PHYSICAL REVIEW B **66**, 033101 (2002)

Thermal hysteresis in the charge-density-wave transition of $Lu_5Rh_4Si_{10}$

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(Received 17 July 2001; revised manuscript received 26 February 2002; published 3 July 2002)

We report the detailed studies of resistivity, magnetic susceptibility, heat capacity, thermal conductivity, and thermoelectric power on the charge-density-wave (CDW) material $Lu_5Rh_4Si_{10}$ in the vicinity of its transition temperature $T_0 \sim 147$ K. Pronounced thermal hystereses loops between heating and cooling cycles have been observed in all measured quantities, making this system very unique as compared to other isostructural compounds such as $Lu_5Ir_4Si_{10}$. The thermal hysteresis features in $Lu_5Rh_4Si_{10}$ are attributed to the presence of metastable states arising from pinning of the CDW phase to impurities. In addition, the measured physical quantities are magnetic field independent up to 8 T, which excludes the possibility of a magnetic coupling to the static CDW structure in $Lu_5Rh_4Si_{10}$.

DOI: 10.1103/PhysRevB.66.033101 PACS number(s): 64.70.Rh, 65.40.−b, 71.45.Lr

$Lu_5Rh_4Si_{10}$ is a well-ordered intermetallic compound with a $Sc_5Co_4Si_{10}$-type crystal structure (space group $P4/mbm$). A previous resistivity and susceptibility study indicated the formation of charge-density-wave (CDW) ground state at around $T_0 \sim 147$ K, in spite of its three-dimensional structure. [1–3] Recently, we observed a spike-shaped specific heat jump $\Delta C_P (\sim 40$ J/mol K) within a very narrow temperature region in $Lu_5Rh_4Si_{10}$ near its CDW transition.[4] Such a result, similar to those found in its isostructural compounds $Lu_5Ir_4Si_{10}$ and $Er_5Ir_4Si_{10}$,[5–7] corresponds to a huge entropy change. Obviously the mean-field description for weakly coupled CDW formations is not appropriate for the transitions found in these materials, and thus the CDW transition of this type was proposed to be first order.[5] However, we have seen no evidence of thermal hysteresis in C_P of $Lu_5Ir_4Si_{10}$ within our measurement resolution.[6] To further explore the nature of the transition in $Lu_5Rh_4Si_{10}$, we performed measurements under heating and cooling cycles to examine the possible thermal hysteresis behavior, a characteristic feature exhibited in a first-order phase transition. Indeed, in the present study, we report the discovery of thermal hysteresis near the transition of $Lu_5Rh_4Si_{10}$ in resistivity (ρ), magnetic susceptibility (χ), heat capacity (C_P), thermal conductivity (κ), and thermoelectric power (S). The observations are attributed to the presence of metastable states arising from pinning of the CDW phase to the transition. In addition, we carried out resistivity, susceptibility, as well as heat capacity measurements with the application of magnetic field to examine the possible origins associated with the observed hysteresis.

The samples studied were prepared by an arc-melting technique described elsewhere.[2] Figure 1 presents the temperature variation of electrical resistivity of $Lu_5Rh_4Si_{10}$ measured during warming process by a standard four-terminal method. Near the CDW transition temperature $T_0 \sim 147$ K, an abrupt increase in ρ was observed, a characteristic response in ρ for CDW formation. The resistivity enhancement $\Delta\rho/\rho$ was estimated to be approximately 15%, consistent with the previously reported value.[2] In this study, we further found an unambiguous thermal hysteresis of about 3 K in the vicinity of the transition. This feature is not affected by external magnetic field up to 8 T, as shown in the inset of Fig. 1.

The magnetic susceptibility was measured using a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer on a sample that was cut from the same batch for ρ measurements. The data displayed in Fig. 2 was obtained during warming process in a dc field of 0.1 T under zero field cooled condition. The drop in χ, consistent with the previous result,[2] is attributed to a reduction of Pauli paramagnetism which is related to a partial opening of an energy gap and thus a loss of electronic density of states at the Fermi level. As shown in the inset of Fig. 2, a well-defined thermal hysteresis loop of about 2 K appears around T_0. In this investigation, dc fields of 0.1, 0.5,

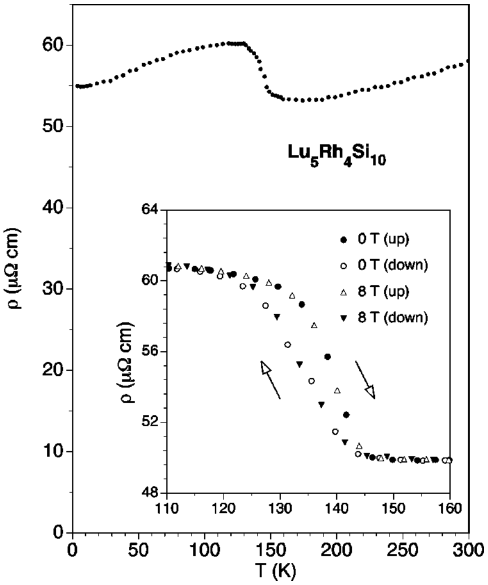

FIG. 1. Temperature dependence of electrical resistivity of $Lu_5Rh_4Si_{10}$. Inset: the thermal hysteresis of electrical resistivity near T_0 in fields of 0 and 8 T.

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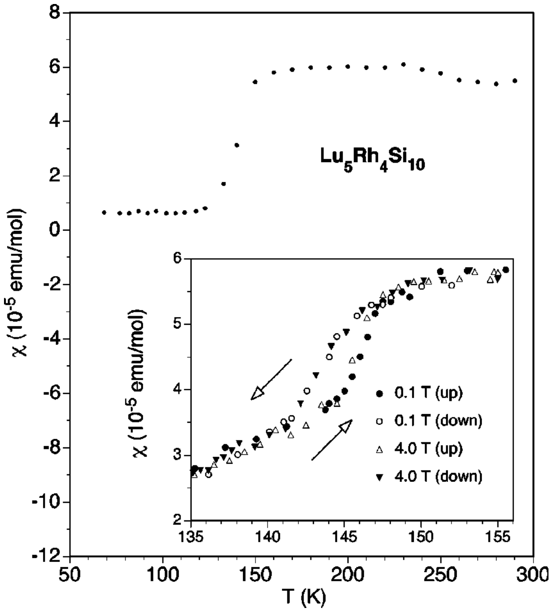

FIG. 2. Temperature dependence of magnetic susceptibility of $Lu_5Rh_4Si_{10}$. The inset shows a clear hysteresis loop in the vicinity of the transition with fields of 0.1 and 4.0 T.

1, and 4 T were applied for χ measurements, but we only present the data measured for 0.1 and 4 T fields. It is clearly seen in this figure that the transition temperature and the hysteretic feature of susceptibility for $Lu_5Rh_4Si_{10}$ are essentially unchanged with field.

For specific heat measurements, relative heat capacity data were obtained by an ac calorimetry, using chopped light as a heat source.[8] The absolute value of the specific heat in zero field was determined by measuring a powder sample (~200 mg) using a differential scanning calorimetry (DSC) with a precision better than 3%. The ac results were thus corrected for their addendum heat capacities (GE varnish and thermocouple wire) and normalized to the DSC data at 180 K. The temperature-dependent specific heat of $Lu_5Rh_4Si_{10}$ upon cooling is illustrated in Fig. 3. Near T_0, a pronounced anomaly in C_p with a huge excess specific heat $\Delta C_p/C_p \sim 15\%$ was observed. In this study, we found that the transition is hysteretic with a loop of about 2 K. In addition, the application of magnetic field up to 8 T has no effects on the hysteresis loop of C_p, as demonstrated in the inset of Fig. 3.

The T-dependent thermal transport measurements including conductivity and thermoelectric power were carried out simultaneously in a close-cycle refrigerator over temperatures from 10 to 300 K, using a direct heat-pulse technique.[6] The representative κ in $Lu_5Rh_4Si_{10}$ obtained by a warming process is shown in Fig. 4. A broad maximum appears at around 30 K which is due to the reduction of thermal scattering at low temperatures. Around T_0, κ has a sharp drop accompanied by a well-defined peak in which a hysteresis loop (~2 K) is observed, as demonstrated in the inset of Fig. 4. The abrupt drop in κ near T_0 can be fit very well with the resistivity data by means of the Wiedmann-Franz law,[4] an

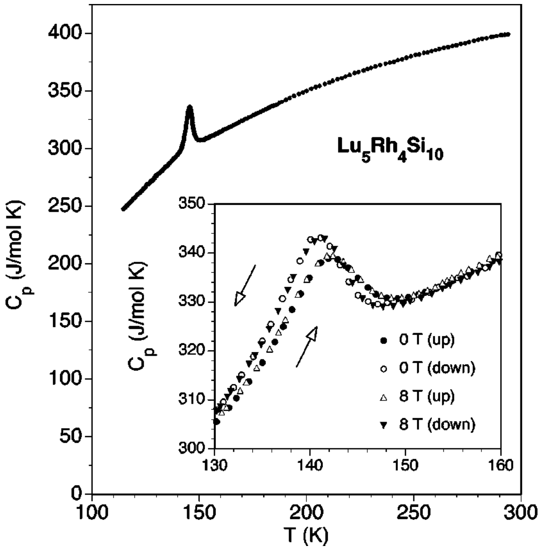

FIG. 3. Temperature dependence of specific heat of $Lu_5Rh_4Si_{10}$. The inset shows the thermal hysteresis of specific heat near T_0 in fields of 0 and 8 T.

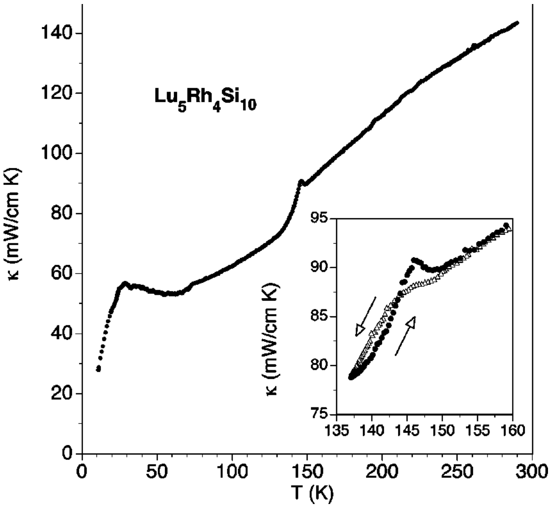

FIG. 4. Thermal conductivity as a function of temperature for $Lu_5Rh_4Si_{10}$. The inset demonstrates the thermal hysteresis near T_0.

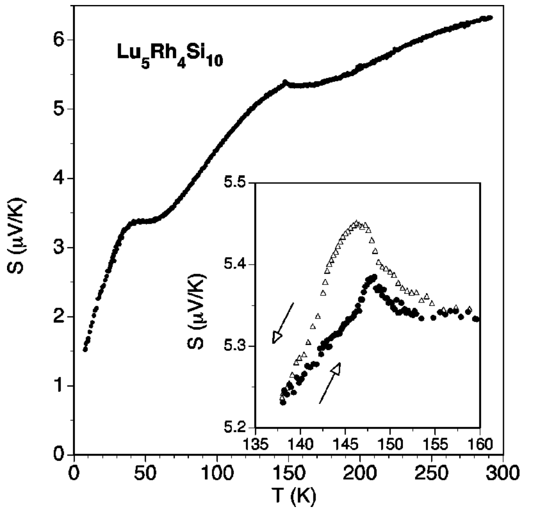

FIG. 5. Thermoelectric power as a function of temperature for $Lu_5Rh_4Si_{10}$. The inset demonstrates the thermal hysteresis near T_0.

indication of the sharp drop is essentially caused by the reduction of electronic contributions. The occurrence of a peak in κ at T_0 could be understood as a result of heat carried by soft phonons occurring during the phase transition.[4]

The T-dependent S of $Lu_5Rh_4Si_{10}$ measured during heating process is plotted in Fig. 5. A broad shoulder at around 50 K is attributed to the phonon drag effect, commonly seen at low temperatures in metals. In the vicinity of T_0, the Seebeck coefficient exhibits a pronounced peak with $\Delta S/S \sim 3\%$, consistent with the value previously reported.[4] The peak in S could be associated with soft phonons which enhance the heat transport. As presented in the inset of Fig. 5, a thermal hysteresis loop of about 2 K also appears in S near the transition. It is worthwhile mentioning that measurements of S in quasi-1D CDW systems such as 2H-$TaSe_2$ (Ref. 9) and $(NbSe_4)_{10}I_3$ (Ref. 10) also show similar hysteresis loops near their transition temperatures. It indicates that the origin of the thermal hysteresis behavior in these systems arises from the same mechanism, presumably due to the pinning of the CDW phase to impurities.

As we should address here, to ensure the reproducibility of the observed thermal hysteresis in $Lu_5Rh_4Si_{10}$, at least two pieces cut from different ingots were measured. All presented features are repeatable for different experimental runs on the same sample, but the observed peaks are somewhat sample dependent. The absolute measured values are slightly different from different measurements, mainly due to the uncertainty on sample dimensions. In spite of this discrepancy, their intrinsic hysteresis features would remain unchanged.

Although similar thermal hysteresis has been discovered in many low-dimensional CDW systems such as 2H-$TaSe_2$ (Ref. 9), $(NbSe_4)_{10}I_3$ (Ref. 10), and TaS_3 (Ref. 11), the hysteretic behavior found in $Lu_5Rh_4Si_{10}$ near its CDW transition is thought to be the first example of this kind in the ternary rare-earth transition-metal silicide system. The hysteretic features in low-dimensional CDW materials are typically interpreted as arising from pinning of the CDW phase to impurities. In this regard, a number of CDW metastable states may appear, due to a freezing of the wave vector to a nonequilibrium average value. The choice of a particular metastable state therefore depends on the thermal history of the sample and the time scale of the experiment, which leads to irreversible characteristics for measured physical quantities. Experimental results obtained from time-dependent resistivity studies in TaS_3 seem to be consistent with this argument.[11,12] This picture is also appropriate to the current case of $Lu_5Rh_4Si_{10}$. For other ternary rare-earth transition-metal silicides such as $Lu_5Ir_4Si_{10}$, the pinning force between the CDW phase and impurities may not be sufficient to result in any irreversible behavior, and thus explains why the hysteresis behavior is visible in $Lu_5Rh_4Si_{10}$ but not in $Lu_5Ir_4Si_{10}$.[6] However, this proposed mechanism for the hysteretic behavior is not exclusively restricted to either first-order or second-order phase transitions. Hence, the true thermodynamic nature of the CDW transition in $Lu_5Rh_4Si_{10}$ has not yet be established by present measurements.

Another class of CDW systems having a 3D structure is CuV_2S_4 which is the most studied material of this type.[13] Multiple phase transitions corresponding to incommensurate, commensurate, and incommensurate states at 90, 75, and 50 K, respectively, have been identified by x-ray diffraction. In addition, a large thermal hysteresis of about 10 K has been observed in both resistivity and magnetic susceptibility at around 50 K, which suggests a first-order phase transition associated with this incommensurate CDW transition. While the 3D structure, the coexistence of superconductivity with CDW features, and the observed thermal hysteretic behaviors in $Lu_5Rh_4Si_{10}$ are reminiscent of those in CuV_2S_4, conclusive evidence for an incommensurate transition in $Lu_5Rh_4Si_{10}$ will have to wait till an exact phase identification of the superlattice by x-ray diffraction.

Now, we turn to the magnetic field dependence on the resistivity, magnetic susceptibility, and specific heat data. In general, CDW materials with magnetic-field-induced phenomena are typically associated with CDW coupling with magnetic impurities, field-induced spin-density wave (SDW) mixed with CDW ground states, or field-modified Fermi surface. For the extensively studied CDW system $NbSe_3$, the large field-enhanced resistance was initially attributed to the mixture of SDW with CDW ground states,[14] but the NMR results indicated a pure CDW enhancement associated with Fermi surface changes.[15] The latter mechanism normally occurs in nearly compensated metals, although the Fermi surface may contain several electron and hole pockets. With the application of an external magnetic field, the Fermi-surface will be modified and thus change the electronic band structures. Apparently $Lu_5Rh_4Si_{10}$ can not be classified as this type of metals. The origin of a mixture of SDW with CDW ground states has been discussed by several authors. Overhauser has mentioned that a SDW component may develop if the elastic stiffness constants are sufficiently anharmonic in a CDW metal.[16] Gor'kov and Lebed have argued that for the case of simple anisotropic metals with two open nesting Fermi surfaces, the tendency to SDW formation could be enhanced by external magnetic field.[17] The observation of a magnetic-field independence in the vicinity of the CDW transition in $Lu_5Rh_4Si_{10}$ suggests that its CDW nature does not have the appropriate characteristics of these various models.

In summary, an unambiguous thermal hysteresis loop in $Lu_5Rh_4Si_{10}$ near its CDW transition has been observed by means of resistivity, magnetic susceptibility, heat capacity, thermal conductivity, as well as thermoelectric power measurements. The hysteretic behavior in $Lu_5Rh_4Si_{10}$ is presumably due to pinning of the CDW phase to impurities, which could result in the relaxation time exceeding any practical time scale for real measurements. In addition, we have demonstrated that there is no coupling between an applied magnetic field (up to 8 T) and the static CDW structure in $Lu_5Rh_4Si_{10}$. Although possible origins and mechanisms have been discussed, a specific extension of the theoretical models to $Lu_5Rh_4Si_{10}$ and additional experimental data based on the single crystal x-ray diffraction study would be required to verify whether the transition is first-order and the true incommensurate nature in this material.

This work was supported by National Science Council, Taiwan, under Grant Nos. NSC-90-2112-M-259-017 (Y.K.K), NSC-90-2112-M-110-012 (H.D.Y), and NSC-90-2112-M-415-002 (C.S.L).

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