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Specific heat of cadmium arsenide (Cd_3As_2) below 30 K

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The low-temperature specific heat of Cd_3As_2 has been measured over the temperature range between 1.7 and 30 K. In this range, the specific heat is dominated by the lattice contribution, which yields a limiting Debye characteristic temperature at absolute zero $\Theta_D(0)=111\pm3$ K. This value is found to be in good agreement with that calculated from the experimental sound velocities.

In recent years, a great amount of work has been done on Cd_3As_2 in order to determine its electronic energy-band structure. It is now established that Cd_3As_2 has an inverted energy-band structure near the Γ point of the Brillouin zone, analogous to that of the well-known narrow-gap semiconductors HgTe and HgSe.[1] An excellent survey of the progress that has recently been made in the understanding of the electronic properties of Cd_3As_2 can be found in a review article by Blom.[2] In contrast, much less attention has been paid to the determination of the lattice properties of Cd_3As_2. In particular, little is known regarding the low-temperature thermal properties of this compound. The purpose of this paper is to report the first measurement of specific heat of Cd_3As_2 at low temperatures.[3]

We had a 3.684-g sample of Cd_3As_2, kindly supplied by Prof. Blom (University of Technology, Eindhoven, The Netherlands). This sample consisted of a few large crystals. The specific-heat measurements were performed in a conventional adiabatic calorimeter in the temperature range from 1.7 to 30 K. The sample was fixed by copper clips and isolated from the calorimeter by nylon threads. A mechanical heat switch was used to cool the sample. The temperature was measured with a carbon resistance thermometer calibrated with an accuracy of 10^{-3} K. The experiment involved about 90 data points over the temperature range investigated. The precision of an individual specific-heat measurement was estimated to be better than 3%.[4]

The results of our specific-heat (C) measurements are shown in Fig. 1, where C/T^3 (given in $\mu J/K^4\,g$) is plotted against temperature (T). As we can see, the lowest-temperature data do not show any evidence of the contribution of an electronic term linear in the temperature to the measured C values. This is consistent with the fact that Cd_3As_2 should normally have a very small electronic contribution (γT) to its low-temperature specific heat. In fact, using the known physical parameters for this material, we readily obtain the estimated value $\gamma\sim0.014$ $\mu J/K^2$ g.[5] With this value of γ, the electronic specific heat is indeed insignificant in the temperature range covered in this experiment as compared to the measured C values (for example, at $T\sim2$ K, $C\sim25$ $\mu J/K\,g$). As a consequence, we are thus led to the conclusion that the analysis of our C vs T data can be carried out essentially in terms of a lattice contribution only. Now, as can be seen in Fig. 1, starting at about 2–3 K, C shows a rapid deviation from the low-temperature asymptotic T^3 behavior expected from the Debye lattice model. This deviation is at the origin of the large, well-defined maximum in the C/T^3 vs T curve near 9–10 K, as shown in Fig. 1. In fact, for an ideal Debye solid, namely, for a pure ω^2 lattice frequency distribution, the low-temperature C/T^3 vs T plot would strictly result in a horizontal line at $C/T^3=\alpha$, where α is related to the limiting Debye characteristic temperature at absolute zero $\Theta_D(0)$ through the well-known

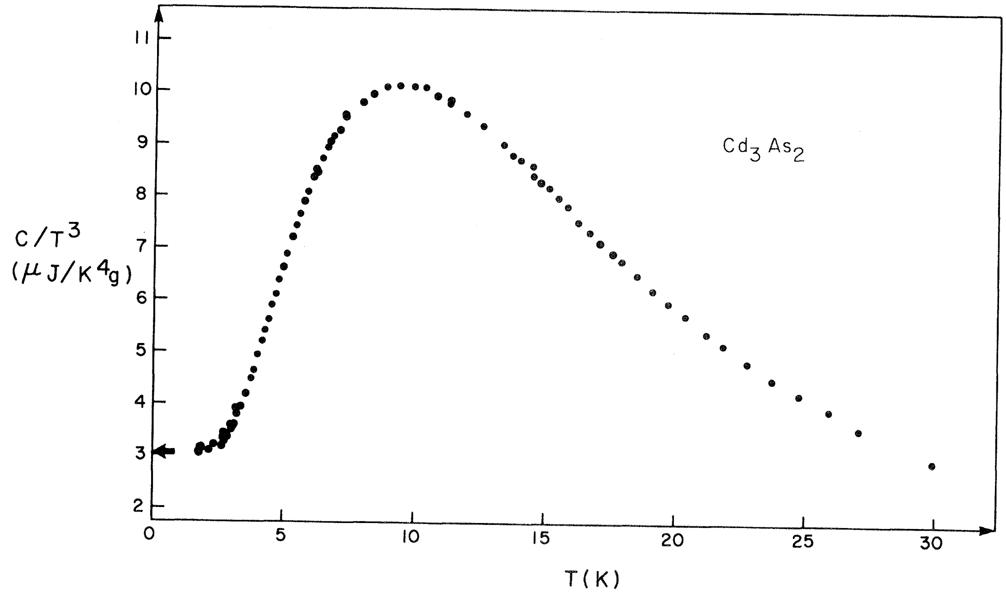

FIG. 1. C/T^3 as a function of T for cadmium arsenide. The arrow indicates the asymptotic value $\lim(C/T^3)$ as $T \rightarrow 0$ K, as determined from the experimental sound velocities.

asymptotic expression (valid in the limit $T \rightarrow 0$ K) (Ref. 6)

$$\Theta_D(0) = \left[\frac{12\pi^4 R}{5M\alpha}\right]^{1/3}, \tag{1}$$

in which $R = 8.314 \times 10^6$ μJ/K mole is the universal gas constant, M is the molecular weight of the solid, and α is given in μJ/K^{4}g. For Cd_3As_2 ($M = 487.0$), Eq. (1) reads

$$\Theta_D(0) = \left[\frac{3.991 \times 10^6 \ \mu\text{J/K g}}{\alpha}\right]^{1/3}. \tag{2}$$

As is well known,[7] such a deviation of the low-temperature lattice specific heat from the strict asymptotic form αT^3 generally occurs in the temperature region beyond about $\Theta_D(0)/50$, so that we can roughly estimate the value of $\Theta_D(0)$ for Cd_3As_2 to be somewhere in the range 100–150 K. Unfortunately, this marked non-Debye-like nature of the lattice contribution or, alternatively, the relatively low value of $\Theta_D(0)$, makes it difficult to analyze accurately our specific-heat data for Cd_3As_2.

The analysis of our C vs T data is carried out using the usual power series expansion in the temperature[7,8]

$$C = \sum_n a_{2n+1} T^{2n+1}, \quad (n = 0,1,2,3,\ldots). \tag{3}$$

Since the exact value of the $a_1 = \gamma$ coefficient has little effect on the analysis, the various terms $a_3 = \alpha, a_5, a_7$, etc., are obtained by forcing a_1 to have the value estimated theoretically (namely, 0.014 μJ/K^2 g) (Ref. 5) and by next using a least-squares computer fitting procedure. Due to the fact that Cd_3As_2 has a relatively low $\Theta_D(0)$ value, our lowest temperature (~ 1.7 K) is relatively high, so that many terms are required in Eq. (3) to fit the experimental data over the temperature range in which we are interested. Since the terms a_5, a_7, etc., have no easily identifiable physical significance, we have used, alternatively, overlapping fits in the liquid-helium region, over limited temperature ranges, to analyze our data in terms of Eq. (3). The values for the leading coefficients, namely, $a_3 = \alpha$ and a_5, which result from these analyses, appear to be essentially independent of the temperature ranges used, which thus gives some confidence to the uniqueness of the coefficients. These are $\alpha = 2.9 \pm 0.2$ μJ/K^{4}g and $a_5 = 0.06 \pm 0.03$ μJ/K^{6}g. Substituting this value of α into Eq. (2), we readily deduce $\Theta_D(0) = 111 \pm 3$ K for the limiting Debye characteristic temperature at 0 K of Cd_3As_2. This value of $\Theta_D(0)$ can be compared with that calculated from the experimental sound velocities, according to the asymptotically exact (as $T \rightarrow 0$ K) result[6,9]

$$\lim_{T \rightarrow 0\,\text{K}} \left[\frac{C}{T^3}\right] = \frac{2\pi^2}{15} \frac{k_B^4}{\hbar^3 \rho} \left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right], \tag{4}$$

where v_l and v_t are the longitudinal and transverse acoustical phonon velocities, and the other quantities are defined in Ref. 5. Taking the observed values $v_l = 3.5 \times 10^3$ m/s and $v_t = 1.65 \times 10^3$ m/s for Cd_3As_2,[10] we readily obtain from Eqs. (2) and (4), $\Theta_D(0) = 109.1$ K. As we can see, this calculated value of $\Theta_D(0)$ is in good agreement with that deduced from our specific-heat fitting analyses.

To conclude this paper, we should emphasize the need for extending the present specific-heat measurements on Cd_3As_2 to lower temperatures, for example, to $0.1-0.3$ K. In fact, such measurements would make it possible not only to obtain a better (that is to say, more accurate) determination of α and, consequently, of $\Theta_D(0)$, but also to extract a measure of γ, the coefficient of the linear term in the electronic specific heat. If the measurements are performed on well-characterized single crystals of Cd_3As_2 of known electron concentrations, an accurate knowledge of this latter coefficient would be of great importance in providing further information about the electronic energy band structure of Cd_3As_2.

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[2] F. A. P. Blom, in *Proceedings of the International Summer School on Narrow-Gap Semiconductor Physics and Applications, Nîmes, 1979* (Springer-Verlag, New York, 1980), p. 191.

[3] Specific-heat measurements on Zn_3P_2, Cd_3P_2, Zn_3As_2, and Cd_3As_2, over the temperature range from 300 to 55 K, were reported previously by A. F. Demidenko, G. N. Danilenko, V. E. Danilenko, V. B. Lazarev, V. Ya. Shevchenko, S. F. Marenkin, and S. E. Kozlov, in Izv. Akad. Nauk SSSR Neorg. Mater. 13, 214 (1977) [Inorg. Mater. (USA) 13, 181 (1977)]. A brief review of this work is given by V. Ya. Shevchenko, in *Proceedings of the First International Symposium on the Physics and Chemistry of II-V Compounds, Mogilany, 1980* (Eindhoven University of Technology, Eindhoven, 1981), p. 15. We should recall here that Cd_3As_2, along with Zn_3P_2, Cd_3P_2, and Zn_3As_2, belongs to a class of materials with the general formula A_3B_2, where A is a group-II and B a group-V element, that have the tetragonal crystal structure [M. von Stackelberg and R. Paulus, Z. Phys. Chem. (Leipzig) B 28, 427 (1935); G. A. Steigmann and J. Goodyear, Acta Crystallogr. B 24, 1062 (1968)].

[4] For a complete description of the experimental details, see J. C. Michel, Thèse de Doctorat-ès-Sciences, Grenoble, 1967 (unpublished).

[5] We can readily estimate the electronic contribution (γT) to the specific heat of Cd_3As_2 at low temperatures by simply calculating the value of γ for a degenerate Fermi gas of electrons in a spherical parabolic energy band, using the well-known expression (see

Ref. 6, Chap. 2, p. 29)

$$\gamma = A \left[\frac{m^*}{m_0} \right] \frac{N^{1/3}}{\rho},$$

where $A = (\pi/3)^{2/3} k_B^2 m_0/\hbar^2 = 1.610 \times 10^{-6}$ μJ/K^2 cm^2, k_B is Boltzmann's constant, $\hbar$ is the Planck constant divided by 2π, m_0 is the free-electron mass, N is the number of electrons per cm^3, ρ is the mass density, and m^* is the electron effective mass. Assuming that N is typically of the order of 2×10^{18} cm^{-3}, which corresponds to a Fermi energy $E_F = 0.20$ eV and to a conduction-electron effective mass at E_F $m^* = m^*(E_F) = 0.043$ [see J.-P. Jay-Gerin, M. J. Aubin, and L. G. Caron, Solid State Commun. 21, 771 (1977)], and using $\rho = 6.21$ g/cm^3 [see, for example, W. Żdanowicz and L. Żdanowicz, in *Annual Review of Materials Science* (Annual Reviews, Palo Alto, California, 1975), Vol. 5, p. 301], we obtain $\gamma = 0.014$ μJ/K^2 g. Obviously, a more accurate determination of this parameter would be complicated by the necessity of taking properly into account the known anisotropy and the strong nonparabolicity of the Cd_3As_2 conduction band.

[6] See, for example, N. W. Ashcroft and N. D. Mermin, in *Solid State Physics* (Holt, Rinehart and Winston, Philadelphia, 1976), Chap. 23, p. 451.

[7] See, for example, T. H. K. Barron and J. A. Morrison, Can. J. Phys. 35, 799 (1957).

[8] T. C. Cetas, C. R. Tilford, and C. A. Swenson, Phys. Rev. 174, 835 (1968); T. C. Cetas, J. C. Holste, and C. A. Swenson, *ibid.* 182, 679 (1969); J. C. Holste, Phys. Rev. B 6, 2495 (1972).

[9] Strictly speaking, Eq. (4) applies only to amorphous or truly isotropic solids. In fact, the calculation of $\Theta_D(0)$ from acoustical velocity measurements is, in general, much more complex even for cubic crystalline solids. Although Cd_3As_2 has the tetragonal crystal structure (see Ref. 3), the values of the longitudinal and transverse sound velocities reported in the literature for this material and used in Eq. (4) were obtained on polycrystalline Cd_3As_2 samples, so that the application of Eq. (4) is justified here.

[10] I. Rosenman, Solid State Commun. 3, 405 (1965); J. P. Saint-Martin, in *Proceedings of the 9th International Conference on the Physics of Semiconductors, Moscow, 1968* (Nauka, Leningrad, 1968), Vol. 2, p. 878; A. Lebourgeois, quoted in M. T. Clavaguera, J. Phys. Chem. Solids 36, 1205 (1975); A. A. Lakhani (unpublished results); L. Opilska and A. Opilski, Phys. Status Solidi A 35, K183 (1976).