

and adding  $(\psi, v\psi) = (|\psi|, v|\psi|)$  to both sides yields Eq. (3).

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<sup>1</sup>See, e.g., K. Jörgens, *Math. Z.* **96**, 355–372 (1967);

P. R. dos Santos and H. S. Brandi, *Phys. Rev. A* (to be published); R. Lavine and M. O'Carroll, to be published.

<sup>2</sup>T. Kato, *Israel J. Math.* **13**, 135–148 (1973). Kato proves that  $H(0)|\psi| \leq \text{Re}[(\text{sgn}\psi)H(a)\psi]$ , whence (3) follows by multiplying by  $|\psi|$  and integrating.

<sup>3</sup>Since  $|\psi|$  is not differentiable, one should really prove (3) as Kato does, letting  $\psi_\epsilon = (|\psi|^2 + \epsilon^2)^{1/2}$  and then taking  $\epsilon$  to zero.

## Saturation of the High-Temperature Normal-State Electrical Resistivity of Superconductors

Z. Fisk\* and G. W. Webb†

*Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093*

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The high-temperature, normal-state resistivity of strong-coupled superconducting transition-metal compounds saturates at a value corresponding to an electron mean free path of the order of the interatomic spacing in the compound. This accounts for the nonlinear temperature dependence of the resistivity observed in these compounds at high temperature.

The normal-state electrical resistivity ( $\rho$ ) of a large class of transition-metal superconductors, including the high- $T_c$  A-15 structure compounds, is known to have a temperature dependence very different from that predicted by the Bloch-Grüneisen theory or Wilson's modification thereof.<sup>1-4</sup> Near  $T_c$  the electrical resistance varies approximately as  $T^3$ , consistent with Wilson's theory<sup>5</sup>; this regime joins smoothly to one of strong negative curvature ( $d^2\rho/dT^2 < 0$ ), the inflection point,  $d^2\rho/dT^2 = 0$ , being quite generally of order 100°K; at high temperature the resistivity rises less rapidly than a linear  $T$  dependence. We ask how this curvature in the resistivity is related to the occurrence of superconductivity.

One ingredient of the answer is that the electron-phonon coupling ( $\lambda$ ) in such materials is large. This follows from the magnitude of the observed resistivities: The room-temperature value is high, typically 50–70  $\mu\Omega$  cm. In addition, the inflection point of the resistance curve moves to lower temperature as  $T_c$  increases in closely related sequences of compounds,<sup>6</sup> consistent with an increased  $\lambda$ . Anomalous curvature occurs, then, when  $\lambda$  is large.

Large  $\lambda$  itself, however, does not account for the curvature. Two plausible explanations have been proposed for this curvature. One is the Cohen, Cody, and Halloran model<sup>3</sup>: A rapid temperature dependence of the density of states at

the Fermi level resulting from a nearly empty or full high-density-of-states  $d$  band overlying a low-density-of-states  $s$  band leads to resistance curves of the kind observed. This model successfully correlates the resistance with a number of other temperature-dependent properties of Nb<sub>3</sub>Sn, V<sub>3</sub>Si, and V<sub>3</sub>Ga. The other explanation is that of Allen *et al.*<sup>7</sup>: Hardening of lattice vibrational modes as  $T$  increases results in a resistivity which rises with less than a linear  $T$  dependence. On the basis of neutron data for V<sub>3</sub>Si, they can account for about half the curvature observed in the resistivity of V<sub>3</sub>Si from  $T_c$  to room temperature.

We believe that, while the above treatments are appropriate to these materials, at high temperatures a different effect dominates. Figure 1 shows data on the electrical resistivity of A-15 structure Nb<sub>3</sub>Sn ( $T_c = 18^\circ\text{K}$ ) and single crystal Nb<sub>3</sub>Sb ( $T_c = 0.2^\circ\text{K}$ ). Data for Nb<sub>3</sub>Sn were read from a graph in Ref. 1. Knapp, Bader, and Fisk have measured the heat capacity of both these compounds between 2 and 400°K.<sup>8</sup> The electronic specific heat  $\gamma$  for Nb<sub>3</sub>Sb is 1.1 mJ/°K<sup>2</sup> gram-atom, more than a factor of 10 less than that of the isostructural Nb<sub>3</sub>Sn. In addition, analysis of the anharmonic contribution to the heat capacity shows that the Nb<sub>3</sub>Sb lattice softens as  $T$  increases, opposite to Nb<sub>3</sub>Sn. It is unlikely, therefore, that the previous two explanations apply to Nb<sub>3</sub>Sb, yet its resistivity is very similar to that of Nb<sub>3</sub>Sn

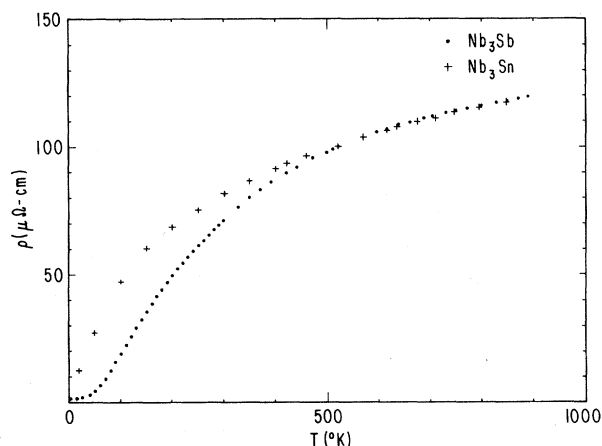


FIG. 1. The resistivities of  $\text{Nb}_3\text{Sb}$  and  $\text{Nb}_3\text{Sn}$ . The data for  $\text{Nb}_3\text{Sn}$  were taken from Ref. 1. Not all points are plotted. The  $T_c$  of  $\text{Nb}_3\text{Sn}$  is 18°K while that of  $\text{Nb}_3\text{Sb}$  is 0.2°K. Note that the two curves are nearly identical above 500°K. At lower temperatures, e.g., 50°K, different residual resistivities can account for less than half the difference between the two resistivities; the remainder of the difference we ascribe to the stronger electron-phonon interactions in  $\text{Nb}_3\text{Sn}$ .

in both shape and magnitude above room temperature. The resistivity for both compounds appears to be saturating at  $\rho_{\text{sat}} \sim 150 \mu\Omega \text{ cm}$ . One may interpret such a limit as a lower limit to the electron mean free path in the solid. Ioffe and Regel<sup>9</sup> and Mott<sup>10</sup> point out that this lower limit would be of order of the interatomic spacing of the material. There is no theory at present predicting a functional form for the approach to saturation.<sup>11</sup>

The value we find for  $\rho_{\text{sat}}$  in these compounds is not unreasonable in light of the detailed calculations for Nb by Yamashita and Asano.<sup>12</sup> They find that a resistivity which they calculate at 290°K to be about  $20 \mu\Omega \text{ cm}$  corresponds roughly to a mean free path of 30 Å. This implies a  $\rho_{\text{sat}}$  for Nb of some  $200 \mu\Omega \text{ cm}$ . We expect  $\rho_{\text{sat}}$  for the A-15 structure compounds to be of the same order of magnitude. A free-electron estimate using the Drude formula yields a similar value.

The large room-temperature resistivity of the poor superconductor  $\text{Nb}_3\text{Sb}$  is somewhat surprising and something we do not fully understand.<sup>13</sup> At low temperature the phonon resistivity of  $\text{Nb}_3\text{Sn}$  is much larger than that of  $\text{Nb}_3\text{Sb}$ . But it is difficult to make a comparison based on  $\lambda$ 's which differ by a factor of 3.3<sup>8</sup> since the functional form of the resistivity for the two compounds is completely different, being  $T^2$  for  $\text{Nb}_3\text{Sn}$  and  $T^{3.6}$  for  $\text{Nb}_3\text{Sb}$ .<sup>14</sup>

For a cubic metal we can write

$$\rho = \frac{12\pi^3\hbar/e^2}{\int \tau v dS}.$$

The relaxation time  $\tau$  and the magnitude of the electron velocity  $v$  are functions of the wave vector. The integral is over the Fermi surface. At saturation the mean free path,  $\tau v$ , will be a function of wave vector determined by the interatomic distances in the crystal. The fact that  $\rho_{\text{sat}}$  for  $\text{Nb}_3\text{Sn}$  and  $\text{Nb}_3\text{Sb}$  are roughly the same indicates that the averaged mean free path times the Fermi surface area for the two compounds is nearly the same at high temperature.

Our conclusion is that the resistivity at high temperatures of those superconductors whose resistivity is strongly curved is so large that the electron mean free path saturates at a lower limit, the interatomic spacing. The region of extended negative curvature in the resistivity is a result of the mean free path not depending linearly on the scattering perturbation. It is a further consequence of these ideas that the magnitude of the temperature-dependent (phonon) contribution to the resistivity will be decreased if the mean free path in the absence of phonons is already short, because, for example, of spin fluctuations or the atomic disorder produced by alloying or defects. This is observed. In the case of atomic disorder, Mooij has noted that  $d\rho/dT$  for concentrated transition-metal alloys decreases to zero in the vicinity of  $150 \mu\Omega \text{ cm}$  and concludes that the mean free path is then of order of the interatomic spacing.<sup>15</sup> Similar considerations can be applied to rare-earth and actinide intermetallic compounds with large resistivities.

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<sup>8</sup>G. S. Knapp, S. D. Bader, and Z. Fisk, in Proceedings of the International Conference on Low Lying Lattice Vibrational Modes and Their Relationship to Superconductivity and Ferroelectricity, San Juan, Puerto Rico, 1975 (to be published).

<sup>9</sup>A. F. Ioffe and A. R. Regel, Prog. Semicond. 4, 237 (1960).

<sup>10</sup>N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974), p. 23 ff.

<sup>11</sup>Empirically we find that over the range 500 to 1000°K the resistivity of both compounds appears to be approaching saturation as  $T^{-1}$ .

<sup>12</sup>J. Yamashita and S. Asano, Prog. Theor. Phys. 51, 317 (1974).

<sup>13</sup>Part of the answer for the high room-temperature resistivity of Nb<sub>3</sub>Sb is probably to be found in the fact that its Fermi surface is quite complicated, having at least four sheets (A. Arko and Z. Fisk, to be published).

<sup>14</sup>G. W. Webb, Z. Fisk, J. J. Engelhardt, and S. Bader, to be published.

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## Polariton Effects in the Exciton Absorption of GaSe

A. Bosacchi

*Laboratorio Materiali Speciali per Elettronica e Magnetismo, Consiglio Nazionale delle Ricerche, 43100 Parma, Italy*

and

B. Bosacchi

*Istituto di Fisica dell'Università, Parma, Italy, and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Parma, Italy*

and

S. Franchi

*Laboratorio Materiali Speciali per Elettronica e Magnetismo, Consiglio Nazionale delle Ricerche, 43100 Parma, Italy*

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An anomalous temperature and thickness dependence in the optical absorption of the lowest direct exciton of GaSe is reported. The effect, which is interpreted as a result of the competition between exciton-photon interaction and exciton dissipation mechanisms (phonon and surface scattering), provides strong experimental evidence for the polariton description of the exciton absorption process in semiconductors.

Hopfield has shown that the creation of an exciton by a photon in a crystal does not in itself lead to any absorption of light, unless the exciton undergoes a scattering process.<sup>1</sup> A very direct consequence of this result, which, however, has not received much attention so far, is the possibility of a substantial reduction of the exciton absorption in comparison with the corresponding value of the semiclassical theory.<sup>2</sup> In fact, this has to be expected when the "polariton" frequency  $f$  (i.e., the rate of exchange of energy back and forth between the excitonlike and photonlike states of the polariton excitation) is fast compared with the frequency  $\gamma$  which characterizes phenomenologically the exciton (polariton) scattering processes. In this Letter we present and

discuss some data on the optical absorption of the lowest direct exciton in GaSe, which provide strong experimental evidence for the above effect.

GaSe is an indirect gap semiconductor: There is, however, a direct transition only  $\sim 50$  meV higher, to which the lowest direct exciton is associated.<sup>3</sup> Since when the electric field  $\vec{E}$  of the radiation is perpendicular to the  $\vec{c}$  axis both the direct and indirect transitions are allowed only if the spin-orbit interaction is taken into account, this exciton has a relatively low absorption strength, and is therefore well suited for experimental investigation. We have performed a detailed study of the temperature dependence of its optical absorption, on several samples of vari-