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MÖSSBAUER STUDIES OF TERNARY SUPERCONDUCTORS

by

C.W. Kimball, G.L. Van Landuyt, C.D. Barnet,
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Mössbauer Studies of Ternary Superconductors

C. W. Kimball, G. L. Van Landuyt, and C. D. Barnet
Northern Illinois University, DeKalb, Illinois 60115†

and

G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin
Argonne National Laboratory, Argonne, Illinois 60439*

ABSTRACT

Mössbauer studies of the ternary Chevrel phase and rare earth rhodium boride superconductors have been made. Anomalous phonon properties at the Sn site in $SnMo_6S_8$, $SnMo_6Se_8$, and $La_{0.98}Sn_{0.02}Mo_6Se_8$ have been investigated. Studies of polarization of conduction electrons at the site of the magnetic ion have been made by means of the ^{151}Eu Mössbauer effect in $Eu_xSn_{1-x}Mo_6S_8$ and the effects of such polarization on superconducting properties discussed. The Mössbauer effect in ^{166}Er has been used to investigate the electronic ground state in the ternary compound $ErRh_4B_4$ both in the superconducting and magnetically ordered states.

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RESUMÉ

Des etudes Mössbauer de phases de Chevrel et rare earth rhodium boride supraconductrices sout discutées. On a étudié des anomalies de phonons au site de Sn dans $SnMo_6S_8$, $SnMo_6Se_8$ et $La_{0.98}Sn_{0.02}Mo_6Se_8$. La polarisation des electrons de conduction par les ions Eu a été étudiée dans $Eu_xSn_{1-x}Mo_6S_8$ et les conséquences de cette polarisation pour les propriétés supraconductrices sont discutées. La configuration électronique de Er^{3+} dans le superconducteur ternaire $ErRh_4B_4$ a été étudiée par spectroscopie Mössbauer de ^{166}Er.

1. Introduction

The ways in which the Mössbauer effect can be used to elucidate superconductivity has been a longtime subject of interest. Most of the early experiments [1,2] attempted to observe changes in the resonance fraction or the shift at the superconducting transition. It has subsequently become clear that important information relevant to the determination of superconducting properties can be obtained by a wide range of Mössbauer studies dealing with (i) phonon properties, (ii) the influence of paramagnetic impurities or (iii) the coexistence of superconductivity and magnetism.

The relevance to superconductivity of vibrational properties obtained from Mössbauer data received considerable attention following McMillan's [3] application of BCS theory to strong-coupled superconductors [4,5]. This is so because the electron-phonon coupling parameter, λ, which appears in McMillan's expression for the superconducting transition temperature, depends on a ratio of phonon moments which can be obtained directly from careful measurements of the temperature dependences of the resonance fraction $f(T)$ and the second-order Doppler shift $\delta(T)$. In addition, either $f(T)$ or $\delta(T)$ may show anomalies related to changes in phonon properties which frequently occur in high temperature superconductors at low temperatures. Several investigations of both binary and pseudobinary systems [5] have suggested the importance of anharmonic effects and phonon mode softening in high T_c superconductors.

The influence of paramagnetic impurities on superconducting properties has been discussed briefly in the Mössbauer literature [6]. Studies to present in most systems indicate that a strong depression in T_c occurs if magnetic impurities are present because spin-flip scattering of conduction electrons from magnetic spins causes a breaking of Cooper pairs [7]. Paramagnetic relaxation rates, however, for the impurity spins in metallic systems are usually dominated by the same scattering mechanism. Hence, a study of relaxation phenomena in these systems has a direct bearing on the effect of magnetic impurities on the superconducting properties.

The question of whether or not superconductivity and long-range magnetic ordering can co-exist has been a subject of considerable interest for many years [8]. Mössbauer spectroscopy, in combination with other techniques, can be used to investigate this area. Examples of such studies are reported by Erickson et. al. [9] and by Gumprecht et. al. [10].

In most of the above cited studies, the Mössbauer probe has been an impurity in the superconducting hosts. This has been necessary since most of the interesting superconductors (with a few notable exceptions, such as Nb_3Sn) did not contain the Mössbauer atom as an intrinsic component of the material. The recent discovery of new classes of ternary superconductors has provided materials where the Mössbauer atom is one of the natural constituents and plays a major role in determining the superconducting properties [11]. Studies of these materials provide more direct information on superconductivity from Mössbauer studies and are the subject of the present review.

Two groups of ternary compounds have been discovered in recent years which have very promising superconducting properties. The group of ternary molybdenum sulfides and selenides are known as the Chevrel phase compounds. The sulphides have the general formula $M_xMo_6S_8$, where M stands for a large number of metals, e.g., Sn, Dy, Eu, and Er, and x can vary from 1 to 4, depending on M. These materials have high T_c and exceptionally large critical field, H_{c2}, values. Some appear to show coexistence of long-range magnetic order and superconductivity in the same volume elements [11]. The second group of ternary superconductors have the general formula R Rh_4B_4 where, e.g., R = Y, Er, Tm, and Lu. These have moderately high T_c and rather low H_{c2}. In $ErRh_4B_4$, a superconducting transition is found at T_c = 8.5 K; at lower temperatures, a magnetic transition occurs (T_M = 0.95 K) which quenches the superconductivity and causes a re-entrance to the normal state [12].

The present review is based on extensive measurements of ternary superconductors of the type $M_xMo_6S_8$, $M_xMo_6Se_8$, and $ErRh_4B_4$ by the present authors [13,14]. These studies have utilized Mössbauer spectroscopy of various isotopes in combination with NMR, magnetic susceptibility, specific heat and neutron diffraction measurements. The only other Mössbauer studies of ternary superconductors are those of Bolz et. al. [15,16], and their results will be included in this review.

2. Lattice Properties

In addition to their interesting magnetic properties the ternary Chevrel phases show a very large pressure dependence of the superconducting transition temperature [17] and a tendency to undergo low temperature crystallographic transitions [18]. The Chevrel phase compound most extensively studied by the Mössbauer effect is $SnMo_6S_8$ [13,15]. The Chevrel phase has a rhombohedral structure with the Sn atom surrounded by eight Mo_6S_8 units such that the Sn point symmetry is axial. The isomorphic binary compound $SnMo_6Se_8$ has a transition temperature of ~6 K compared with that of 13 K in $SnMo_6S_8$. It is of interest to see if the difference in T_c between these compounds is associated with soft lattice modes due to the Sn.

Measurements of both f(T) and δ(T) in $SnMo_6S_8$ have been performed by Kimball et. al. [13] and by Bolz et. al. [15]. The Sn nucleus with trigonal symmetry experiences a large field gradient. The quadrupole doublet measured with ^{119}Sn Mössbauer effect displays a large Goldanskii-Karyagin effect which permits the measurement of the lattice vibrational anisotropy and the components of the resonance fraction parallel and perpendicular to the threefold axis, $f_{||}(T)$ and $f_{\perp}(T)$. Consideration of both these quantities as well as δ(T) has led us to the following conclusions: (i) The vibrational spectrum of Sn atoms is highly anisotropic and anharmonic. (ii) An anomalous temperature dependence is observed in all three quantities near 80 K, implying a soft-mode transition in the Sn phonon spectrum. (iii) The soft vibrational modes of the Sn contribute significantly to

the electron-phonon coupling parameter λ, thus leading to an increased T_c [13]. Subsequent inelastic neutron measurements [19] showed the mode-softening to also be associated with the external modes of the Mo_6S_8 units. The Mössbauer and neutron data can, however, be understood by invoking a hybridization of Sn resonance modes and the soft-modes of Mo_6S_8 units [20].

In order to contrast the phonon anomalies in a low T_c and a high T_c compound, data have also been obtained for ^{119}Sn in $SnMo_6Se_8$. In that case the quadrupole interaction is about 40% smaller than in the sulphide, primarily due to an increase in the lattice constant. Because the two lines of the quadrupole doublet are unresolved, the decomposition of f(T) into parallel and perpendicular components was not possible. However, both f(T) and δ(T) show mode-softening around 80 K. These anomalies are weaker than in the sulphide, in keeping with the difference in their T_c values (6.5 K for $SnMo_6Se_8$ vs. 13 K for $SnMo_6S_8$) as can be seen from the temperature dependence of the recoilless fraction shown in Fig. 1. The solid lines indicate the behavior expected on the basis of a Debye model fitted to the high temperature data. Similar weak phonon anomalies have been observed by us in $LaMo_6S_8$ (T_c = 7 K) doped with 2% Sn.

3. Magnetic Interactions

In a large number of binary and pseudobinary superconducting alloys the influence of magnetic impurities has been studied by bulk measurements [21] and an excellent agreement with the Abrikosov and Gor'kov theory [7] has been obtained. Generally in such cases both T_c and the upper critical field H_{c2} are lowered by the presence of the pair-breaking due to the magnetic impurities.

Recently, very unusual behavior has been observed in ternary superconductors containing magnetic impurities [22]. For example, in $Sn_{1-x}Eu_xMo_6S_8$, the Eu^{2+} ions carry a magnetic moment of 7 μ_B. In spite of this, the value of T_c is almost unchanged up to concentrations $x \simeq 0.5$. Even more curious, the H_{c2} value actually increases from 275 kG for x = 0 to 390 kG for x = 0.4. These peculiar (but technologically useful) properties have both been examined microscopically using the ^{151}Eu Mössbauer effect and ^{95}Mo Knight shift measurements.

The ^{151}Eu resonance measurements in samples with x = 0.25 and 0.5 gave linewidths at low temperature which were considerably broader than the high temperature widths. The temperature dependence of the excess linewidth (the broadening over the minimum observable width) is indicative of paramagnetic relaxation effects. If we presume spin-spin interactions are weak, the spin relaxation rate is dominated by exchange scattering from the conduction electrons (the Korringa process). This rate can be written

$$W = \frac{2\pi}{h} (g_J-1)[J_{sf}N_s(0)]^2 kT, \qquad (1)$$

where J_{sf} is the s-f exchange coupling, and $N_s(0)$ is the s density of states at the Fermi level, which can be obtained from band calculations, e.g., Jarlberg et. al. [23] or Anderson et. al. [24]. In the fast relaxation regime, the excess linewidth $\Delta\Gamma$ is expected to be inversely proportional to the rate in Eq. (1) and hence should be inversely proportional to temperature. This behavior is obeyed well for $\Delta\Gamma$ in $Eu_{0.25}Sn_{0.75}Mo_6S_8$ over a wide temperature range (15-200 K) as shown in Fig. 2. These results provide a direct observation of a small density of states at the Eu site, and/or a small exchange coupling J_{sf}. Both these observations are in agreement with weak dependence of T_c on the Eu concentration for $x \lesssim 0.5$.

The mechanism responsible for the increase in the H_{c2} value on adding Eu atoms to $SnMo_6S_8$ is slightly more involved. The result is that the presence of Eu atoms generates an internal field at the 4d superconducting electrons of Mo which counteracts the effects of the external magnetic field. Our ^{151}Eu Mössbauer measurements of the magnetic hyperfine field in $Eu_{0.5}Sn_{0.5}Mo_6S_8$ (obtained by applying an external field) indicate that the s-conduction electron polarization at the Eu site is positive and small compared to other metallic systems. A small value for the total s-electron density is also reflected in the isomer shift value of -14.0 mm/sec. On the other hand, the ^{95}Mo Knight shift shows the conduction electron polarization at the Mo site to be negative, implying a spatial dependence of the direction of the spin density in the material. Thus, the effect of polarizing the Eu moments in the external field is to produce an effective field at the Mo site which partially compensates the applied field. The essential idea for this mechanism was proposed by Jaccarino and Peter [25] many

years ago on the basis of a uniform polarization model and in a more complex form appears to be operating in these new ternary superconductors.

The above understanding of the behavior of $(Eu,Sn)Mo_6S_8$ leads to a two-band-picture of this material--an "s-band" and a "d-band". The superconducting properties are dependent on the d-band, presumably derived largely from the Mo atoms. Below T_c the Fermi level electrons in the d-band form Cooper pairs, causing the observed change in the ^{95}Mo Knight shift at T_c. When the Eu atoms are added to the material, a weak exchange interaction occurs largely in the s-band. In addition, the Mo d-electrons are shielded from Eu spins by a cage of sulphur atoms, resulting in a small J_{df} coupling. Thus, T_c is weakly dependent on the presence of the Eu atom and the Eu concentration. In an external field Eu^{2+} spins polarize the s-band. This polarization is parallel to the external field direction at the Eu site, but shows a spatial dependence such that it is negative at the Mo site. Below T_c, no gap opens in the s-band so that the polarization is maintained. As a result, the externally applied field is compensated by the s-band polarization at the Mo site resulting in an enhancement of H_{c2}.

4. Spin Ordering in the Superconducting State

Can long range magnetic spin ordering occur simultaneously with superconductivity? This question has been asked since the late fifties, but still does not have a completely clear answer [26]. Much of the early work on the "coexistence" problem utilized bulk measurements such as a.c. susceptibility and specific heat. For example, in LaGd alloys [27] and $Ce_xGd_{1-x}Ru_2$ alloys [28], bulk measurements strongly supported

the simultaneous occurrence of magnetic order and superconductivity in appropriately chosen concentration ranges. The Mössbauer effect can be an important supplementary tool since it provides a microscopic probe of magnetic order which is rather insensitive to superconductivity.

Experiments of Taylor et. al. [29] on iron-doped $Ce_xGd_{1-x}Ru_2$ and of Steiner et. al. [30] on LaEu showed hyperfine splitting at very low temperatures which supported the arguments for the coexistence of magnetic ordering and superconductivity. On the other hand, neutron scattering experiments on $Ce_{0.8}Tb_{0.2}Ru_2$ [31] and $Ce_{0.73}Ho_{0.27}Ru_2$ [32] showed only short-range magnetic order, with magnetic correlation lengths ranging up to 40 Å. The coexistence of short-range magnetic order and superconductivity can be understood if the magnetic correlation length is small compared to the coherence length for Cooper pairs [33]. Of course, the presence of a magnetic hyperfine splitting in a Mössbauer spectrum does not necessarily imply long-range magnetic ordering. For example, magnetically split spectra can arise from slow paramagnetic relaxation rates, as observed in studies of spin-glasses and small particles. Magnetic domains containing as few as ten spins can lead to a split magnetic pattern at low enough temperatures. On the basis of current measurements, the magnetic order for all the cases discussed above appears to be of a spin-glass type rather than long-range magnetic ordering [26] . In a very careful study at ^{151}Eu nuclei at temperatures between 0.05 and 4.2 K Bolz et. al. [16] conclude that the magnetic ordering in $Eu_xSn_{1-x}Mo_6S_8$ is of the spin glass type.

In the rare-earth rhodium boride compounds, it is clear that there is no coexistence in the sense that magnetic ordering and superconductivity occur at the same temperature. However, both kinds of ordering are seen in the same material at different temperatures. For example, $ErRh_4B_4$ is superconducting with T_c = 8.5 K, in spite of the large concentration of paramagnetic Er ions present in the material. At lower temperatures, long-range ferromagnetic ordering occurs (T_M = 0.95 K), at which point the superconductivity is quenched. Recent neutron diffraction measurements have indicated that the magnetic state is ferromagnetism, with Er ions lying in the basal plane of the tetragonal structure and having a magnetic moment about 60% of the free-ion value [34].

Mössbauer experiments using the ^{166}Er resonance in $ErRh_4B_4$ between 0.1 and 4.2 K give a moment nearly equal to the free-ion value [35]. The difference between the Mössbauer and neutron diffraction results can be understood by assuming that only a component of the Er moment is magnetically ordered, with the other components being disordered down to 0.1 K. Since the neutron diffraction experiment measures a spin-pair-correlation function, it will see only the ordered component. The Mössbauer experiment, on the other hand, measures an autocorrelation function and so may observe the full moment. The Mössbauer studies and neutron diffraction results together indicate a unique ground state with partial magnetic order, the magnetic correlations are sufficient, however, to destroy the superconducting behavior.

5. Conclusions

In this review we have illustrated the usefulness of the Mössbauer effect in studying the properties of superconductors. The important aspects of superconducting materials that can be investigated with the Mössbauer effect are:

(i) Phonon properties, such as the electron-phonon coupling, anharmonicity, and soft-modes;

(ii) the strength of magnetic spin scattering by the superconducting electrons;

(iii) measurement of conduction electron polarization effects due to paramagnetic ions; and

(iv) microscopic studies of the interrelationship of superconductivity and magnetism.

The ternary superconductors investigated here are of considerable importance for their technological applications and at the same time are ideally suited for fundamental studies of the behavior of superconducting materials.

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Figure Captions

Figure 1. Temperature dependence of the relative recoilfree fraction for ^{119}Sn in $SnMo_6S_8$ and $SnMo_6Se_8$. The solid lines are Debye fits to the high temperature data.

Figure 2. Line width of ^{151}Eu absorption as a function of temperature in $Sn_{0.75}Eu_{0.25}Mo_6S_8$ showing the inverse dependence of $\Delta\Gamma$ on temperature.

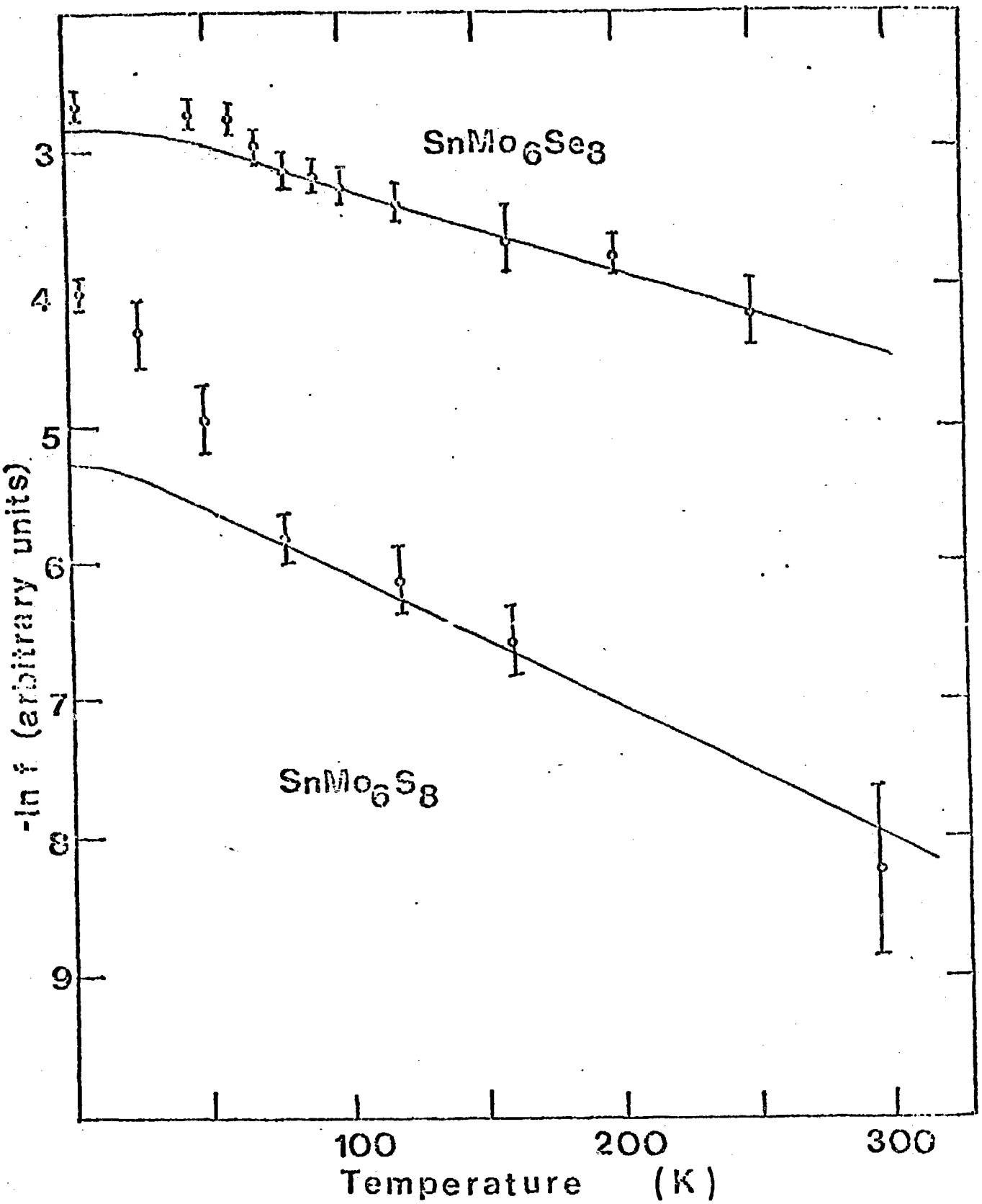
SnMo6Se8
SnMo6S8
-ln f (arbitrary units)
3
4
5
6
7
8
9
100
200
300
Temperature (K)

FIGURE 1

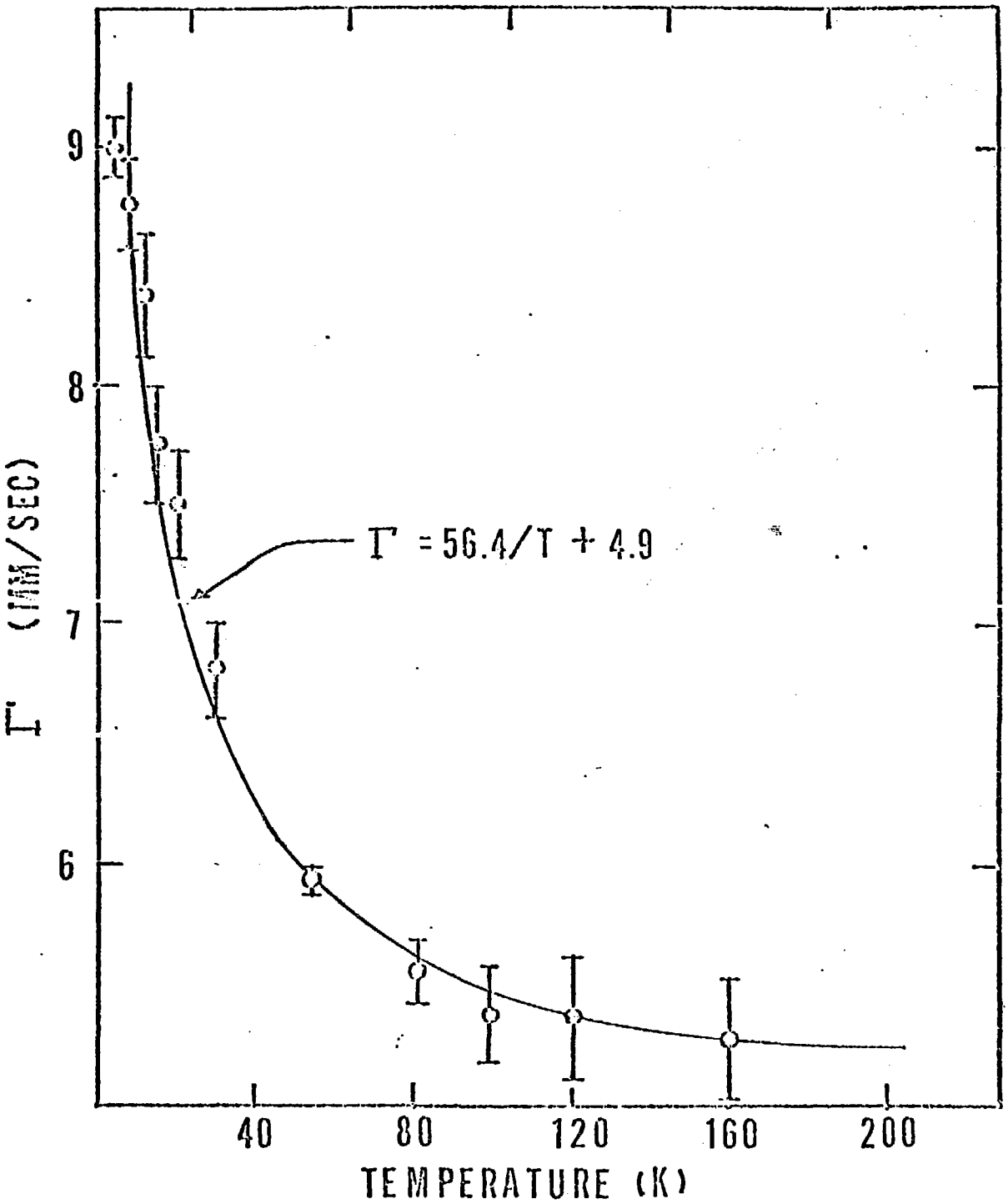

FIGURE 2