid line above T_{JT}, was obtained keeping the $\Delta = 10.5$ cm^{-1} parameter constant and varying the phase transition temperature to best fit the points measured below T_{JT}. As is shown in figure 3, it was necessary to take in the calculations a transition temperature of $T_{JT}^{theo} = 8.25$ K to achieve a good agreement between the theoretical curve and the experimental points. This is in agreement with reference [12], in which the authors stated that the molecular-field theory usually gives values for the cooperative Jahn–Teller transition temperature that are too high, especially for dysprosium compounds, and illustrated this fact using the examples of $DyVO_4$ and $DyAsO_4$.

In order to illustrate the relation between the theoretical temperature dependence of the specific heat and the temperature dependences of the other quantities appearing in the theoretical model, we have calculated, for the parameters $T_{JT} = 6.4$ K and $\Delta = 11.5$ cm^{-1}, and presented in figure 3 and figure 4 the following functions:

(i) the specific heat versus temperature, $C(T)$, calculated according to relations (C7) and (B1), drawn in figure 3 as a dotted line,

(ii) the distance between the lowest two doublets of dysprosium ions versus temperature, $W(T)$, calculated by solving the entangled relation (C6), drawn in figure 3 in the inset, and

(iii) the components and modulus of the pseudo-spin versus temperature: $\sigma_{1x}(T)$, $\sigma_{1z}(T)$, $\sigma_1(T)$, calculated according to relations (C3) and (C4), drawn in figure 4.

In [8] the theoretical $W(T)$ dependence has been presented, according to which W reaches the value 19.5 cm^{-1} at $T = 0$ K. It should be stressed that none of the theoretical sets of parameters used in the present paper leads to so large a theoretical splitting of the lowest two doublets at $T = 0$ K, i.e. neither $\Delta = 11.5$ cm^{-1} and $T_{JT} = 6.4$ K, which gives $W(T = 0) = 13.4$ cm^{-1}, nor $\Delta = 10.5$ cm^{-1} and $T_{JT}^{theo} = 8.25$ K, which gives $W(T = 0) = 14.5$ cm^{-1}. This is caused by the fact that the authors of reference [8] have not calculated the $W(T)$ function according to expression (C6); they have used their own expression (2), derived under assumption that the $\sigma_{1z}(T)$ dependence is determined by the Brillouin function, like the spontaneous magnetic moment in the classical Weiss theory of ferromagnetism, and obtained $\sigma_{1z}(T = 0) = 1$. As is illustrated in figure 4, this assumption is incorrect for the case of the pseudo-Jahn–Teller effect, i.e. for the case where $\Delta \neq 0$,
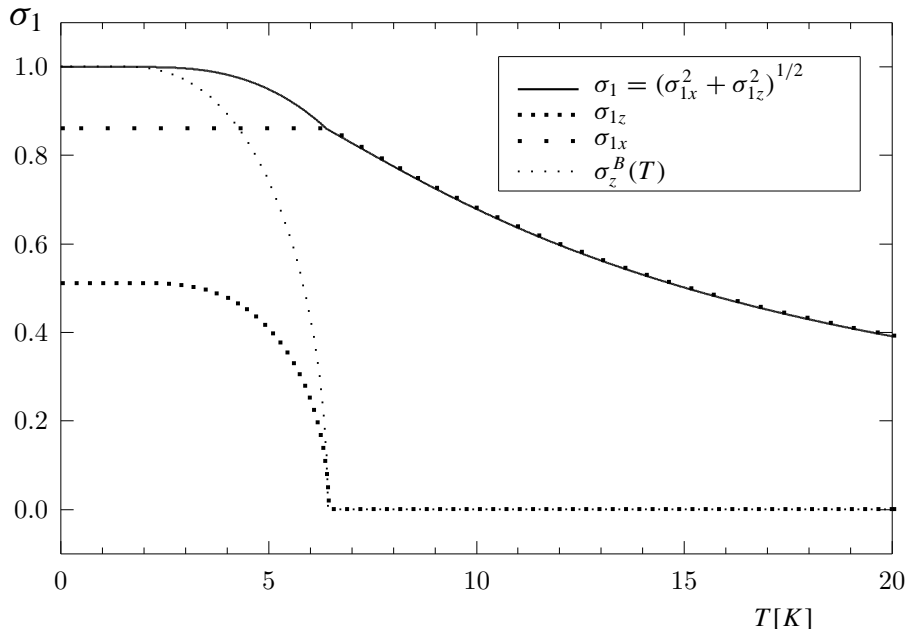
Figure 4. Temperature dependences of the pseudo-spin components, σ_{1x} and σ_{1z}, and the modulus, σ_1, calculated according to (C3) and (C4) for $\Delta = 11.5$ cm^{-1} and $T_{JT} = 6.4$ K. The $\sigma_z^B(T)$ curve, i.e. the $\sigma_{1z}(T)$ dependence calculated using the Brillouin function for $S = 1/2$, is plotted as a thin dotted line. It is evident that it differs significantly from the $\sigma_{1z}(T)$ function.

because the $\sigma_{1z}(T)$ dependence calculated in an appropriate way differs significantly from the dependence determined from the Brillouin function. On the other hand, in [8], the large value of the splitting of the lowest two doublets of dysprosium ions at low temperatures has been also found experimentally. However, this result is based on just two experimental points, bearing rather large experimental error. Thus, either the two experimental points are overestimated, or the molecular-field theory, used in the present paper and in [8], is too rough an approximation for describing the cooperative Jahn–Teller transition in KDy(WO$_4$)$_2$ properly.

4. Conclusions

The specific heat of KDy(WO$_4$)$_2$ has been measured over a wide temperature range, and no indications of a second structural phase transition, above $T_{JT} = 6.4$ K, were found up to 200 K. The phonon specific heat was assumed to be the main component of the specific heat measured above 20 K, and it was analysed in the framework of the Debye model. A strong temperature dependence of the Debye temperature was observed. Extrapolation of this dependence down to 4.7 K appeared to be an adequate method for estimating the lattice specific heat at low temperatures. It allowed us to separate the Schottky contribution to the specific heat, originating from the population of the lowest two doublets of the dysprosium ions, and the contribution connected with the phase transition driven by the cooperative Jahn–Teller effect. The theoretical Schottky specific heat calculated using the value of the splitting of the lowest two doublets of the dysprosium ion known from the literature [8]

was found to agree very well with the experimental points. The λ-anomaly appearing at the Jahn–Teller transition temperature has been described satisfactorily in the molecular-field approximation. The temperature dependence of the splitting of lowest two doublets of the dysprosium ion has been calculated in an appropriate way.

Acknowledgment

Appendix A. The lattice contribution to the specific heat

It is well known that the Debye model, taking into consideration the harmonic vibrations of the crystal lattice, does not describe the effect of thermal expansion of crystals. As is pointed out in many books, e.g. in reference [6] (chapters 4, 5, 9, 10), assuming that thermal expansion results in a change of the phonon frequencies of the crystal is the simplest method for taking this effect into account. The direct consequence of the change in the phonon spectrum is a change of the Debye frequency and the Debye temperature. As a result, the lattice specific heat of a real crystal can be analysed using the expression derived in the framework of the Debye model for one mole of the material:

$$C_{Deb}(T, \theta_D) = n \, 9 N_A k_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \tag{A1}$$

provided that the Debye temperature, θ_D, is treated as a parameter depending on temperature. N_A and k_B denote Avogadro's number and Boltzmann's constant, respectively. n denotes the number of atoms in the molecule of the compound considered, e.g. $n = 12$ for $KDy(WO_4)_2$. So, knowing the molar specific heat measured at temperature T, $C_{meas}(T)$, and solving the entangled relation

$$C_{meas}(T) = C_{Deb}(T, \theta_D) \tag{A2}$$

with respect to θ_D, one obtains the dependence $\theta_D(T)$.

Appendix B. The Schottky anomaly

The Schottky anomaly, i.e. the temperature dependence of the specific heat of an ensemble of N_A two-level objects, is given by the well known formula [6]

$$C_{Sch}(T) = N_A k_B \left[\frac{\Delta}{k_B T} \frac{1}{2 \cosh\left[\Delta/(2 k_B T)\right]} \right]^2 \tag{B1}$$

where Δ denotes the spacing between the two energy levels.

Appendix C. The contribution of the cooperative Jahn–Teller effect to the specific heat

The simplest approximations which allow one to determine the contribution of the pseudo-Jahn–Teller effect to the specific heat of the material are the pseudo-spin formalism for $S = 1/2$ and the molecular-field approximation [10, 11]. As was mentioned above, the

pseudo-Jahn–Teller effect is the phenomenon in which the lowest two doublets of the Jahn–Teller-active ions are non-degenerate and the cooperative Jahn–Teller effect just increases the distance between them. Because in the case of KDy(WO₄)₂ the Jahn–Teller effect can lead to the occurrence of an antiferrodistortive deformation, the simplest two-sublattice model of the antiferrodistortive ordering [3] has been assumed, and the Hamiltonian describing two dysprosium ions belonging to the different sublattices has been written in the form

$$\hat{H} = -(J_s \langle \hat{\sigma}_{1z} \rangle + J_i \langle \hat{\sigma}_{2z} \rangle) \hat{\sigma}_{1z} - \frac{\Delta}{2} \hat{\sigma}_{1x} - (J_s \langle \hat{\sigma}_{2z} \rangle + J_i \langle \hat{\sigma}_{1z} \rangle) \hat{\sigma}_{2z}$$

$$- \frac{\Delta}{2} \hat{\sigma}_{2x} + \left[\tfrac{1}{2} J_s (\langle \hat{\sigma}_{1z} \rangle^2 + \langle \hat{\sigma}_{2z} \rangle^2) + J_i \langle \hat{\sigma}_{1z} \rangle \langle \hat{\sigma}_{2z} \rangle \right] \qquad \text{(C1)}$$

where the indices 1 and 2 denote ions belonging to two different sublattices. The pseudo-spin x- and z-components are represented by the Pauli matrices $\hat{\sigma}_x$ and $\hat{\sigma}_z$, and they describe the crystalline-electric-field effect and the Jahn–Teller deformation, respectively. J_s and J_i are molecular-field constants describing intrasublattice and intersublattice interactions between dysprosium ions, respectively. Hereafter, thermal averages of the operators $\hat{\sigma}_{ju}$, where $j = 1, 2$ and $u = x$, y, or z, will be denoted by $\langle \hat{\sigma}_{ju} \rangle$ or σ_{ju}. Next, the method based on the non-equilibrium thermodynamic potential [13, 3] has been applied, and the following expression, describing the non-equilibrium free energy per mole of KDy(WO₄)₂, has been obtained:

$$F(\sigma_{1x}, \sigma_{1z}, \sigma_{2x}, \sigma_{2z}, T) = \{ -(J_s/2)(\sigma_{1z}^2 + \sigma_{2z}^2) - J_i \sigma_{1z} \sigma_{2z} - 2k_B T \ln(2)$$

$$+ \tfrac{1}{2} k_B T [(1 - \sigma_1) \ln(1 - \sigma_1) + (1 + \sigma_1) \ln(1 + \sigma_1)$$

$$+ (1 - \sigma_2) \ln(1 - \sigma_2) + (1 + \sigma_2) \ln(1 + \sigma_2)] \} N_A / 2 \qquad \text{(C2)}$$

where $\sigma_j = (\sigma_{jx}^2 + \sigma_{jz}^2)^{1/2}$. As a result of minimizing equation (C2) with respect to σ_{ju}, i.e. by solving the system of equations $\partial F / \partial \sigma_{ju} = 0$, the following formulae, analogous to those derived in reference [10] for the one-sublattice case, have been obtained: for $T < T_{JT}$,

$$\sigma_{1z} = \pm \sigma_{2z} \qquad \sigma_{1z}^2 = \left[\tanh \left(\frac{[4(J_s \pm J_i)^2 \sigma_{1z}^2 + \Delta^2]^{1/2}}{2k_B T} \right) \right]^2 - \frac{\Delta^2}{4(J_s \pm J_i)^2} \qquad \text{(C3)}$$

$$\sigma_{1x} = \sigma_{2x} \qquad \sigma_{1x} = \Delta / [2(J_s \pm J_i)]$$

and for $T > T_{JT}$,

$$\sigma_{1z} = \sigma_{2z} = 0$$

$$\sigma_{1x} = \sigma_{2x} \qquad \sigma_{1x} = \tanh [\Delta / (2k_B T)] \qquad \text{(C4)}$$

where the upper and lower signs refer to the cases of ferrodistortive and antiferrodistortive ordering, respectively. The relation between T_{JT} and the molecular-field constants has the form

$$J_s \pm J_i = \frac{\Delta}{2 \tanh [\Delta / (2k_B T_{JT})]}. \qquad \text{(C5)}$$

The temperature dependence of the distance between the lowest two doublets is given by the entangled relation

$$W = \begin{cases} 2(J_s \pm J_i) \tanh [W/(2k_B T)] & \text{for } T \leqslant T_{JT} \\ \Delta & \text{for } T > T_{JT}. \end{cases} \qquad \text{(C6)}$$

By substituting expressions (C3) and (C4) into (C2), the formula for the equilibrium free energy of the system considered has been obtained. Next, the entropy $S = -(\mathrm{d}F/\mathrm{d}T)$,

internal energy $U = F + TS$, and specific heat $C = T(dS/dT)$ per mole of $KDy(WO_4)_2$ were calculated. Above T_{JT}, the dependence of the specific heat on temperature is given by equation (B1), whereas below T_{JT} it has the form

$$C(T) = N_A k_B \frac{(J_s \pm J_i)^2 \sigma_{1z}^2 + \Delta^2/4}{T(k_B T \cosh^2([\sqrt{4(J_s \pm J_i)^2 \sigma_{1z}^2 + \Delta^2}]/2k_B T) - (J_s \pm J_i))} \tag{C7}$$

It should be emphasized that, according to (C5), the molecular-field constants enter all formulae in the form of the expression $J_s \pm J_i$, which is determined by T_{JT} and Δ only. Thus, as was pointed out in reference [3], the theoretical temperature dependence of the specific heat has the same shape for both kinds of distortive ordering. As a result, the antiferrodistortive and ferrodistortive orderings cannot be distinguished by measuring the specific heat in zero magnetic field.

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